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REVIEW ARTICLE

15 YEARS OF STRONG METAL SUPPORT INTERACTION

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Introduction

Though the concept of metal support interaction was known ever since Adadurov[1] proposed in 1935 that metals would be polarized by oxides surfaces containing cations of high charge and Schwab *et al.*[2] postulated that respective Fermi levels of metal and support are the key parameters for catalysis for metals supported on semiconductors, Tauster and his coworkers[3] brought out a new observation in 1978 that hydrogen and carbon monoxide chemisorption capacity was suppressed completely and the system showed altered catalytic activity for hydrogenation or hydrogenolysis reactions after reduction of the supported system at 773 K and termed this phenomenon as Strong Metal Support Interaction (SMSI). With this a complete distribution[4] (weak, medium and strong) of interactions have come into discussion. Even though, one can realize that there can be a gradation in the extent of interaction, no clearcut limits appear to have evolved for these three stages of interaction. After the publication of the paper by Tauster *et al.*[3] in 1978, various efforts have been constantly made to decipher the causes of this phenomenon as well as to exploit the consequences of this phenomenon favourably. However, what appeared to be a feasible proposition in 1978, namely tailoring of supported metal systems, still eludes us and the initial enthusiasm is waning out with frustration setting in. The purpose of this presentation is to reflect on the reasons for this state of affairs in the understanding of SMSI phenomenon and how to counter this trend with vigorous thinking and action in our future research efforts.

Characteristics of SMSI

The basic criterion used to characterize the onset of SMSI is compete suppression of hydrogen or carbon monoxide chemisorption at room temperature after reduction at 773 K. This criterion has been questioned especially for those systems like supported iron where hydrogen chemisorption is activated[5]. For the systems which exhibit activated adsorption, the proposal for the criterion is the suppression of chemisorption capacity at the temperature of maximum in the isobar. Though there seems to be some convergence regarding the reduction at 773 K as the appropriate treatment temperature for the onset of SMSI state, slightly lower or higher temperatures say upto 873 K are also used depending on the nature and the precursor used for the preparation of the support. It should be pointed out that the interaction can be turned off if ion-exchange[6] or microemulsion methods[7] methods are used to disperse the metal onto a low surface area support. Secondly, in the case of carbon monoxide chemisorption, complete suppression is not observed on certain supported systems like supported iron, where one can visualize more than one adsorption state for CO and hence this criterion also has to be used with caution. In Table I and Table Ia summary of the essential data (representative ones) generated and reported in literature on the chemisorption of hydrogen/carbon monoxide on supported metal systems exhibiting SMSI state is given.

Table I

Data relating to suppression of hydrogen and carbon monoxide adsorption in SMSI state

System	[H/M]		Ref
	at low temperature reduction	at high temperature reduction	
1% Fe/TiO_2 (c)	0.05[673]	0.00[798]	8
1.5% Fe/TiO_2	0.09[573]	0.00[773]	5
1.4% Fe/La_2O_3	0.60[698]	0.00[998]	5
2.4% Fe/Sm_2O_3	0.15[748]	0.00[1123]	5
1.5% Co/TiO_2	—	0.048[723]	9
10% Ni/TiO_2	0.46[523]	0.022[723]	10
1% Ni/TiO_2	0.042[573]	0.005[773]	6
4.7% Ru/TiO_2	0.35[475]	0.128[750]	11
1.01% Ru/ZrO_2	0.80[573]	0.61[773]0.46[973]	12
Ru/SiO_2	0.45	0.26	13
Ru/TiO_2	0.18	<0.015	11
Ru/TiO_2	0.54	0.11	11
3.8% $Rh/V/SiO_2$	0.49[573]	0.12[773]	14
	0.22[573]	0.06[773]	14
	0.02[573]	0.02[773]	14
1% Rh/ZrO_2	0.72[523]	0.4[773]	15
2.03% Pd/TiO_2	0.31[448]	0.02[773]	16
Pd/CeO_2	0.41	0.021	17
0.3% Ir/TiO_2	1.00[473]	<0.01[773]	18
2% Ir/TiO_2	1.60[473]	0.00[773]	3
2% Os/TiO_2	0.21[473]	0.11[773]	3
5% Pt/Al_2O_3	0.52[573]	0.40[773]	19
5% Pt/Al_2O_3	0.80[573]	0.50[773]	20
1% Pt/TiO_2	0.60[513]	0.00[773]	20
0.2% Pt/TiO_2	1.15	0.04	21
2% Pt/TiO_2	0.59[573]	<0.02[773]	22
2% Pt/TiO_2	0.12[573]	0.17[773]	22

It is necessary that one is able to distinguish between SMSI and non-SMSI supports. This means that certain supports loaded with metals are capable of exhibiting SMSI state on reduction at 773 K or above, while some supports do not exhibit the suppression in chemisorption capacity measured at 300 K for either hydrogen or carbon monoxide even after reduction at 773 K or at high-

Table Ia

Data relating to suppression of carbon monoxide adsorption in SMSI state

System	[CO/M]		Ref
	at low temperature reduction	at high temperature reduction	
1.01% Fe/TiO_2 (c)	0.13[673]	0.08[798]	8
6.3% Fe/TiO_2	0.022[643]	0.001[873]	23
1.5% Co/TiO_2	–	0.037[773]	9
10% Ni/TiO_2	0.15[523]	0.008[723]	10
1% Ru/TiO_2	0.13[523]	0.03[773]	24
1% Rh/ZrO_2	0.16[523]	0.00[773]	15
1% Rh/TiO_2	0.75[523]	0.24[773]	24
1% Pd/TiO_2	0.36[523]	0.07[773]	24
2% Ir/TiO_2	1.19[473]	0.00[773]	3
1% Ir/TiO_2	0.29[523]	0.005[773]	24
5% Pt/Al_2O_2	0.58[573]	0.35[773]	19
5% Pt/Al_2O_3	0.35[573]	0.35[773]	20
1% Pt/TiO_2	0.8[573]	0.50[773]	20
1% Pt/TiO_2	1.04[523]	0.00[773]	24
$Rh/V/SiO_2$	0.49	0.12	

The figures in the brackets refer to the temperature of reduction.

er temperatures for prolonged periods. In other words, these systems retain their chemisorption capacity whether the reduction was carried out at 573 K or at or above 773 K. To substantiate this point, the data on hydrogen/carbon monoxide chemisorption on Pt/SiO_2 system are given in Table II together with the data on Pt/TiO_2 system for comparison. It is seen that the Pt/SiO_2 system retains its chemisorption capacity whether the system is reduced at 573, 673 or 773 K and that the size of the platinum crystallites are small. However, in the case of Pt/TiO_2 (C) (where (C) denotes that the sample of TiO_2 used is from commercial sources), complete suppression of carbon monoxide/hydrogen chemisorption is observed after reduction at 773 K. Viswanathan *et al.*[26] have attempted to distinguish between SMSI and non-SMSI supports on the basis of the magnitude of the heat of the phase transition of the support. They argued that supports like TiO_2, Nb_2O_5, La_2O_3 and Sm_2O_3 which undergo phase transition in the temperature interval 723-873 K with the heat of phase transition in the range 60-80 KJ mol^{-1} will exhibit SMSI effect while supports like SiO_2, Al_2O_3, ZrO_2 which undergo phase transition at higher temperatures (>1073 K) with low heat of phase transition (<20 KJ mol^{-1}) will not exhibit SMSI characteristics as a result of reduction at 773 K. The phase transition is also known to be catalyzed by the metal loaded on the support[27]. Even though the catalytic role of the metal in phase transition of the support is recognized long ago, it is not clear whether there is any selectivity (i.e., only certain metals catalyze the phase transition) for this behaviour. The phase transition of the support is not a universal phenomenon and depends on both the nature of the

Table II

Comparison of hydrogen and carbon monoxide chemisorption on platinum supported on silica and titania [25]

System	Temp.of reduction	Hydrogen Uptake in μ mole $(g.cat)^{-1}$	Carbon monoxide uptake in μ mole $(g.cat)^{-1}$	Percentage dispersion		Particle size (nm)	
				H_2	CO	H_2	CO
0.7% Pt/SiO_2	300	6.6	6.6	35	35	3.1	3.1
	400	6.6	6.6	35	35	3.1	3.1
	500	6.6	6.6	35	35	3.1	3.1
1% Pt/TiO_2 (C)	300	7.4	7.4	29	29	3.7	3.7
	400						
	500	0.0	0.0	—	—	—	—

metal supported as well as on the nature of the precursors used for the preparation of the support. Generally, supports prepared from freshly precipitated precursors are susceptible to exhibit the phase transition and the catalytic role of group VIII metals is perceptible in the phase transformation of freshly precipitated supports. However, the generalization that all group VIII metals can catalyze the phase transition of the support cannot be fully substantiated at present. The concept of phase transformation as a cause for the observation of SMSI effect[23,28] could have originated from the observation of Dickenson *et al.*[29] who reported that titanium cations of the hexagonal form of barium titanate formed direct chemical bonds with several transition metal ions by the overlap of the respective *d*-orbitals. The presence of strong bonding between heteronuclear cations that is between Ti^{4+} and metal cations like Pt^{4+}, Ir^{4+}, Mn^{2+}, Co^{2+} is responsible for the stabilization of hexagonal form over the tetragonal form of barium titanate. It is clear that only when the metal ions are dissolved in the support lattice and yield strong cation-cation interactions by suitable overlap of *d*-orbitals, the phase transition of the support will be observed[25]. This means that in such supported metal systems where, the extent of reduction is considerably lower than 100% and support material texture allows the dissolution of metal ions in subsurface layers, one will observe the phase transition of the support as a result of reduction at high temperatures. The role of high temperature reduction in this case is to aid the dissolution of metal ions as well as to generate the reduced cations of the support (Ti^{3+} in the case of TiO_2) which can effectively function as donor cations while reduced state of metal ions or Ti^{4+} cations can function as acceptor cations, to give rise to strong cation-cation interactions. In order to substantiate this point, the XRD data of Fe/TiO_2, Fe/La_2O_3, Fe/Sm_2O_3 and Pt/TiO_2 systems are given in Table III. Since the presence of rutile form of TiO_2 is observed in the case of TiO_2 (gel) support alone in the case of Fe/TiO_2 system, the extent of dissolution of metal ions into the subsurface layers of the support has been monitored by studying the variation of I_{Fe}/I_{Ti} as a function of sputtering time and the data generated for TiO_2(c) as well as TiO_2 (gel) system are given in Fig. 1[25]. It is seen that considerable amount of iron is present in the subsurface layers of TiO_2 (gel) support while the concentration of iron in the subsurface layers of TiO_2 (C) support is low. Secondly, it has been shown that the extent of reduction of iron is only 25% for 9.2% Fe/TiO_2 (gel) system as compared to the value of 75% reduction for 9.5% Fe/TiO_2 (C) catalyst. The anatase to rutile phase transformation in pure TiO_2 is reported to occur[30,31] approximately at 973 K while this transition is reported[30,32-34] between 973-1075 K for Pt, Rh, Co, Ni and Ag loaded TiO_2 thus indicating that the catalytic role of group VIII metals on the phase transformation of TiO_2 from anatase to rutile is not universal. Therefore, the role of phase transformation of the support in the onset of SMSI state is only incidental and thus cannot be considered to be the real cause of the effect observed.

Table III

XRD data of Fe/TiO_2, Fe/La_2O_3, Fe/Sm_2O_3 and Pt/TiO_2 systems at various temperatures of reduction[25,5]

System	Phases identified by XRD
9.5% *Fe/TiO_2 (c)*	TiO_2-A
(a) Fresh TiO_2	TiO_2-A, Fe_2O_3
(b) Fresh Fe/TiO_2	TiO_2-A, Fe_2O_3, $\alpha-Fe$
(c) Fe/TiO_2 reduced at 573	TiO_2-A, $\alpha-Fe$, Fe_2O_3
(d) Fe/TiO_2 reduced at 773	TiO_2-A, $\alpha-Fe$, Fe_2O_3
9.2% *Fe/TiO_2 (g)*	
(a) Fe/TiO_2 reduced at 573	TiO_2-A, Fe_3O_4, $FeTiO_3$
(b) Fe/TiO_2 reduced at 773	TiO_2-A, Fe_3O_4, $FeTiO_3$, TiO_2-R
4% *Fe/La_2O_3*	
(a) Fe/La_2O_3 reduced at 698	La_2O_3-B, La_2O_3-A, $LaFeO_3$, Fe_2O_3, $\alpha-Fe$
(b) Fe/La_2O_3 reduced at 998	La_2O_3-B, La_2O_3-A, $LaFeO_3$, $\alpha-Fe$
2.4% *Fe/Sm_2O_3*	
(a) Fe/Sm_2O_3 reduced at 673	Sm_2O_3-C, $\alpha-Fe$, Fe_2O_3
(b) Fe/Sm_2O_3 reduced at 848	Sm_2O_3-B, $\alpha-Fe$, $SmFeO_3$
4.8% *Pt/TiO_2*	
(a) Pt/TiO_2 reduced at 573	Pt, TiO_2-A
(b) Pt/TiO_2 reduced at 773	Pt, TiO_2-A

TiO_2-A—anatase; TiO_2-R—rutile; La_2O_3-B—monoclinic form of La_2O_3; La_2O_3-A—hexagonal form of La_2O_3; Sm_2O_3-C—cubic form of Sm_2O_3; Sm_2O_3-B—monoclinic form of Sm_2O_3.

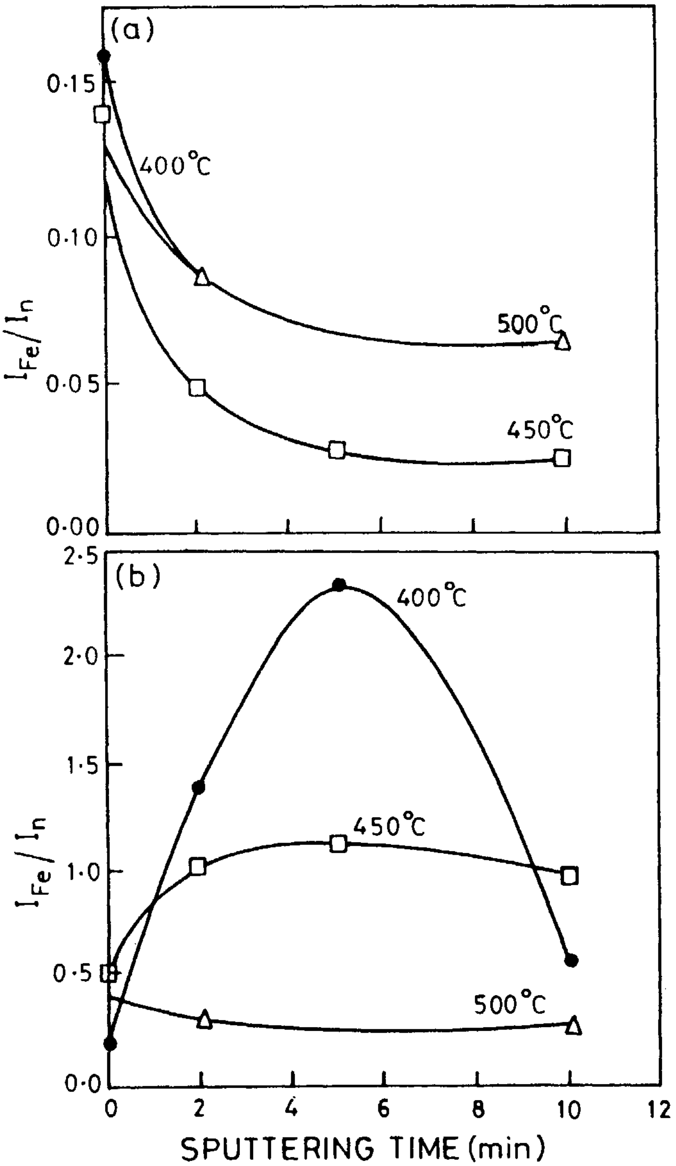

Fig 1 Variation of I_{Fe}/I_{Ti} as a function of sputtering time for Fe/TiO_2 catalysts reduced in H_2 at various temperatures (a) commercial and (b) gel[25] sample of TiO_2

Models for SMSI State

There are essentially four major models for strong metal support interaction namely, electron transfer, morphological effects, encapsulation/decoration and alloying. Among these models, electron transfer and encapsulation/decoration models have received considerable attention in the last 15 years.

Charge Transfer Model

Horsely[35] performed X_α SCF−SW calculations to estimate the extent of bonding between Pt and TiO_2. The inadequacy of the models considered in this study for representing metal (Pt) supported on reduced TiO_2 surfaces has also been pointed out[36]. However, similar calculations have also been carried out by Madhusudan Rao *et al.*[37] for clusters representing Pt supported on titania and silica. According to these calculations the occupied metal *d*-states split off from the top of the band arising out of oxygen $2p$-states, because of the strong repulsive interaction between metal *d*-states and oxygen $2p$ non-bonding states in the case of silica supported systems, while in the case of titania supported systems the metal *d*-states are pinned towards the top edge of the oxygen $2p$-band. Though in both cases one can visualize molecular orbitals with contributions of orbitals of the cations of the support (Ti^{4+} and Si^{4+}) as well as *d*-orbitals of the metals (Fe or Pt) the strong repulsive interaction between the metal atom and the nearest neighbour oxygen ions in the case of silica supported system can prevent the close approach necessary for metal-metal bonding. However, the metal-metal bonding may be possible in the case of titania supported system. Viswanathan and Lakshmi[38] used the arguments of metal orbital contributions to HOMO band LUMO levels of model clusters containing iron and Ti in both +4 and +3 state and concluded that encapsulation of iron occurs only in reduced support systems and in this state alone facile dissociation of carbon monoxide is possible which will account for the increased CO hydrogenation activity normally observed in SMSI state. The same can be argued, that when there is direct bonding (by virtue of mixing of metal *d*-orbitals with that of the support cations in the occupied states) then the dispersion of the metal on the support will be high and in the case of systems where such a mixing is not possible, the dispersion will be lower or the metal particle size will be higher. The formation of metallic clusters of varying sizes is envisaged as the reason for SMSI state[38,39]. However, the point that emerges from the concept of mixing of the orbitals of metal with those of support is that, one should observe some kind of charge delocalisation between the metallic centres and the species of the support. This model, means that as a result of charge transfer, there must be some initial state effects in the binding energy of the core levels of the metallic species. This expectation was probed by observing the shifts in the core level binding energies of supported metal systems. Since the observed binding energy shifts necessarily contain both the initial state chemical shift and final state relaxation component, it is necessary to extract out the component of the shift in binding energy due to the initial state chemical shift. This has been attempted by a number of workers[40-43]. The inadequacy of the expressions used by them, namely

$$\Delta(BE) = \Delta E - \Delta R - \Delta E_{\text{bending}}$$

and

$$\Delta(KE) = \Delta E + 3\Delta R + \Delta E_{\text{bending}}$$

where $\Delta(BE)$ and $\Delta(KE)$ are the binding energy and kinetic energy shifts, ΔE and ΔR are the chemical and the relaxation shifts respectively and $\Delta E_{\text{bending}}$ is the extent of band bending at the interface for evaluating the initial state chemical shift has been pointed out[44-46]. Thomas[47] has shown that the simple relationship that the Auger parameter $\Delta \alpha = 2\Delta R$ may not be sufficient and should include higher order terms (i) for the change in the core ionization energy with respect to electron removal or addition in the valence level (~ 0.2 eV) (ii) the change in the valence charge as a result of core ionization (~ 1 eV) and (iii) the change in external potential due to charge transfer from and polarization of surroundings. It appears that corrections upto ~ 3 eV may be required in the Auger parameter in some cases. This point has been established by the experimental results of White *et al.*[64] as well as of Toyoshima *et al.*[48]

Takasu *et al.*[49] have reported that particle size differences can also account for the observed binding energy shifts to higher values. Mason *et al.*[50] postulated that binding energy shifts for small clusters can be due to initial state effects only, though for less interactive substrates, they expect a higher binding energy values for clusters with respect to bulk metals. Therefore, observation of binding energy shifts alone may not be adequate to evaluate the electronic effect of SMSI. In fact, many of the electron spectroscopic investigations have failed to observe any shift in the binding energy of the core levels of the supported metals. In spite of these limitations in the interpretation of the observed binding energy shifts, the data reported in literature relevant for SMSI are summarized in Table IV. The following points emerge from the values given in this table:-

(*i*) The observations by Sexton *et al.*[56] as well as by Chien *et al.*[55] that at least one oxidation-reduction cycle is necessary before a reproducible value in the shift can be obtained show that the effect observed in the first high temperature reduction is due to a combination of one or more effects normally associated with SMSI state. The cycling removes probably the components due to contributions from these other effects other than the electronic effect.

(*ii*) The extent of binding energy shift due to electronic effects is mostly of the order of 0.2 ± 0.1 eV denoting that the net charge on the metal atoms is very small ~ 0.1 to 0.2 e only.

(*iii*) The differences that exist in the observed values have therefore to be reckoned with the inadequate quenching of the effects in the measurements. For example, majority of the shift of 1.6 eV observed by Fung[63] may have to be ascribed to effects due to morphology changes and increase in crystal size.

Sadeghi and Henrich[58] have fabricated a model system with deposited rhodium on a well characterized TiO_2 surfaces. They have also observed a shift in the binding energy of the $3d_{5/2}$ core level of Rh by about 0.4 to 0.5 eV. They presume that this shift could arise dominantly from the changes in the extent of screening of the core hole as a function of Rh coverage ($\Theta = 0.1$ to 0.5). They propose that part of the shift can arise out of the charge transfer but it was not possible to separate out only the charge transfer component as there was simultaneous change in particle size. Another observation recorded by them is that the model system after high temperature reduction (673 K; 10^{-3} torr hydrogen) showed no UPS peaks due to adsorbed CO indicating that the model system passed on to the SMSI state. This observation is similar to the one reported by Tanaka *et al.*[67] on *n*-$Si/SiO_x/Ni$ system.

Table IV

Observed Binding Energy Shifts of the core levels of Supported Metals in SMSI State

Metal	Support	Level probed	Binding energy or shift eV	Cause	Ref
Fe	TiO_2	$2p_{3/2}$	706.7	Diffusion of iron into the support	51
Ni	TiO_2	$2p_{3/2}$	-0.4	Charge transfer	40-42
Ni	Si/SiO_x	$2p_{3/2}$	-0.4	Charge transfer	43
Ru	TiO_2/SiO_2	$3d_{5/2}$ $3p_{3/2}$	~ 1.0 -0.75	Charge transfer, alloy, dispersion	53
Ru	Al_2O_3	$3d_{5/2}$	2 < to Ru^0	Alloy with Ru negatively charged	52
Rh	ZnO	$3d_{5/2}$	307.1	Rh – Zn bond	54
Rh	TiO_2	$3d_{5/2}$	-0.7*; -0.2@	Charge transfer	55
Rh	TiO_2	$3d_{5/2}$	-0.6*	Charge transfer	56
Rh	V_2O_5	$3d_{5/2}$	-0.3*	Charge transfer	56
Rh	Nb_2O_5	$3d_{5/2}$	-0.3	Charge transfer	56
Rh	Si/SiO_x	$3d_{5/2}$	-0.3	Charge transfer	48
Rh	TiO_2	$3d_{5/2}$	0.0	Encapsulation and spalling	45
Rh	Al_2O_3	$3d_{5/2}$	0.0	Encapsulation and spalling	45
Rh	TiO_2	$3d_{5/2}$	307.8; 307	Presence of Rh^+ and Rh^0	57
Rh	TiO_2	$3d_{5/2}$	-0.4; -0.5	Charge transfer and particle size	58
Rh	TiO_2	$3d_{5/2}$	-0.3	Charge transfer and sintering	59
Pd	ZnO	$3d_{5/2}$	336; 337.1	Pd – Zn bond	60
Pd	La_2O_3	$3d_{5/2}$	-0.7	Encapsulation, $LaPdO_x$ formation	61
Pt	TiO_2	$4f_{7/2}$	-0.5	Charge transfer	62
Pt	TiO_2	$4f_{7/2}$	-1.6	Charge transfer	63
Pt	TiO_2	$4f_{7/2}$	-0.4*	Charge transfer	56
Pt	TiO_2	$4f_{7/2}$	0.0	Encapsulation and spalling	45
Pt	Al_2O_3	$4f_{7/2}$	0.0	Encapsulation	45
Pt	Al_2O_3	$4f_{7/2}$	0.0	Encapsulation and spalling	45
Pt	TiO_2	$4f_{7/2}$	0.4	Morphology electronic effect	64
Pt	$SrTiO_3$	$4f_{7/2}$	-0.3	Charge transfer	40
Pt	ZnO	$4f_{7/2}$	-0.7	Charge transfer atomic rearrangement	65
Pt	TiO_2	$4f_{7/2}$	-0.3	Charge transfer and sintering	59
Pt	TiO_2	$4f_{7/2}$	< 0.3	Variation in work function	66

*initial value
@ after cycling

(*iv*) The observations of Huizinga *et al.*[45] that even a positive binding energy shift is observed as a result of reduction of M/TiO_2 system at 1015 K with increase in dispersion shows encapsulation and spalling of the metal particles as a result of high temperature treatment.

(*v*) The relative positions of the donor levels in the reduced support and the available unoccupied levels of the metal species dispersed can also control the extent of charge transfer. This aspect has not yet been clearly investigated.

Most of the studies reported in literature concern the Pt/TiO_2 system wherein differences in dispersion and the extent of reduction of the support can account for the differences in the results reported. In systems where Pt is dispersed in atomic state and where the reduction of the support is not extensive the effect could be small.

Mansour *et al.*[68] have examined the charge transfer model by X-ray absorption spectroscopy in which they observed the L_{II} and L_{III} X-ray absorption edges for Pt supported on either SiO_2 or Al_2O_3. They have deduced the values of *d*-level vacancy of supported Pt with respect to that of pure Pt. It has been observed that the *d*-level vacancy is increased in the supported system and the extent of vacancy depends on the nature of the support and the extent of reduction. These results have been interpreted in terms of charge transfer from the metal to the reduced support opposite to what is proposed on the basis of electron spectroscopic observation of binding energy shifts.

Most of the electron spectroscopic studies on supported systems involved Pt metal because of the consequent changes in binding energies seem to be within observable limits in this system. The small magnitude of the changes can also be the reason why some of the authors have failed to observe any changes in the binding energy of the metal core levels in the SMSI state. These observations, no doubt point out the difficulties involved in using this technique for this aspect.

The charge transfer model as applied to SMSI effect stems from the original proposals of Schwab *et al.*[2] some fifty years ago in the name of the 'synergetic.promotion' by the support. Repeatedly[69], this postulate has been used to explain anomalous support effects though most often convincing direct proof could not be obtained and only indirect effects in the form of alteration of activity or activation energy for the catalyzed reaction or change in the heats of adsorption of hydrogen or carbon monoxide could be observed. However, when a metal is brought in contact with a metal oxide especially a semiconductor there can be alignment of Fermi levels. Depending on the value of the work function of the support and the metal and the height of the Schottky barrier, the charge flow will occur in one of the two directions. Since the values of the work function of the support and metal in the case of Pt/TiO_2 system ($Pt = 5.36$ eV and $TiO_2 = 5.5$ eV) are almost the same, there is no net transfer of charge in either directions in the low temperature reduced state or non-SMSI state.

As a result of high temperature reduction, the support phase also undergoes reduction considerably. There are many experimental evidences to show that the support phase undergoes reduction as a result of high temperature hydrogen treatment. In brief they are: (*i*) observation of Ti^{3+} by ESR[70]; (*ii*) the identification of Ti_4O_7 phase by electron diffraction[71]; (*iii*) identification of reduced Ti^{3+} species as revealed from the binding energy of 2*p* level of Ti[72]; (*iv*) Martens *et al.*[73,74] showed that the model in which metal particles rest on a [001] layer of reduced TiO_2, a layer that closely resembles a shear plane in Ti_4O_7 could fit to the experimental EXAFS and HRTEM observations; (*v*) correlation of SMSI effect with ease of reducibility of the support; (*vi*) deduction of the composition of non-stoichiometric phase by oxygen consumption experiments[75]; and (*vii*) from electrical conductivity measurements and from a consideration of the heat of formation, Herrmann[76] deduced that in Pt/TiO_2 system in SMSI state contains only singly ionized anionic vacancies instead of the suboxide formation as a result of reduction at higher temperatures. In the reduced state, the work function of the support will be smaller than that of the unreduced support (because of the increase of *n*-type conductivity in the case of TiO_2) and hence charge flow occurs in the direction of the metal for the alignment of the Fermi levels. In fact, SMSI behaviour has been correlated with the nature of charge carriers of the support oxide, those systems with *n*-type semiconducting behaviour alone promote SMSI behaviour. Relevant data are given in Table V. Meriaudeau *et al.*[77] favouring this charge transfer model in terms of the collective property of the electron, consider that the filling up of the *d*-band of the metal transforms it from the active state to almost a non-reactive one. They have supported this model based on the collective properties from the measurements of increase of conductivity as a result of high temperature reduction of Pt/TiO_2 and its decrease as a result of subsequent oxidation. However, this naive model cannot account for the differences observed in the catalytic activity of Pt supported on TiO_2 and CeO_2 though both being *n*-type semiconductors. Chen and White[78] have considered this model for a number of supports with various carrier types (*n*,*p*, insulator and metal) and have concluded that the support with relatively high electrical conductivity and a work function lower than that of the deposited metal will exhibit SMSI effect. The chinese group[65] considers the conventional SMSI behaviour as a consequence of the enhanced metal-semiconductor interaction. They have observed that the reduction of Pt/ZnO system with hydrogen at 573 K caused the change of rectifying behaviour to ohmic property and the appearance of PtZn lattice could be deduced from XRD. These results were considered to indicate the occurrence of atomic rearrangement at the Pt−ZnO interface in the samples treated at 573 K. The metal semiconductor interaction related to an

Table V

Correlation of SMSI behaviour with the nature of charge carriers in the support oxides[35,76]

Support	Carrier type	Electrical conductivity (cm^{-1})	SMSI
TiO	metal	10^{-1}	yes
Ti_2O_3	n	10^{-3}	yes
TiO_2	n	10^{-11}	no
Nb_2O_5	n	10^{-1}	yes
HfO_2	p	10^{-5}	no
ZrO_2	p	10^{-5}	no
Sc_2O_3	p	10^{-7}	no
MgO	n	10^{-12}	no
SiO_2	insulator	10^{-12}	no
SiO	metal	10^{-3}	yes

atomic interaction and/or interfacial layer formation between the metal and the semiconductor is considered by them to be the cause of the conventional SMSI state. Chung *et al.*[40-42] have deduced the extent of charge transfer from the shifts of the core levels of Pt or Ni supported on single crystals of $SrTiO_3$ or TiO_2 and proposed the concept of localized charge transfer model which has attracted attention in contrast to the treatment in terms of the collective behaviour of electrons. Though EXAFS studies of Short *et al.*[79] support the direction of charge transfer, for the Pt/TiO_2 system, they predict a lesser amount of charge transfer than 0.6 electron (compare with a value of 0.5 electron for Rh/TiO_2[80]) per platinum atom (of the order of 0.02 electron per platinum atom) a value deduced by theoretical calculations by Horsley[35]. However, as pointed out earlier the validity of the models used for the computation by Horsley has however, been questioned[36]. Sadeghi and Heinrich[80] have considered Rh/TiO_2 system specially designed so as to minimize the effects of morphological changes and encapsulation that occur simultaneously when the catalysts are reduced at high temperatures. The reduced form of the support was obtained by inert gas ion bombardment on which the rhodium metal was deposited. They have essentially provided the following three experimental observations in support of the postulate that the reduced titania species bond to rhodium through a somewhat ionic bond (the charge transfer envisaged is of the order of 0.5 electron per rhodium atom) with charge transferred to the rhodium from reduced Ti cations.

(*i*) There is an attenuation of the titanium *d-d*-transition peak in ELS as a result of rhodium deposition on reduced TiO_2 indicating a decrease in the number of Ti $3d$ electrons on the reduced support through interaction with rhodium.

(*ii*) The ratio of the intensity of LMV_{Ti} to LMV_0 Auger transitions decreases with coverage of reduced titania surfaces by rhodium which is indicative of the oxidation of the surface Ti ions on rhodium deposition suggesting that electrons are transferred from the reduced Ti ions to the rhodium metal.

(*iii*) The 0-$2p$ derived valence band shifts towards the Fermi level as a function of rhodium coverage which is in the same manner and by the same amount as it does for the oxidation of reduced TiO_2 by oxygen thus pointing the direction of charge transfer from the reduced support to metal.

Sanz *et al.*[81] examined Rh/TiO_2 system reduced at high temperatures by ^1H NMR technique and postulated that support held hydrogen produces SMSI effects in Rh/TiO_2 system because of electronic changes (rehybridisation) induced in the small metal particles by interaction with the support stabilized hydrogen, thus causing a lesser density of states near the Fermi level of the metal which are involved in hydrogen chemisorption, thus accounting for the reduction in hydrogen chemisorption capacity in SMSI state. Herrmann[76] from thermodynamic considerations postulate that electrons originating from the ionization of anionic vacancies of the support are partially trapped by the metal thus resulting in the enrichment of electrons at the metal site which could account for decreased adsorption of donor species like hydrogen and carbon monoxide. The existence of SMSI effects induced by replacing the high temperature reduction of Pt/TiO_2 either by introducing an alkali additive[82] or by doping titania with penta- (Ta^{5+}, Sb^{5+}) or hexa- (W^{6+}) valent heterocations also supports the charge transfer model[83]. Kelly *et al.*[84] however, consider that the SMSI effect is not due to the extent of charge transfer from TiO_2 to Pt but can be due to more subtle and specific changes in the electronic structure of the Pt atoms which occur as a result of high temperature hydrogen reduction. In this connection it is interesting to note the two direct experimental evidences observed by Chung and Weissbard[85] which support the localized charge transfer concept. They are: (i) the surface Ti^{3+} species were removed as evidenced from the disappearance of the 1.2 eV energy loss transition as a result of the deposition of Pt on $SrTiO_3$ and (ii) the work function of $SrTiO_3$ increased from 4.2 eV when $\Theta_{Pt} = 0$ to 5.0 eV when $\Theta_{Pt} = 1.0$.

There are other indirect evidences available for the charge transfer postulate as the cause of SMSI state. The IR absorption band of linearly absorbed CO on Pt/MgO shifted from 2080 to 2085 cm^{-1} with increase of reduction temperature. This observation has been accounted for in terms of a Pt – MgO complex formed as a result of reduction at higher temperatures in which electron transfer occurs from Pt to MgO[86].

In an earlier study Jiang *et al.*[87] argued that SMSI is due to the presence of electronegative TiO_x species on the surfaces of titania supported metal particles which could decrease the strengths of hydrogen and CO adsorption as well as could account for the decreased rate of dissociative hydrogen adsorption. They have argued that the charge transfer direction should be opposite of what is normally considered that is from the reduced support to the metal, on the basis of comparison of the effect of addition of alkali metals or electronegative species like O, C, S, P, Cl to iron for the adsorption of nitrogen.

In spite of the overwhelming evidences in favour of charge transfer model, arguments can still be given against this concept. It is known that Ti^{3+} is formed whether the reduction is carried out at 473 K or at 773 K but SMSI effect is observed only after reduction at 773 K for TiO_2 supported systems. If charge transfer were to be due to the presence of Ti^{3+} with '*d*' level occupancy as is usually argued it would have occurred even at 473 K reduction when Ti^{3+} could have formed. Rh supported on Y-zeolite exchanged with Ti^{3+} (in this system Rh and Ti^{3+} can be in the neighbourhood in the super cages) has shown hydrogen and carbon monoxide adsorption capacity as well as hydrogenating properties whatever was the reduction temperature. This result can probably indicate the absence of SMSI when only isolated Ti^{3+} ions are in the proximity of the metal. By virtue of charge transfer, Pt attains the *d*-character of Au and hence shows similar to gold no hydrogen adsorption capacity. This type of reasoning has already been questioned by Bond and Burch[88]. It is known that the variations in the *d*-character is only a few percent around 40 and hence these small variations cannot have any perceptible effect. The indirect effect of the support observed in the case of Pt-silver strongly supporting the spill-over process[89] cannot be accounted for on the basis of charge transfer model. It is not clear at present how this model can be extended to the SMSI behaviour observed with phosphate supported nickel catalysts[90]. Ponec[91] argues that small particles of metal (say 2nm diameter) will have of the order of 10^3 delocalized electrons and whether such small change in their number (one per 10^3 electrons) can cause such pronounced support effects as found experimentally? In addition, charge transfer model predicts a change in activation energy while experimentally variations in frequency factor alone were observed in the case of kinetics of catalytic reactions in the SMSI state.

Thus it appears at the moment, the available evidences of SMSI are unable to substantiate the charge transfer postulate. The environmental changes with or without inclusion of hydrogen arising out of migration, reduction and redistribution as a result of high temperature reduction could have altered the local density of states of metal particles or cluster species. The interaction in the dispersed catalysts should therefore be considered as though between metal clusters and the reduced catalyst. In the case of cluster model, charge transfer mechanism cannot result in individual metal atoms acquiring an electronic configuration (example Pt obtaining the '*d*' electron configuration of gold or cobalt that of nickel) which could account for the loss in sorption capacity. One should probably consider the interaction between the cluster and the support and see the net effect of charge transfer to such a cluster. This has not yet been attempted, probably because of lack of information on the nature and geometry of cluster species obtainable on supported systems as a result of high temperature reduction. Such a synthesis model can probably account for some of the observations of SMSI state as far as charge transfer concept is concerned. A first attempt in this direction has been made[92]. It is interesting to note that Haller *et al.*[93] consider SMSI state of catalytic interest can be more of subtle interaction than that described theoretically by Horsley[35] or physically by experiments on metals supported on single crystals by Chung *et al.*[40-42].

Geometric Effects

Extensive electron microscopic studies by Baker *et al.*[94-96] and others[97,98] showed that there can be variations in the particle size of the metal with significant differences in the morphological details of the metal particles. Typically platinum on titania support has been shown to take an hexagonal outline with extremely thin and of uniform thickness across the particle with a 'pill-box' morphology as a result of high temperature reduction. However, it is known that the metal particles on other supports are globular or spherical (example Rh/TiO_2)[99] in outline and have a hemispherical geometry. Baker argues that this difference between titania and other supports arises due to concomitant reduction of titania to Ti_4O_7 or similar phases with high values of surface tension γ_{gs} (interfacial tension at the solid gas interface) which facilitates the formation of thin flat crystallite structures as a result of wetting and spreading of the metal on the support. This postulate is supported by the observation[100] that the rate of ammonia synthesis is hardly affected showing that the thin iron particles formed during reduction at temperatures above 773 K possess flat surfaces which resemble those on large particles of metallic iron.

The redistribution of thickened platinum metal aggregates supported on titania into flat 'pill-box' hexagonal structures with few atoms thick can be considered as some sort of 'melting' wherein the cohesive forces in metal aggregates are overcome. The driving force for the redistribution can be conceived to arise from the strength of metal-support interaction. However, it is not clear how this redistribution is obtainable preferentially in some supports alone since Baker *et al.*[94-96] have not recorded this redistribution for Pt on silica after treatment at higher temperatures (1073 K). The argument that titania is capable of undergoing reduction to its next member of the crystallographic shear oxide of composition Ti_4O_7 and thus causes the redistribution cannot however be extended to other supports where SMSI effect has been observed. No detailed information is yet available on the nature and composition of the reduced states of other supports causing SMSI effect[101-103].

Normally one would expect an increase in particle size of the metal as a result of high temperature reduction. Though this expectation seems to be true in the case of Pt on Al_2O_3, SiO_2, carbon and a few other oxide supports, the situation in the case of meals on titania seems to be contradictory[104], though in the case of Pt/TiO_2 little change in particle size is observed after reduction at 773 K. The simultaneous reduction of TiO_2 to Ti_4O_7 as evidenced by electron diffraction[92] and ESR data[70] as the cause for this anomalous behaviour of titania has to be reexamined since a study[34] on the redistribution of cobalt on titania showed that the support underwent only a phase transition from anatase to rutile as a result of high temperature reduction. These authors[34] argue that the difference in the values of activation energy for redistribution and the transformation temperature are lowered by the presence of foreign metal like cobalt. In addition Kelly *et al.*[84] have observed in their ISS measurements that the Pt peak intensity is decreased after reduction at 673 K which is not in agreement with the view that the onset of SMSI is associated with the conversion of multilayer particles into monolayer rafts since such a situation should have led to more Pt to be visible in the SMSI state.

It is known that particle size and shapes of metal clusters can have an influence on the extent of dispersion[106]. SMSI can therefore be considered as a manifestation of a different particle shape when such an interaction occurs between metal and oxide[107]. Catalytic probes employing structure sensitive reactions can be used for evaluating the role of geometric effects in SMSI[108,109]. Since the interaction between the support oxide and metal may be specific, the shape changes for small metal particles on different support may not be always apparent[110]. These situations can mislead when the catalytic probes are used as a means of probing geometric effects in SMSI. Little *et al.*[11] though could identify the presence of free and precursor nickel oxide with different binding modes on alumina, titania, and alumina/titania, they could not find any apparent differences in the methanation activity on a weight percent basis of nickel.

Extended X-ray absorption fine structure (EXAFS) studies by Konigsberger *et al.*[74,112-114] showed the development of distinct Rh – Rh bonds due to metal crystallites and Rh-oxygen bonding involving interfacial zero valent rhodium atoms and oxygen anions of the TiO_2 support as a result of reduction at high temperatures. The onset of Rh – O interaction as a result of high temperature reduction has also been invoked by Haller *et al.*[108,115] to explain their EXAFS results. Sankar *et al.*[116] have deduced the presence of two Ni – Nb (Ni – Ti) distances, one of which (2.65/2.62 A compare this with the observed value of 2.56 A for Rh – Ti distance) is comparable to that obtainable in the alloy. They accordingly propose that structural reorganization of the support (Nb_2O_5 or TiO_2) occurs in the neighbourhood of Ni particles. However, Koningsberger *et al.* find a longer Rh – Ti distance (3.42 A) in Rh/TiO_2 and proposed the alloy formation may not occur even if one were to observe shorter Rh – Ti distance.

It should be remarked that the attempts to elucidate the role of geometric effects in SMSI have often been masked by the concomitant oxide migration and metal encapsulation. There is growing evidence that encapsulation is the main cause of SMSI state, resulting from the high temperature reduction used: This aspect of the geometric effect is considered in the next section.

Encapsulation Model

Encapsulation of the metal particles following reduction at temperatures greater than 773 K can occur either due to extensive loss in the surface area of the support or due to the migration of the support on the metal particles or due to interdiffusion of the metal and the support. Powell and Wittington[117] have developed a model for encapsulation based on the reduction of the surface free energy of supported system (in this particular case Pt/SiO_2) as a result of changes in the areas of the Pt surface, interface as well as that of the support on high temperature reduction. Ruckenstein and Lee[118] have accounted for the changes in crystallite shapes as a result of heating in purified hydrogen at 773 or 973 K in terms of extension or contraction of the particles caused by the changes in the interfacial tension values of γ_{ca}, γ_{cg}, and that of γ_{sg} for the reduced support. The changes in γ_{cg} could be brought out by the migration of the reduced TiO_{2-x} over the surface of the crystallites because of strong interactions between the two. Equilibrium and surface segregation calculations by Spencer[119] show that SMSI effects in Pt/TiO_2 catalysts are due to strongly adsorbed titanium suboxide on the platinum surface. The reduction of the support leads to the formation of PtTi alloy which on oxidation yields reduced support oxide over layer or Pt diffuses into the reduced support. According to Cairns *et al.*[120] the modified support interface as a result of high temperature reduction becomes incompatible with the metal layer and hence tends to lose contact and breaks up. This cracking process facilitates access to hydrogen at the interface and causes local reduction of the support and consequent interdiffusion between the elements of the reduced support and the metal. This interdiffusion affects the chemical composition and environment of the metal thus accounting for the alteration in hydrogen chemisorption. According to this model, the high temperature hydrogen reduction causes the metal to break up in islets with elements diffused from the support. Subsequent exposure to oxygen leads to the formation islets of oxidized support leaving the active metal exposed again. However, the oxidation step cannot completely regenerate the metal surface area due to (*i*) the globules of the support phase partly covers the metal and (*ii*) if the diffusion of the elements of reduced support were to be extensive then subsequent oxidation would have resulted in the complete loss of metal surface area. This model thus, cannot however fully account for the experimentally observed total regain of sorption capacity after oxidation and low temperature reduction of the SMSI state. In addition, Tauster *et al.*[3] observed that the surface areas of the samples were essentially the same regardless of whether the reduction was carried out at low temperatures or at high temperatures. This observation however is not universal. Using field emission technique Vanselow and Mundschau[121] have shown that there can be layer and/or face specific reduced support oxide precipitate formation as well as island formation with high surface mobility of the oxide molecules. The creation of these strong electric patch fields could account for the alterations in the adsorptive and catalytic properties observed in the SMSI state. That is reactions in which the dipole moment of the activated molecule is larger than the sum of the dipole moments of the reactants will be accelerated by the creation of these patch fields.

Dumesic *et al.*[87,100,122] have deduced that SMSI state is induced in iron titania system after reduction at 800 K from the observation of increase in the values of activation energy and ammonia partial pressure dependence for ammonia synthesis. The metal support interaction in this case, according to them is due to spreading of reduced TiO_x species over the α-iron particles (size ~20nm) either by the dissolution of titanium species during impregnation in aqueous solutions or by spreading of the reduced titanium species, since the mobilities of TiO_x and group VIII metals may be comparable, instead of the metal spreading over the reduced titania. The subsequent oxidation of both metal and the reduced titania species probably provide the necessary heat for the mobility of titanium species and renucleation of three-dimensional TiO_2 islands leads to a state which on low temperature reduction restores the sorption capacity. Raupp and Dumesic[123] showed that coverage of nickel sites by titania reduced carbon monoxide adsorption on strongly bound sites while it enhanced adsorption at weakly bound sites while the adsorption of hydrogen is strengthened by the presence of titania coverage over nickel. They have even postulated that the spreading of the support and the consequences in the adsorption behaviour may be applicable to irreducible oxide supports like alumina. It is however, true, that the disappearance of metal particles to a small extent has been observed in some cases, but the extent of metal encapsulation if it were present cannot account for the total loss of sorption capacity normally observed experimentally.

Another model of encapsulation can be that the poisonous impurities like, sulphur, phosphorus, and chlorine migrate over the metal particles as a result of high temperature reduction. Wang *et al.*[124] using various purity MgO or with addition of impurities like sulphate showed that hydrogen sorption capacity and activity for ethane hydrogenolysis decreased as a result of reduction at higher temperatures (773 K). However, little effect of reduction temperature was observed when high purity MgO was used as a support for Rh metal. They have therefore, deduced that the impurities especially of sulphate providing sulphide poisoning are responsible for the apparent metal-support interaction in the Rh/MgO system. Kunimori *et al.*[19,125] have reported a phenomenon called sulphur aided SMSI. The role of sulphur impurities is presumably to promote partial reduction of alumina support thus leading to a redox reaction

$$Pt + Al_2O_3 \rightleftharpoons PtAl_{2/3} \cdot 2/3\,Al_2O_3$$

However, Apesteguia *et al.*[126] consider another redox reaction

$Pt + (SO_4)^{2-}_{support} \rightleftharpoons PtS + (O^{2-})_{support}$

which of these reactions predominates depends on Pt/S ratio, the nature of sulphate in alumina support and the temperature of hydrogen treatment. Whatever, may be the redox process, the species formed can account for the suppression in hydrogen chemisorption[126].

Chen and white[78,127] report that they could not detect any of these impurities by XPS both on oxidized and non-oxidized Pt/TiO_2 samples which showed different hydrogen chemisorption properties. If poisoning especially by sulphur were to be the cause for SMSI state, then the amount of sulphur impurity normally found (typically ~25 micromol g^{-1} of TiO_2) in the supports cannot account for the total amount of the metal present on most of the supports. In addition, a second high temperature oxidation could have removed the impurities and one would have expected a normal behaviour following reduction at high temperatures. Experimentally the effect on the sorption capacity as a result of SMSI state has been observed whether the support used is of high purity or not. It is, therefore, less likely that encapsulation by impurities can be the exclusive cause for the observation of SMSI state.

Vannice and Chou[128] have favoured the encapsulation postulate for the SMSI state on the basis of the observation that the heats of adsorption of hydrogen and carbon monoxide are of comparable magnitude for Pd/TiO_2 catalysts reduced at low temperatures (LTR) or high temperatures (HTR). They suggest that the support effect on the catalytic properties of Pd involving carbon monoxide as substrate may be due to direct involvement of support in the catalytic sequence but are unlikely to be a consequence of changes in the electronic properties of Pd in the SMSI state[16]. This postulate is similar to the proposal of Burch and Flambard[33] who invoke activation of substrate molecules simultaneously bonded to the metal site and the reduced support sites. In this connection it is interesting to compare the activation energy for desorption (E_d) of carbon monoxide and hydrogen from the metal surfaces in SMSI state. This comparison is made by the data given in Table VI, wherein it is seen that the values of E_d is considerably different from those observed on pure metals.

The AES studies by Sadeghi and Henrich[58] briefly referred to earlier and SSIMS investigation on Rh/TiO_2 system by Belton *et al.*[44] have led to numerous similar studies on supported group VIII metal systems. Takatani and Chung[132] observed by AES intensity profiles as a function of sputtering time that titanium and oxygen enriched on the surface of nickel deposited on TiO_2 as a result of high temperature reduction. Another result supporting this enrichment hypothesis is the Auger intensity of nickel decreased and that of titanium increased with square root dependence on reduction time, which is in agreement with the earlier observation of Resasco and Haller[109] that the ethane hydrogenolysis activity of Rh/TiO_2 follows a square root dependence on the reduction time. This functional dependence indicates that the migration of titania is a diffusion controlled process. Takatani and Chung[132] showed that the enrichment of titania on the metal particles have remarkable deactivating influence (for every titanium ion at the surface approximately nine nickel atoms are deactivated) on CO chemisorption. This observation[133] agrees with the earlier observation that the CO methanation activity on TiO_x/Ni (111) showed a maximum at a titanium coverage (i.e., $\Theta \sim 2 \times 10^{14}/cm^2$) at which the effect of surface titania on CO chemisorption is most pronounced. Fleish *et al.*[134] have shown that the fraction of Pd crystallite surface covered by LaO_x (La_2O_3 is the support) increased with Pd dispersion. In order to account for the weaker CO adsorption bond on Pd/LaO_x as compared to that on Pd/SiO_2 they still invoke the charge transfer from LaO_x particles to Pd crystallites which might have weakened the sigma component of the adsorption bond[101]. Rieck and Bell[102] postulate that the LaO_x species decorated on the Pd particles alters the adstate of CO in favour of its dissociative form which can account for its subsequent rapid methanation.

Table VI

Heats of Adsorption and Activation Energy of Desorption in KJ mol^{-1} for supported catalysts in SMSI state.

Adsorbate	Surface	Strength of adsorption		Ref.
		ΔH	E_d	
CO	Ni		136-117 (Θ-> 1)	129
	TiO_x/Ni		69-85 (α_1)	129
			42-56 (α_2)	129
	2.03% Pd/TiO_2 (448 K)	10		128, 16
	2.03% Pd/TiO_2 (773 K)	71		128, 16
	Ni/TiO_2	134-139 (on top)		123
		91-107 (Bridged CO)		123
H_2	Ni		89 (β_1)	130, 129
	TiO_x/Ni		75 (β_2)	129, 130
			108 (β_3)	
			133	
	2.03 Pd/TiO_2 (448 K)	138		128, 16
	2.03% Pd/TiO_2 (773 K)	109		16, 128
	1.5% Pt/TiO_2 (LTR)	84		131
	1.5% Pt/TiO_2 (HTR)	98		131

Sedeghi and Henrich[58] have continued their original AES studies[135] and found in their model system consisting of Rh/TiO_2, normal chemisorption behaviour could be restored when the surface is sputtered till Rh Auger signal intensity reached a maximum. Their contention is that the suboxide migration over Rh does not necessarily require the high temperature hydrogen treatment and the UHV conditions or hydrogen retained can be sufficiently 'reducing' environment for the process. Their view probably supports the hypothesis that the deduction of charge transfer process through the observation of the shift in the binding energy of the core level of the supported metal is possible only when the secondary effects are kept to a minimum or completely eliminated[43,48].

Takatani and Chung[136] have carried out AES and HREELS measurements on a 12 nm nickel film deposited on TiO_2. The results of variation of titanium and oxygen Auger signal intensities as a function of sputtering time though could provide evidence for oxide migration over the metal particles by a diffusion controlled process with a diffusion coefficient of 2×10^{-16} cm^2/s at 973 K and an activation energy of 97 KJ mol^{-1}, could not distinguish between two models namely the migrated titanium oxide partly covers the nickel islands formed as a result of high temperature reduction or the oxide migration leads to homogeneous distribution of oxide within the nickel layers except the surface. However, the interesting deduction of this work based on the analysis of coverage of carbon monoxide variation with coverage of titanium is that approximately five to six surface nickel atoms are deactivated for CO adsorption by the presence of one titanium species. The observation of the decrease of concentration of bridge bonded CO relative to that of on-top CO with increasing titanium coverage could lend support to the oxide migration hypothesis. They have identified yet another adsorption mode for CO with a stretching frequency of 1850 cm^{-1} which survived even after extended reduction. They postulate that the close proximity between nickel and titanium oxide and the resultant strong interaction could activate CO simultaneously which might be responsible for the interesting catalytic transformations. It is necessary to point out that Burch and Flambard[137,138] have considered the possibility of Ni/TiO_x periphery site to be the active centres in these systems, though they have not invoked the oxide migration explicitly. Vannice and Sudhakar[139] have also considered this synthesis model of specific active sites being generated as a result of reduction at high temperatures. The implications of the generation of specific active sites in the SMSI state will be considered in a subsequent section.

Ko and Gorte[140] have devised a model system consisting of a titania layer covered on Pt foil. From an Auger analysis, they showed that oxidized titanium diffused reversibly into a clean Pt foil between 700-900 K. The diffusing species has been identified to be some partially oxidized form of 'titanium oxide' since titania desorbed irreversibly when the titania covered Pt surface was heated in oxygen. The adsorption properties of Pt contaminated with this titanium oxide species correspond to those observed on SMSI catalysts. The migration of titanium species to the surface of Pt has also been invoked in the case of Pt_3Ti alloy[141]. It was shown that CO chemisorption was completely suppressed only when titania segregated to the surface on heating the Pt_3Ti in oxygen atmosphere at higher temperatures.

From a model system study of CO hydrogenation on nickel deposited on reduced or oxidized TiO_2, Chung *et al.*[133] attributed the SMSI behaviour to the presence of titania on the metal surface induced by high temperature treatment and the hydrogen retained on surface or subsurface layers during the reduction which act synergistically accounting for the enhanced activity. Recently, Komaya *et al.*[11] examined Ru/TiO_2 system by TEM, ^1H NMR and hydrogen chemisorption and deduced that as the reduction temperature rises from 573 K to 773 K the average particle size of Ru remains the same, but the surface of the particle is covered to an increasing extent by an amorphous layer of titania. It is also considered that the amorphous TiO_2 overlayers are formed in Rh/TiO_2 reduced at higher temperatures[142,143].

Spencer[144] analyzing the data on potassium promoted Pt/TiO_2 catalysts proposes that the inhibition of hydrogen chemisorption is caused by a redistribution of TiO_2 promoted by K_2TiO_3. The migration of support phase on the active metal is also substantiated by the observation of more Rh – O interactions after high temperature reduction from EXAFS studies of Rh – Ag/SiO_2 and Rh – Ag/TiO_2 systems[108].

Tesche *et al.*[14] examined vanadia promoted Rh/SiO_2 system after low and high temperature reduction by microscopic techniques and showed that the highly dispersed Rh^0 particles is decorated and blocked by VO_x species as a result of high temperature reduction under extreme conditions of pretreatment, the encapsulation of Rh^0 species seems to be complete.

IR spectral observation that there was gradual disappearance of bridge bonded species first and subsequently linear and gem dicarbonyl species as a function of reduction temperature and time was considered to be supporting the postulate of the migration of the support on the active metal[108]. It is interesting to note that Burch and Flambard[137,138] accounted for the increased reactivity of supported systems by invoking the adsorption and dissociation of CO in the periphery sites involving the metal atom and the reduced support, which could be similar to bridge bonded species.

Though there are overwhelming evidences for the encapsulation model, Dumesic *et al.*[145] propose that migration of both reduced titania and metal species may be involved in the initiation of SMSI interactions during high temperature reduction. This is in contrast to the general belief that the reduced titania species alone diffuse into and over metal particles.

Conesa *et al.*[146,147] have considered a similar metal-oxide border line site for the activation of molecular hydrogen involving the 'pushing' of the electron through Rh particle to the TiO_2 support and resulting in an atomic adsorption of hydrogen as a proton on the support oxide. As stated earlier, these concepts regarding the nature of active sites involved in SMSI state are interesting and deserve separate consideration though the available data are limited. It is interesting at this point to refer to the recent work of Knozinger[148]. He has shown by the application of several surface analysis techniques on Rh/TiO_2 model system that encapsulation of Rh particles occurs by the wetting of the Rh surface preferentially by TiO_2 which is more mobile $\geqslant 800$ K than the reduced forms of TiO_2. This leads us to the original question that what is the driving force for this encapsulation and what is the nature of the encapsulating species. At this point we seem to have come one full circle.

Other Secondary Effects

(*a*) *Direct Metal-Metal Bonding or Alloy Formation*—Taking the lead given by Tauster *et al.*[3] that SMSI state can be due to the creation of metal-metal bonds similar to the one in $BaTiO_3$, Horsley[35] as stated earlier, has carried out X_a calculations on model clusters and has concluded that the model involving platinum insertion in the surface oxygen vacancies of the support with direct ionic bonding by charge transfer between titanium cations and the platinum atoms can describe the SMSI state. The basis for the postulate of metal-metal bonding as the cause for the SMSI state is that only reducible metal oxide supports[149] showed SMSI behaviour. The temperature of reduction for the onset of SMSI state correlated with the reducibility of the support. Prauliaud and Martin[150] have obtained a ferromagnetic state with a specific magnetization value of 16.2 emu at 77 K in Ni/SiO_2 system as a result of reduction at 1120 K with low heating rate. They proposed that this system should have contained $Ni-Si$ alloy with Curie point between 77 and 300 K since the value of the specific magnetization was zero at 300 K. However, in the case of titania supported and in other reducible oxide supported systems, surface phenomena may be important than affecting the bulk properties. Den Otter and Dautzenberg[151] considered alloy formation as the cause for the loss of hydrogen uptake observed when Pt/Al_2O_3 catalysts were reduced at high temperatures (~ 950 K).

Experimental support for this deduction comes from the observation of down field Knight shift by 1.2% (similar to $PtAl_2$—4.2%) in the case of Pt/Al_2O_3 samples reduced at higher temperatures. Kunimori *et al.*[152] have deduced the following reaction on the basis of their measurement of hydrogen and oxygen consumption

$$Pt + Al_2O_3 \underset{1/2\,O_2,\ 723\ K}{\xrightarrow{H_2,\ 773\ K}} PtAl_2O_2\ [\text{or}\ PtAl_{2/3}2/3\,Al_2O_3]$$

Similar hydrogen/oxygen consumption measurements on the system Pt/TiO_2 showed[75] that a non-stoichiometric titania with composition $TiO_{1.992}$ is produced as a result of high temperature reduction (773 K). This corresponds roughly to 10^{14} vacancies/cm^2 (10% of the total surface) if the reduction were to be confined only to the top most layer of the support. Even if alloy formation were to be present in the SMSI state it must be confined to a part of the surface layer alone.

Yao[153] argues on the basis of decreased redispersion in oxygen at 773 K for $Pt/CeO_2/\gamma\text{-}Al_2O_3$ and no redispersion in $Pt/MoO_2/\gamma\text{-}Al_2O_3$ that strong metal support interactions in these cases is due to a stable Pt_x-MoO_x or $Pt-CeO_x$ complex on alumina. Renyuan *et al.*[154] employing a repetitive TPR experiment and *n*-heptane conversion data on Pt/Al_2O_3 catalysts suggest that high temperature reduction normally used for inducing SMSI behaviour can give rise to $Pt-Al$ alloy formation so that the second TPR profiles have reduced area due to diminishing Pt rich alumina phase as well as the isomerization and cracking of *n*-heptane follow the same course with increasing Pt content as has been observed in 0.47% $Pt-Sn/Al_2O_3$ catalysts wherein $Pt-Sn$ alloy formation is known to occur. Bardi *et al.*[141] argue that intermetallic formation cannot account for the SMSI effect since though hydrogen chemisorption was absent on the intermetallic, the chemisorption of CO was suppressed only when TiO_2 segregated (as deduced by AES) to the surface on heating Pt_3Ti in oxygen at elevated temperatures.

Badyal *et al.*[155] have grown Ti films on Ru(0001) surface and have shown that it affects carbon monoxide uptake. The hydrogen chemisorption of exposed titanium leads to the formation of surface TiH_3 which decomposes at 600 K with the formation of Ru–Ti surface alloy. TiH_3 itself could also be responsible for the enhanced activity for carbon monoxide hydrogenation.

From the studies[156] on sputtered $Pt-TiO_2$ model system it is deduced that as a result of high temperature reduction (~ 773 K) in hydrogen Ti^{2+} and Ti^{3+} are generated which diffuse into platinum in the form of TiO_x with x close to 1. Interdiffusion of Pt into reduced TiO_x is also envisaged. A surface compound of the composition Pt_nTiO_x with $n > 1$ is generated which could be reduced to a surface alloy Pt_3Ti. The formation of surface compound of composition Pt_nTiO_x is considered to the cause of SMSI.

The formation of alloy as the cause for SMSI has to be evaluated carefully in the light of the following considerations:-

(*i*) Normally, the reduction of the support to the metallic phase is not observed at temperatures used for getting the SMSI state. For example, reduction of TiO_2 to metallic Ti as well as the formation of intermetallic compound such as Pt_3Ti, Ir_3Ti occur only above 2000 K. However, the reduction of the supports can be catalyzed by group VIII metals by hydrogen spill-over process.

(*ii*) Intermetallic alloys are stable in oxygen and would not be decomposed by treatment with oxygen at low temperatures but are known only to lead to phase segregation.

(*iii*) XPS studies have not so far identified the presence of the metallic state of the support.

(*iv*) Intermetallic alloy formation results in isolating the active metal atoms rather than modifying its intrinsic activity per atom. Therefore, alloy formation should result in the suppression of reactions which require ensembles but should not affect reactions occurring on single atoms. For example, one would expect a decrease in hydrogenolysis activity as a result of alloy formation in the SMSI state, but should not observe any change in dehydrogenation activity. This is not in conformity with experimental observations.

(*v*) Titanium based alloys are known to be good hydrogen storage materials and hence the loss of hydrogen sorption capacity in the SMSI state cannot be easily reconciled with alloy formation model.

(*b*) *Hydrogen Retention and Hydrogen Spill-over*—Menon and Froment[157,158] have observed that the desorbed amount of hydrogen is greater than the amount adsorbed for supported Pt catalysts reduced at higher temperatures and thus deduced that hydrogen is retained by the system at high temperature reduction. According to them, Pt and other metals covered by or retaining the strong hydrogen species will be inaccessible for further hydrogen, thus accounting for the SMSI state. Wang *et al.*[159] have observed that hydrogen retained at higher temperatures could not be desorbed completely by a single TPD run upto 773 K. According to them, this indicates that the spillover of hydrogen onto the surface of the support remained as residual hydrogen in the surface layer or diffused into the interior. The possibility of back spillover of hydrogen and more strongly held hydrogen by the metal could account for the loss of hydrogen sorption capacity in the SMSI state. Chung *et al.*[133] from the observation that both the catalysts TiO_x/Ni(111) and Ni/TiO_2(100) have similar methanation activity concluded that the presence of titania on the metal induced by high temperature treatment and the possible incorporation of surface and subsurface hydrogen act synergistically to modify and maintain the activity of titania supported catalysts.

From model system studies on Ni/TiO_2 system typically generated by depositing Ti over nickel foil and subsequently treating in oxygen Gonzalez Elipe *et al.*[160] propose that hydrogen has a positive role in enhancing the diffusion of TiO_x species into metallic nickel as well as that of nickel atoms through the defective TiO_x lattice. Sanchez and Gazquez[161] in an earlier study proposed that metal atoms are anchored in oxygen vacancies in the surface of the support which on progressive reduction leads to the burial of metal particles with increase in oxygen vacancies.

Conesa *et al.*[146,147] propose another process of spillover namely reversible spillover at 295 K resulting from weakly bonded hydrogen in samples of Rh/TiO_2 reduced at temperatures less than 573 K and slow black spillover in the case of samples reduced at temperatures greater than 573 K. They have tried to substantiate the presence of two types of adsorbed hydrogen species in Rh/TiO_2 from the observations of (*i*) generation of Ti^{3+} species as identified by ESR (*ii*) the displacement of the shifted NMR line due to strongly adsorbed hydrogen (H_s) species with increase in pressure and (*iii*) the decrease in infrared transmittance. However, they conclude that in the SMSI situation a series of different phenomena occur simultaneously, charging and spreading of the metal particles, extensive reduction of the support, migration of atomic or molecular entities including TiO_x species to and from the metal.

No doubt, there are evidences for the retention of hydrogen in the subsurface layers of metal catalysts, but this uptake is continuous with increase of temperature and cannot account for the setting in of the SMSI state at a particular temperature (773 K for Pt/TiO_2). Further, a slow uptake of hydrogen on titania supported metal samples (Ni and Pt) at 298 K was deduced from the difference between hydrogen adsorption measurements and desorption studies after prolonged exposure[87]. This observation can be taken to mean that in the SMSI state, only the heats and rates of hydrogen and CO adsorption are decreased. These expectations are not supported by the observations of Chou and Vannice[16].

Another observation worth considering at this point is that the square root time dependence of H/M ratio which can be considered to mean that the slow diffusion of hydrogen atoms on the support is controlling the overall process[162].

It is therefore, not clear at the moment to what extent hydrogen retention by supported metal systems can account for the SMSI state. It is interesting to note the conclusion of Menon and Froment[157,158], who proposed this postulate that the various possible mechanisms for the SMSI state need not be mutually exclusive; two or more of these may occur simultaneously in many cases. This contention agrees with that of Conesa *et al.*[146,147] as stated earlier.

(*c*) *Interfacial Phenomenon or Active Site Concept*—As stated earlier, Burch and Flambard[137] have proposed an alternative model based on the considerations of the interface between the metal and partially reduced support that new active sites are created at the interface and these are responsible for the high specific activity of these catalysts for the CO/hydrogen reaction. In view of this proposal they name this phenomenon as Interfacial Metal Support Interactions (IMSI). Their proposal is based on the observation that the supported Ni, Pd and Ir catalysts on TiO_2 or SiO_2 exhibited enhanced activity for CO hydrogenation even after low temperature reduction (non-SMSI state) and retained the same level of activity for this reaction even after reduction at high temperature (SMSI state) (See Table VII). However, they recorded the normal characteristics of SMSI state namely suppressed hydrogen or CO chemisorption and considerable reduction of ethane hydrogenolysis activity in the SMSI state (See Table VIII). They have therefore, proposed that the high activity of titania supported catalysts in CO/hydrogen reaction is not due to SMSI, but is due to creation of new active sites at the interface between the metal and the support. The location of these new sites is such that they have the capacity to activate or assist in the adsorption of CO in a reactive form. They even go one step further and postulate that the use of benzene hydrogenation data rather than hydrogen chemisorption data may be more reliable for determining specific activities and hence for evaluating the extent of metal-support effects.

Table VII

Catalytic Activity of Supported Ni, Pd and Ir Catalysts for Co Hydrogenation

Catalyst[a]	Specific activity[b]	Ref.
Ni/S/623[548]	8.0	33
Ni/S/723[548]	11.0	33
Ni/S	7.0	163
Ni/S	5-14.4	164
Ni/S	14.8	165
Pd/S/573(1)[573]	1.24	166
Pd/S/773(3)[573]	0.91	166
Pd/T/473(0.5)[573]	5.71	166
Pd/T/573(1)[573]	6.2	166
Pd/T/773(3)[573]	6.28	166
Pd/T/non SMSI	9.9-10.5	167
Pd/T/SMSI	7.2-10.7	167
Ir/S/573[573]	0.17	168
Ir/S/773[573]	0.10	168
Ir/T/573[573]	3.0	168
Ir/T/773[573]	6.0	168

(a) Metal Support/Reduction temperature (time in hours) [reaction temperature S stands for silica and T for titania

(b) In units of × 10^3 molecules/second/surface metal atom

The activation of CO can take place according to this model on both sites—(1) the metal site where the carbon end of CO is attached and (2) the reduced support site where oxygen end of CO is attached. This multipoint activation can occur on the reduced support and the metal, whether the support is migrated over the metal or not. As stated earlier, Poels *et al.*[169,170] consider a similar combination of active sites in silica supported Pd systems involving Pd ions and the metal species. Burch and his coworkers[137,138] propose that instead of the metal ions, the reduced support cations themselves can fulfill this function.

Table VIII

Catalytic Activity of Supported Ni, Pd and Ir Catalysts for the Hydrogenolysis of Ethane

Catalyst[a]	Specific activity[b]	Ref.
Ni/T/723(1)[478]	0.73	33
Ni/T/823(0.5)[478]	0.34	33
Pd/S/673(0.5)[673]	11.9	166
Pd/S/773(3)[673]	9.5	166
Pd/S/773(16)[673]	11.6	166
Pd/T/673(0.5)[673]	5.86	166
Pd/T/773(3)[673]	0.5	166
Pd/T/773(16)[673]	0.35	166
Ir/S/573[573]	90.4	168
Ir/S/773[573]	28.2	168
Ir/T/573[573]	36.4	168
Ir/T/773[573]	0.01	168

(a) Metal Support/Reduction temperature (time in hours) [reaction temperature S stands for silica and T for titania

(b) In units of × 10^3 molecules/second/surface metal atom

Hicks and Bell[171] have studied the hydrogenation of CO on Pd/SiO_2 and Pd/La_2O_3 catalysts with varying compositions of Pd. The specific activity for methanol synthesis is a factor of 7.5 greater for La_2O_3 supported system than for silica supported Pd. They have recorded *in situ* IR spectra of adsorbed CO under different reaction times. The main conclusions of this study are—(*i*) when supported on SiO_2, Pd sinters under reaction conditions while sintering is observed for Pd loading less than 1 percent on La_2O_3.and (*ii*) there are two forms of bridge bonded CO characteristic of adsorption on Pd(100) and Pd(111) surfaces. From the intensities of these two bands after exposure to reaction mixture for 330min it is deduced that Pd crystallite are composed of approximately 90% Pd (100) and 10% Pd(111) surfaces. However, under initial conditions the adsorption on Pd(111) is strongly inhibited when loaded on La_2O_3 due to coverage of the Pd(111) surfaces of the freshly reduced catalyst by patches of partially reduced support. As a function of reaction time the interaction between the metal and the patches decreases and one could observe the IR absorption band due to CO adsorption on Pd(111) sites. Thus, this study favours a model wherein the metal support interactions seem to affect the morphology of the dispersed metal and the specific activities observed are due to the preferential exposure of certain types of sites with different crystallite sizes and roughness.

The active site model fails short to account for the observed effect of SMSI in terms of the changes in the bulk properties of the metal. The proposals of Burch and Flambard[137,138] though could account for the observed enhanced activity of CO hydrogenation its utility for explaining the other observed properties of SMSI state is not immediately apparent though they have studied extensively the hydrogenolysis of hexane and ethane and the hydrogenation of benzene on these supported catalysts. These aspects will be considered in a later section.

(*d*) *Compound Formation*—In order to account for the interfacial sites normally invoked to account for the altered activity of SMSI state, even compound formation between the metal and the reduced support has also been envisaged. Greenlief *et al.*[172] propose on the basis of XPS studies of titania on platinum that a compound of platinum with oxide is formed at the interface. The supporting evidence for this postulate is that the oxide forms an even layer on the metal. Baker *et al.*[173] proposed that instead of the migration of TiO_x species over the metal, the formation of a highly mobile phase (a mixed surface oxide of $PtTiO_x$) accounts better the behaviour of SMSI state. This may be possible for Pt/TiO_2 system but cannot account for the behaviour of other metals supported on titania. Surface complexes of the form $Ti-O-Fe$ or $Ti-O-O-Fe$ have also been proposed by Nobile and Davies[23] as the possible cause of SMSI state. The interaction between metal ions with the reduced support yielding ternary oxide phase (in the case of Rh on Nb_2O_5 $RhNbO_4$[174], for Pt/TiO_2, Pt_nTiO_x[175], for Fe/La_2O_3, $LaFeO_3$ and for Fe/TiO_2, $Fe_2TiO_{5,5}$) which migrate and block the metallic sites has also been proposed as possible explanation of SMSI behaviour.

Catalytic Consequences of SMSI State

Having seen that the SMSI state in supported systems arises out of two factors namely (*i*) electronic effect due to charge transfer and (*ii*) other secondary or apparent effects due to encapsulation/decoration, hydrogen retention, metal-metal bond formation and so on, it is essential to consider the catalytic consequences of SMSI state and see whether one can distinguish between non-SMSI state from SMSI state. However, this is not possible immediately with the available data because—(*i*) the conditions for obtaining the same degree and state of dispersion for the different metals on the same support are not yet established. (*ii*) Even when the estimated dispersions were nearly the same for different metals, the state of the support (i.e., extent of reduction, and encapsulation, or oxide migration etc.) need not be identical since the extent of metal catalyzed reductions of the support by spillover and other processes could have been different for different metals under the same experimental conditions employed to induce SMSI state. Because of these limitations, the reports dealing with model system studies will be considered first.

The catalytic studies reported by Kao *et al.*[41] on model systems may be suitable to estimate the effect due to electronic effects. In fact, as stated earlier, they have extracted the chemical shifts for nickel on $TiO_2(100)$ sinlge crystals and deduced a charge transfer of 0.1 electron to nickel atom form the support. However, these studies are confined only to nickel on TiO_2 (100). They observed that the CO hydrogenation activity is increased by 3.5 times as compared to that of Ni(111) with an accompanying change in selectivity towards higher hydrocarbons. This is one clear example of catalytic consequence of SMSI state due to electronic effect. Another study using model system was reported by Vannice and Sudhakar[139] using Pt with one or 10 monolayers of TiO_x which showed a 4 or 40 fold increase in turn over frequency values for CO hydrogenation. Though they have discounted the charge transfer model and preferred the presence of special active sites at the interface as a possible explanation, their data cannot completely rule out the possibility of charge transfer. Resasco and Haller[109] have considered the trend of variation of ethane hydrogenolysis (decrease) and cyclohexane hydrogenation (unaltered) as a function of either reduction temperature in the case of Rh/TiO_2 catalyst or atomic percent Cu in copper nickel alloys. Since in the latter case i.e., group VIII-group Ib alloys localized interactions has been proposed as the cause for the depression of activity in a structure sensitive reaction (ethane hydrogenolysis) Resasco and Haller[109], believe that localized interaction between the support and the metal which could be altered by varying the extent of reduction, might account for the observations of SMSI state.

Burch and his coworkers[33,138,166] attempt to dispense away SMSI state as the cause for enhanced CO hydrogenation activity and propose a model wherein the support provides active sites for direct adsorption or for assisting in the adsorption of CO or CH_xO intermediates. According to them the interface between the metal particles and the support is the seat of special catalytic significance. This proposal is similar to that of Poels *et al.*[169,170] who conceived that the metal ions can contribute to the activity of catalysts for the CO hydrogen reaction. The only difference being that the ions of the support, not the ions of the metal as proposed by Poels *et al.*[169,170] are involved in the activation of CO or CH_2O intermediates. Similar proposal has also been made by Vannice and Sudhakar[139], from their model system studies considered earlier. Dumesic *et al.*[122] consider that the addition of potassium to iron catalysts lowers the local work function with consequent increase in the binding energy of molecular nitrogen and its dissociation. In this connection, it is interesting to quote two studies[72,176] dealing with the activation of nitrogen (isoelectronic with CO) on SMSI catalysts wherein it has been argued that similar to carbon monoxide suppression nitrogen chemisorption can also be used as a criterion for the characterization of SMSI state. Another surface science study deals with the elucidation of state of nitrogen activation on metal surfaces as probed by photoemission studies which showed that annealed Ni/TiO_2 (probably corresponding to SMSI state) surface exhibited extensive dissociative adsorption of nitrogen while molecular adsorption predominates on non SNSI system at 80 K[72]. Normally presence of electronegative species on the surface of iron decreases the strength of hydrogen and carbon monoxide chemisorption. Therefore, Dumesic *et al.*[122] consider that SMSI state which exhibits decreased strength for CO and hydrogen binding should be caused by the presence of electronegative TiO_x species on the surface of titania supported metal particles. Similar deductions have been made by monitoring Ti^{3+} species by ESR in Pt/TiO_2 system as a result of addition of potassium[82].

Fang and White[177] recorded a decrease in tne IR band at 1760 cm^{-1} intensity due to adsorption of NO on open sites of Pt and TiO_2 as a result of overnight reduction at 773 K with hydrogen. However, prolonged reduction decreased the intensity of both IR bands due to adsorption of NO on open and close packed sites. They have accounted this depression of NO chemisorption as a result of filling Pt *d*-levels by electron transfer as well as due to morphology changes which decreases the number of open sites.

Chung *et al.*[125] have prepared various model systems of nickel on TiO_2 by depositing before and after oxidation and reduction and showed that reduction with hydrogen at 773 K before and after nickel deposition on TiO_2 (100) resulted in an enhanced steady state activity for CO hydrogenation (the steady state TOF for methane increases by a factor of 2). These results according to them indicate the synergistic effect of surface or subsurface hydrogen in the exhibited activity of the system. However, the altered activity in SMSI state can also be due to a decrease in surface coverage on the active metal surface.

Boffa *et al.*[178] studied CO/CO_2 hydrogenation on model systems fabricated by depositing oxides of Al, Ti, V, Fe, Zr, Nb, Ta and W on Rh foil and observed that the maximum increase in the rate of methane formation occurs at an oxide coverage of approximately half the monolayer. They propose that this enhanced activity is the result of Lewis acid-base complex between the oxygen end of adsorbed substrate (CO/H_2CO) with exposed metal centres of the oxide located at the boundary between the oxide and rhodium. This proposal has close resemblance to the proposal of Burch and Flambard[137].

The kinetic parameters obtained for CO hydrogenation on various supported systems are assembled in Table IX. Though mostly the CO hydrogenation activity is increased as a result of the inducement of SMSI state, this does not seem to be universally true. In certain cases, the increase is marginal. It is therefore not clear whether the activity variation for this reaction can be used as a criterion for identifying the SMSI state. In addition, mostly, there appears to be no variation of the activation energy for either methane formation or CO conversion, between SMSI and non-SMSI states. On the other hand ethane hydrogenolysis is decreased (refer to data in Table X) as a result of high temperature reduction (SMSI state) but in this case also there is no difference in the values of the activation energy for the systems reduced at low or high temperatures. The observation that the value of activation energy remains the same whether the system is either in SMSI state or not may have certain implications in understanding the microscopic nature of the active sites involved but such an analysis has not been carried out.

Table IX

Kinetic parameters for CO/H_2 reaction on supported catalysts

Catalyst	TOF $N_{CH4} \times_1 10^3$ sec^{-1}	E_{CO} KJ mol^{-1}	E_{CH4} KJ mol^{-1}	Relative activity	Ref.
1.5% Ni/TiO_2 (Cabot)	...	111	115	...	179
10% Ni/TiO_2 (Cabot)	...	132	114	...	179
1.5% Ni/TiO_2 (P_{25})	...	116	113	...	179
10% Ni/TiO_2 (P_{25})	...	116	136	...	179
30% Ni/SiO_2	8.6(548)	104	112	...	180
10% Ni/Nb_2O_5	19.0(548)	112	116	...	180
3% Co/SiO_2	2.6(498)	67	109	0.011	181
10% Co/SiO_2	2.6(498)	69	158	0.11	181
3% Co/Al_2O_3	0.8(498)	96	137	0.03	181
10% Co/Al_2O_3	3.8(498)	98	143	0.16	181
3% Co/TiO_2	6.1(498)	96	167	0.25	181
10% Co/TiO_2	24(498)	142	150	1.0	181
3% Co/MgO	inactive 673				181
10% Co/MgO	0.05(498)	164	155	0.002	181
3% Co/C (uu type)	0.065(498)	157	178	0.0008	181
10% Co/C (uu type)	...	176	183	...	181
3% Co/C (Spheron)	0.3(498)	153	167	0.05	181
10% Co/C (Spheron)	3.6(498)	121	175	0.16	181
5% Co/SiO_2	3.6	131	149	...	182
4% Co/SiO_2	3.8	95	133	...	183
2% Co/Al_2O_3	1.7	112	113	...	184
6% Co/Al_2O_3	...	106	...	...	185
2% Pd/SiO_2, 573 (1)	0.89^+(573)	...	...	0.15	166
2% Pd/SiO_2 773 (3)	0.69^+(573)	...	...	0.12	166
2% Pd/TiO_2 473 (0.5)	5.54^+(578)	...	...	0.95	166
2% Pd/TiO_2 573 (1)	6.05^+(573)	...	...	1.04	166
2% Pd/TiO_2 773 (3)	5.82(573)	...	...	1.0	166
0.5% Pd/Nb_2O_5 non SMSI	0.16(473)	...	...	...	181
	0.31(523)	...	...	...	181
0.5% Pd/Nb_2O_5 SMSI	0.16(473)	...	...	...	181
0.5% Pd/TiO_2 non SMSI	0.16(473)	...	...	...	181
0.5% Pd/TiO_2 SMSI	40	...	...	...	108
Rh/TiO_2 (473)	75	...	...	...	108
Rh/TiO_2 (773)	7.4^+(548)	76^+	...	1.0	186
1.9% Pt/TiO_2 (P_{25})	90^+	86^+	...	12.2	186
1.9% Pt/TiO_2 SMSI	1.6(548)	69^+	...	0.22	187
1.5% Pt/SiO_2 (450)	0.19^+(548)	70^+	...	0.03	187
1.5% Pt/$SiO_2 - Al_2O_3$	1.4(548)	69	...	0.19	187
Pt/TiO_x (monolayer)	0.41(548)	...	105	...	139
Pt/TiO_x (multilayer)	4.2(548)	...	97	...	139

Table IX Contd

Contn. of Table IX

Catalyst	TOF $N_{CH4} \times {}_1 10^3 sec^{-1}$	E_{CO} KJ mol^{-1}	E_{CH4} KJ mol^{-1}	Relative activity	Ref.
Ru/Al_2O_3 (300, 0.2@)	0.3	...	...	...	188
Ru/Al_2O_3 (600, 0.2@)	0.46	...	...	...	188, 189
2% Ni/Nb_2O_5 573 (1)	19(548)	112	112	0.73	189
2% Ni/Nb_2O_5 773 (1)	26(548)	128	99	1.0	189
10% Ni/Nb_2O_5 573 (1)	24(548)	123	123	1.33	189
10% Ni/Nb_2O_5 773 (1)	18(548)	116	112	1.0	189
10% Ni/Nb_2O_5 (573 (1) 773 N_2 (1))	11(548)	126	101	0.61	189
10% Ni/Nb_2O_5 (573(1) 773 Ar(1))	16(548)	112	103	0.89	189
10% Ni/TiO_2 LTR	76(548)	...	138	...	190
10% Ni/TiO_2 HTR	35(548)	...	138	...	190
10% Ni/Ti_2O_3 LTR	14(548)	...	113	...	190
10% Ni/Ti_2O_3 HTR	22(548)	...	130	...	190

Catalyst designation: Percent loading/metal/support/temperature of reduction (time of reduction)
TOF: Number of molecules per surface metal atom per second (temperature of reaction)
@: 2 refer to dispersion 300 and 600 refer to reduction temperature
$^+$ Refer to average values

Table X

Kinetic Parameters for Ethane Hydrogenolysis on Supported Catalysts

Catalyst	TOF molecules per surface atom		E KJ mol^{-1}		Ref.
	LTR	HTR	LTR	HTR	
3% Rh/MgO (98%)	1.05(573)	3×10^{-4}	181	185	124
3% Rh/mgO (99.5%)	2.2 (573)	5×10^{-6}	206	206	124
2% Rh/MgO (99.999)	1.2 (573)	0.52	210	185	124
25 Rh/MgO (1% CaO)	1.75(573)	1.23	202	198	124
2% Rh/MgO (0.5% Fe^{3+})	1.85(573)	1.07	185	193	124
2% Rh/MgO (.3% SO_4^{2-})	1.92(573)	8.3×10^{-4}	210	214	124
2% Ni/Nb_2O_5	1.1×10^{-6} (478)	1.2×10^{-7}	176	180	189
10% Ni/Nb_2O_5	4.9×10^{-6} (478)	1.4×10^{-7}	183	170	189
2% Pd/SiO_2	11.9×10^{-3}	10.5×10^{-3} (673)			166
2% Pd/TiO_2	5.9×10^{-3}	0.4×10^{-3} (673)			166

The activities of supported metal systems for the hydrogenation of benzene and CO, hydrogenolysis of hexane and ethane are given in Table XI for

Table XI

Comparison of Activities of Supported Metal Systems for the hydrogenation of benzene and Carbon monoxide as well as hydrogenolysis of Hexane and Ethane[33,166,168]

Catalyst[a]	Turnover frequency × 10^3 molecules^{-1} metal^{-1}			
	Hydrogenation of		Hydrogenolysis of	
	Benzene	CO	Hexane	Ethane
0.94Ni/S/573	10.8	16.3 (553)	30.5(548)	
1.01Ni/T/573	22.6	305(553)	19.9(548)	
9.8Ni/T/573	12.5	238(553)	43(548)	
0.94Ni/S/723@	14.6	31.9(553)	26.8(548)	
1.01Ni/T/723@	41.5	547(553)	45.6(548)	
9.8Ni/T/723@	23.1	444(553)	55.7(548)	
2Pd/S/673		1.24(573)		11.9 (673)
2Pd/S/773		0.91(573)		9.44(673)
2Pd/T/473		5.71(573)		
2Pd/T/673				5.86(673)
2Pd/T/773		6.28(573)		0.46(673)
2Ir/S/573		0.17(573)		90.4 (535)
2Ir/S/773		0.1 (573)		28.2 (535)
2Ir/T/573		3.0 (573)		36.4 (535)
2Ir/T/773		6.0 (573)		0.01(535)

(a) Catalyst designation percent/metal/support titania (T) or silica (S)/temperature of reduction
The numbers in brackets refer to the temperature of reactions.
@ calcined and reduced at 723 K

both in SMSI and non-SMSI states. Burch has suggested that hydrogenation of benzene may be suitable for evaluating the support effects. It is true that the activity for hydrogenation of benzene is increased in the SMSI state compared to the systems reduced at lower temperatures. But in the case of CO hydrogenation no consistent increase is observed in the SMSI state. In the same way, the activity for the hydrogenolysis of hexane also does not show any definite trend, though the expectation that the hydrogenolysis activity in the SMSI state will be lower than that in the non-SMSI state seems to be true in the case of hydrogenolysis of ethane. The activities for hydrogenation of CO is higher for titania supported systems compared to that of silica supported metal catalysts.

Other Catalytic Reactions

Titania supported group VIII metals exhibit unusual activities and selectivities for several other hydrocarbon reactions, like hydrogenolysis of *n*-butane and cyclohexane and dehydrogenation of cyclohexane[33,93,191,192]. Studies on *n*-hexane reactions over Pt/TiO_2 showed an increase in the amounts of benzene and methyl cyclopentane indicating that on titania supported systems cyclization is preferred over isomerization[166]. Similar studies of *n*-pentane over Pt/TiO_2 showed that while hydrogenolysis is suppressed cyclization is enhanced by a factor of ten[193]. For *n*-butane hydrogenolysis an order of magnitude decrease in rate on Rh/SiO_2 has been reported by Braunschweig *et al.*[194] due to annealing of the oxygen roughened surface. On the other hand three orders of magnitude decrease is reported on Rh/TiO_2 due to site blocking by amorphous TiO_x overlayers (at 473 K).

It has been observed that the loss of catalytic activity for these reactions after high temperature reduction can be restored after by mild oxidation followed by LTR for the same way as the chemisorption capacity is restored[192,195].

Titania supported iron catalysts showed a lower activity for ammonia synthesis after reduction at 700 and 773 K than for Fe/MgO or Fe/SiO_2[190]. The decomposition of formic acid has been found to be more rapid on Rh/TiO_2 than on Rh/SiO_2[196].

The hydrogenolysis of methyl cyclopentane has also been used as a model reaction to compare the activities of titania and silica supported group VIII metals. The essential data are given in Table XII. Generally one observed high turn over frequency on titania supported systems as compared to silica supported group VIII metals.

Table XII

Comparison of activities of silica/titania supported catalysts for the hydrogenolysis of methylcyclopentane

Catalyst	H/M	TON	% Hexane	ln A	Ref.
Pt/SiO_2 [573]	0.12	1.28^{*}(503)	14.3	16.7	197
Pt/SiO_2 [773]	0.17	0.85^{*}(503)	17.6	16.1	197
Pt/TiO_2 [573]	0.59	0.97^{*}(483)	22.2	8.7	197
Pt/TiO_2 [773]	<0.01	...	...		
3% Rh/SiO_2 [473]		3.0^{*}(433)	5.0		198
5% Rh/TiO_2 [473]		46^{*}(433)	8.5		198
5% Rh/TiO_2 [773]		3.5^{*}(433)	7.0		198
2% Rh/TiO_2 [723]		...	1.7[480]		199
3% Rh/TiO_2 [573]		...	4.1[473]		199
3% Rh/TiO_2 [933]		...	3.6[474]		199
3% Rh/TiO_2 [1133]		...	5. [474]		199
25% Pt/TiO_2 [573]		1.6^{+}(472)	14		200
		28.9^{+}(533)	16		200

$^{*}10^3$ molecules $MCPs^{-1}$ per surface atom
$^{+}$molecules $s^{-1}g_{Pt}^{-1} \times 10^{-18}$

A higher activity for reduction of NO by CO was observed on titania supported Rh, Pd, Pt reduced at 723 K compared to the alumina supported catalysts[201]. The formation of ammonia an unwanted byproduct, was also suppressed on titania supported catalysts. From IR studies it was suggested that increased dissociation of NO might have been responsible for the enhanced activity. The promoting action of titania on Rh/SiO_2 for the reduction of NO by hydrogen or CO was studied by Pande and Bell[202,203]. The addition of titania enhanced the activity and was attributed to the creation of new sites namely reduced titania species. The use of CO instead of hydrogen was found to diminish the promoting effect of TiO_2. This was explained as being due to the formation of isocyanate species which can block the TiO_x centres. Similar to CO hydrogenation, the promoting effect of TiO_2 is not related to the high temperature reduction as the HTR caused a lowering of activity compared to LTR.

The enhanced activities and selectivities observed for CO hydrogenation on titania supported group VIII metals prompted Sen and Vannice[204] to study the activation of carbonyl bonds in general on these systems. Very large increases in both turnover frequencies and specific activities for acetone hydrogenation were observed on Pt/TiO_2 after HTR. The authors suggested that the carbonyl bond was polarized to a greater extent on the HTR catalyst leading to higher activity. They extended their investigation to the hydrogenation of α,β unsaturated aldehyde namely crotonaldehyde on support platinum catalysts[205]. It has been well documented in literature that the catalytic hydrogenation of α,β unsaturated aldehydes is a difficult proposition than the hydrogenation producing saturated aldehydes or ketones[21]. The preferential formation of saturated aldehydes has been related to thermodynamic and kinetic factors[206]. From a thermodynamic point of view it should be considered that the energy of the $C=C$ double bond (615 KJ/mol) is smaller than that of the $C=0$ bond (715 KJ/mol). From a kinetic point of view it is well known that hydrogenation of $C=C$ bonds occurs at a faster rate even at low temperatures over platinum metals. The enhanced selectivity to unsaturated alcohols over group VIII metals has been achieved by alloying[207] or by the use of promoters[208] and by utilizing the shape selective features of zeolites[209,210]. However, studies on the effect of metal support interaction for the selective hydrogenation of α,β unsaturated aldehydes are fewer. Wismeijer *et al.*[211] reported that Ru/TiO_2 has greater activity and selectivity than Ru/SiO_2 for $C=0$ bond hydrogenation compared to $C=C$ bond hydrogenation. However, the selectivities for crotyl alcohol during crotonaldehyde hydrogenation were not reported. In a study on the selective hydrogenation of crotonaldehyde on supported cobalt catalysts Nitta *et al.*[212] observed that the activities and selectivities are dependent on the cobalt precursor used than on the nature of the support. The use of a chloride precursor always resulted in a catalyst showing higher selectivity to the alcohol. Moreover, the degree of reduction of cobalt on the catalysts used namely, Co/TiO_2, Co/SiO_2, Co/Al_2O_3, Co/ZrO_2 and Co/C was above 90%. Further more only a marginal increase in the selectivity to alcohol was observed on Co/TiO_2 catalyst after high temperature reduction. The silica and alumina supported catalysts showed comparable selectivities to alcohol as the titania supported catalyst.

Vannice and Sen[204] studied the effect of strong metal support interaction on the selectivity of hydrogenation of crotonaldehyde over supported platinum catalysts. They observed that titania supported systems to be more selective towards crotyl alcohol than silica and alumina supported catalysts which were totally nonselective to crotyl alcohol. Among the titania supported catalysts the overall activities were lower on the HTR catalysts compared to the LTR catalysts whilst the turnover frequencies were just the opoosite. Furthermore, only 1.9% Pt/TiO_2 catalyst showed high selectivity to crotyl alcohol after HTR with all other catalysts exhibiting a lower selectivity after HTR. The authors attribute this to the higher activity for crotyl alcohol hydrogenation to butanol. It is suggested that the optimum catalyst dependent on the $Pt-TiO_x$ interfacial area. From a study[162] of the deuteration of acrolein as well as 3,3,3-trifluropropene on Pt/Nb_2O_5 catalysts Yashitake and Iwasawa[162] propose that in LTR catalyst a conventional associative mechanism involving η^2 (C−C) and η^2(C−O) species is involved while on HTR catalyst a η^4 (C−C−C−O) intermediate species is involved on the peripheral sites of migrated NbO_x islands, thus lending support for the oxide migration concept in SMSI state. However, it should be stated that the proposal of Yoshitake and Iwasawa[162] is opposite to the general belief that dissociative mechanism predominates in SMSI state and associative mechanism is preferred in non-SMSI state at least in the case of activation of carbon monoxide. Increased hydrogenation activity for carbondioxide on HTR (773 K) Pd/CeO_2 (TOF 14.3 at 503 K) is reported as compared to the LTR (473 K) (TOF 0.93 at 503 K) system[162]. It can therefore be deduced that the study of titania based systems for selective hydrogenation reactions is in its infancy. Detailed investigations are necessary to study the influence of metal support interactions on the selective hydrogenation of a host of organic substrates.

Epilogue

The present review has considered only one aspect of SMSI behaviour, namely the possible reasons for this effect. It is clear that though both electronic and geometrical factors contribute to varying extents depending on the nature of the metal and support one cannot exclude completely the other apparent causes like hydrogen spillover and presence of impurities. There is growing convergence for oxide migration and encapsulation of metal particles in supported systems especially in the case of supported rhodium catalysts, but one cannot at this stage postulate on the nature of the microscopic and electronic perturbations caused at the surface sites which can alone account for the observed suppression in chemisorption capacity for hydrogen and carbon monoxide and increased reactivity for carbon monoxide hydrogenation. The proposals of Burch and his coworkers is one such in this direction. The reviewer has to admit that some of the authors including the reviewer himself have attempted to rationalise their results at various stages of their work on the basis of different models instead of attempting to synthesise the results in one unified framework. This may be due to the fact that the scientific community was totally confused and hence resorted to alternate explanations for their experimental observations instead of developing experimental data always to support one of the models chosen for explaining the data initially.

In accordance with the established traditions we conclude with certain posers for which answers are yet to be evolved. Some of them are:-

1. Is there an isolation procedure by which the contribution component of each of the effects to the observed SMSI behaviour can be evaluated?

2. Can at all the SMSI behaviour lead to a process of tailor-making of the catalysts for at least some or even one reaction?
3. What are the criteria that can be used to decide, whether a given reaction or adsorption of a gas will be affected in the SMSI state?
4. Why SMSI behaviour is peculiar to group VIII metals alone?
5. Is there any logistics for the selection of support and reduction conditions for the onset of SMSI behaviour?
6. If SMSI behaviour is removed by subsequent oxidation then can the inherent oxidising atmosphere prevalent during the CO hydrogenation reaction (by the dissociation of CO and the water formed during the reaction) restore the normal properties of the supported metal catalysts?
7. For a given reaction with a chosen support can one predict the trend of activity variation in the SMSI state for a given set of group VIII metals?

True to scientific evolution, further systematic studies with resolve to answer these posers alone can unravel some of the intriguing aspects of SMSI state. At this stage, the available literature leads to an impression that the SMSI state may even be an artifact.

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