CLUSTER MODEL FOR STRONG METAL SUPPORT INTERACTION (SMSI) STATE

B. VISWANATHAN
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

ABSTRACT

The charge transfer from support to the metal in the SMSI state and the observations of chemical shifts of core levels of metals in the SMSI state are rationalised in terms of a cluster model consisting of surface species for the reduced support and metal. The applicability of this model for TiO_2/metal system is considered.

INTRODUCTION

When a group VIII metal is dispersed atomically or in clusters on a support oxide matrix, a model system for practical supported catalysts, the valence state of these dispersed species should be different from that of zero valency due to differences in the environment and consequent chemical interaction. The usual high temperature pretreatments is not suitable for model systems, because it will simultaneously induce other apparent or secondary effects like encapsulation, oxide migration, alloy formation, retention of species used for pretreatment, contamination and segregation of impurities. The studies so far reported on Strong Metal Support Interaction (SMSI) state have this built-in multiplicity and hence could not be unequivocal regarding the chemical interaction and the consequent charge transfer. Experimentally, following the postulates of Exxon group (1,2), SMSI state is identified by the considerable reduction in chemisorption capacity for CO and hydrogen or by altered catalytic activities for ethane hydrogenolysis (decrease) and CO hydrogenation (increase). Electron microsopic examination of this state (3) has revealed that the metal species are dispersed on oxide matrices in a decorative fashion with pill-box morphology. Ideal layer by layer growth model (4) has been shown to be applicable at the initial stages of the formation of model systems for this state. It is known that energetically a two dimensional cluster formation is favourable as against the three dimensional clusters with spherical particle morphology. Horsley (5) considered the inclusion of Pt atoms in the anion vacancies of reduced TiO_2 lattice within the framework of X_α-SCF-SW calculations and has concluded that the platinum atoms should be negatively charged to the extent of 0.6 electron /Pt atom. Titanium dioxide is the common support on which SMSI state has been observed for a number of metals as a result of high temperature reduction. The inadequacy of the cluster size and complexity considered by Horsley for the deductions made, has been pointed out by Henrich (6), though Horsley (7) feels that the representation of SMSI state by a larger cluster model will also yield results similar to his original calculations. Attempts have also been made to identify the valence state of metal atoms or clusters in the SMSI state by X-ray photoelectron spectroscopy. These studies summarized in Table 1 have not led to an unambiguous postulate regarding the charge state of metal atoms in SMSI state, probably because, the SMSI state in model systems has been induced by the same hydrogen treatment at higher temperatures ($>$ 773 K) (21) as has been used for practical systems. As stated earlier, this pretreatment induces other secondary effects thus, sometimes precluding the identification of primary chemical interaction. The observations that a constant Ti^+/Rh^+ SIMS signal intensity is observed after an initial decrease and before a steep increase (22) and the Rh AES signal amplitude (23) increases before the normal declining trend as a function of sputtering time show that in most of the cases the high temperature treatment often results in pronounced secondary effects like encapsulation, oxide migration and so on. Under these circumstances, the identification of electronic effects in SMSI state by experimental methods seems to be difficult. It may be possible only if the SMSI state could be introduced without involving high temperature reduction. This has been attempted by Chung et al. (8,20) who used ion bombardment as a means for producing the reduced state of the support

TABLE 1

Observed binding energy shifts of core levels of metals in SMSI state.

Metal	Support	Level probed	Binding energy or shift eV	Cause	Ref
Ni	TiO_2	$2p_{3/2}$	-0.4	Charge transfer	8
Ni	Si/SiO_x	$2p_{3/2}$	-0.4	Charge transfer	9
Ru	Al_2O_3	$3d_{5/2}$	2.0 lower to Ru (0)	alloy formation	10
Rh	ZnO	$3d_{5/2}$	307.1	Rh-Zn bond	11
Rh	TiO_2	$3d_{5/2}$	-0.7^+ 0.2^*	Charge transfer	12

Metal	Support	Level probed	Binding energy or shift eV	Cause	Ref
Rh(2%)	TiO_2	$3d_{5/2}$	-0.6^+	Charge transfer	
Rh(1%)	V_2O_5	$3d_{5/2}$	-0.3^+	Charge transfer	13
Rh(1%)	Nb_2O_5	$3d_{5/2}$	-0.3	Charge transfer	
Rh	Si/SiO_x	$3d_{5/2}$	-0.3	Charge transfer	14
Rh	TiO_2	$3d_{5/2}$	0.0	Encapsulation and spalling	15
	Al_2O_3	$3d_{5/2}$	0.0		
Pd	ZnO	$3d_{5/2}$	336	Pd-Zn bond	16
Pd	La_2O_3	$3d_{5/2}$	-0.7	Support covers Pd	17
Pt	TiO_2	$4f_{7/2}$	-0.5	Charge transfer	18
Pt	TiO_2	$4f_{7/2}$	-1.6	Charge transfer	19
Pt(1%)	TiO_2	$4f_{7/2}$	-0.4^+	Charge transfer	13
Pt	TiO_2 Al_2O_3	$4f_{7/2}$ $4f_{7/2}$	0.0 0.0	Encapsulation and spalling	15
Pt	TiO_2	$4f_{7/2}$	0.4	Morphology and electronic effect	4
Pt	$SrTiO_3$	$4f_{7/2}$	-0.3	Charge transfer	20

$^+$ Initial value *after cycling.

and by Viswanathan et al. (9,14) who have formed a reduced form of SiO_x on n- and p- Si as the support for identiying the valence state of metal atoms dispersed. The results of these two studies wherein the initial state chemical shift has been employed for deductions made, instead of the observed binding energy shifts, support a localized charge transfer model for the SMSI state. The purpose of this communication is therefore to analyse the validity of this model in terms of the relative position of the energy levels of the support and metal clusters normally formed on supported catalysts.

RESULTS AND DISCUSSION

In figure 1 the energy level scheme for a model cluster of oxidised and reduced forms of TiO_2 (24) are given together with the energy level schemes for 13 atom clusters of typical group VIII metals. For the case of nickel, the electronic energy levels as computed by EHT method are also included for comparison. The choice of 13 atom clusters is based on the EXAFS observation (25) that the metal atoms usually form a cubo-octahedral clusters on support phase as a result of high temperature calcination and reduction. However, since the model system studies (4) and electron microscopic investigations (3) favour a two dimensional cluster formation for metal dispersion on supported phase, this situation is considered in terms of a 5 atom cluster. However, the discussion in this paper will pertain to 13 atom cluster model systems only since the deductions for 5 atom cluster model systems are similar. The selection of TiO_2 as the representative for the support phase is based on the fact that SMSI effect has been observed on this support for almost all group VIII metals (26). However the considerations given are equally applicable to other supports in their reduced forms (9,14). In this presentation, the insertion of metal atoms in the anion vacancies created as a result of reduction is not considered because of the following considerations:

1. The tolerable limits of anion vacancies cannot account for the extent of metal dispersions usually observed on supported catalysts.
2. The computations by Horsley (5) have shown mixing of the 'd' orbitals of Ti and Pt is not considerable compared to the ionic bonding.
3. It is known that metal atoms segregate on the surface in islands due to minimization of surface free energy and the possibility of maximum wetting with the support phase (26,27).,
4. Most of photo-electron spectroscopic observations favour a charge transfer model (8,9,12-14,18-20)
5. The reactivity alterations brought about as a result of SMSI cannot be accounted for by such direct metal-metal bonding alone though Burch and his coworkers (28), Vannice and Sudhakar (29) as well as Ponec et al (30) postulate that the interface is the active site, and the reactants are activated by a cooperative action of the metal and metal ion (of the support).

In the energy level scheme (Fig.1) for the surface cluster representing rutile (110) (the stable phase) the occupied levels are composed of oxygen 2p levels while the empty conduction levels are mostly made up of Ti 3d orbitals. The levels just below

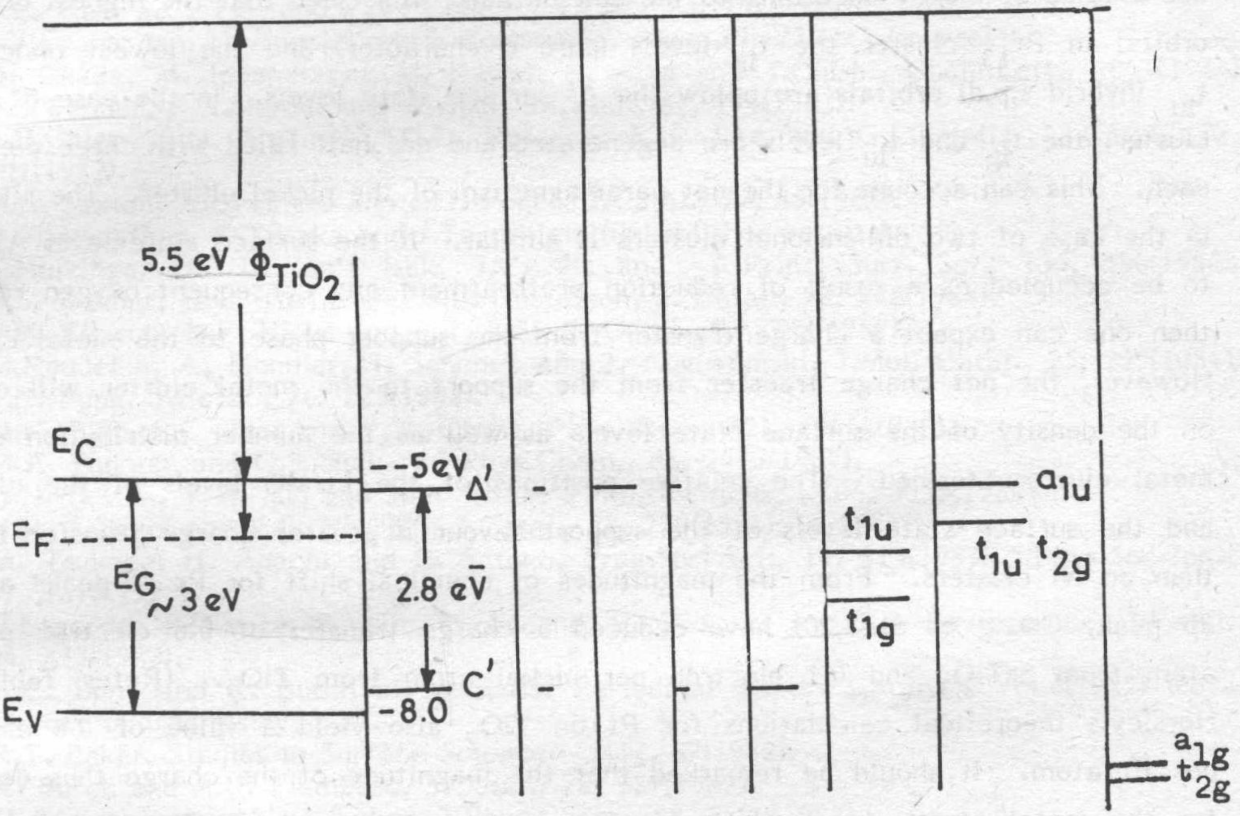

Fig.1 Energy level diagram for bulk TiO_2, surface states of $TiO_2(110)$ an d the extent of contributions to the surface states from coordinatively saturated Ti(1) coordinatively unsaturated Ti(2), oxide ion in normal position 0(1) and protruding oxide ions 0(2). The position of the highest occupied level and the lowest unoccupied levels for Pt_{13} and Ni_{13} clusters as obtained by X_α method and that for Ni_{13} by the EHT method. The t_{1u} and t_{2g} levels are half filled for Ni_{13} cluster while the t_{1u} levels are fully occupied for Pt_{13} clusters as per X_α calculations.

(C') and above (A') Fermi level are contributed predominantly from the 2p states of protruded oxygen ions, and 'd' states of coordinatively unsaturated Ti ions respectively. These levels can be considered to be the surface state levels since the position of these levels lie in the band gap of the bulk cluster. The experimental proof that such surface state levels really exist comes from ELS studies of Chung et al.(31) who have observed a peak at 2.4 eV on Ar bombarded surface which corresponds to transition from oxygen surface state (C') to the titanium surface state levels (A') which has a value of 2.8 eV according to the calculations. It is seen that the highest occupied orbital in Pt$_{13}$ cluster the t$_{1g}$ levels (pure d character) and the lowest unoccupied t$_{1u}$ (hybrid s,p,d) orbitals are below the A' surface state levels. In the case of nickel cluster, the t$_{1g}$ and t$_{1u}$ levels are degenerated and are half filled with three electrons each. This can account for the net paramagnetism of the nickel cluster. The situation in the case of two dimensional clusters is similar. If the surface state level A' were to be occupied as a result of reduction pretreatment and consequent oxygen removal then one can expect a charge transfer from the support phase to the metal cluster. However, the net charge transfer from the support to the metal cluster will depend on the density of the surface state levels as well as the number distribution of the metal clusters formed. The relative positions of the LUMO levels of the clusters and the surface state levels of the support favour a greater charge transfer for Pt than on Ni clusters. From the magnitudes of chemical shift for Pt 4f peaks and Ni 2p peak, Chung et al.(8,20) have deduced a charge transfer of 0.6 electron per Pt atom from SrTiO$_3$ and 0.1 electron per nickel atom from TiO$_2$. (Refer Table 2) Horsley's theoretical calculations for Pt on TiO$_2$ also yield a value of 0.6 electron per Pt atom. It should be remarked that the magnitude of the charge thus deduced for the metal atoms dispersed on supports is an average value. The net charge on the individual metal atoms will depend on the size and geometry of the clusters formed and probably can account for the variation of activity with dispersion.

TABLE 2
Charge state of metal species on TiO$_2$ based supports.

Metal	Support	ΔBE eV	ΔKE eV	ΔE eV	ΔR eV	Charge on metal
Pt	SrTiO$_3$(100)	0.3	-1.9	-0.5	-0.8	0.6± 0.1
Ni	TiO$_2$(100)	0.4	- 2.0	-0.4	-0.8	0.1± 0.05

REFERENCES

1. S.J. Tauster, S.C.Fung and R.L. Garten, J.Am.Chem.Soc., 100, 170(1978).
2. Metal Support and Metal Additive Effects in Catalysis (Ed) B. Imelik, Elsevier, Amsterdam, 1982.
3. A.J. Simoens, R.T.K. Baker, D.J. Dwyer, C.R.F. Lund and R.J. Madon, J. Catal., 86, 359(1984) and references therein.
4. D.N. Belton, Y.M. Sun and J.M. White, J.Phys. Chem., 88, 1690(1984).
5. J.A. Horsley, J.Am.Chem.Soc., 101, 2870(1979).
6. V.E. Henrich, J.Catal., 88, 519(1984).
7. J.A. Horsley, J.Catal., 88,549(1984).
8. C.C. Kao, S.C. Tsai and Y.W. Chung, J.Catal., 73, 136(1982).
9. B.Viswanathan, K. Tanaka and I. Toyoshima, Chem.Phys.Lett., (in press).
10. O. Okada, M. Ipponmatsu, M. Kawai, K. Aika and T.Onishi, Chem.Lett., 1041(1984)
11. P.S.Wehner, P.N.Mercer and G.Apai, J.Catal., 84, 244(1983).
12. S.H.Chien, B.N. Shelimov, D.E. Resasco, E.H. Lee and G.L. Haller, J.Catal., 77, 301(1982).
13. B.A. Sexton, A.E. Huges and K.J. Foger, J.Catal., 77, 85(1982).
14. B.Viswanathan, K.Tanaka and I.Toyoshima (unpublished results).
15. T.Huizinga, H.F.J. Van't Blik, J.C. Vis and R.Prins, Surf. Sci., 135, 580(1983).
16. P.S. Wehner, G.C. Tustin and B.L. Gustafson, J. Catal., 88, 246(1984).
17. T.H. Fleisch, R.F. Hicks and A.T. Bell, J. Catal., 87, 398(1984).
18. M.Koudelka, A. Monniar, J. Sanchez and J. Augustynski, J.Mol. Catal., 25, 295(1984).
19. S.C. Fung, J.Catal., 76, 225(1982).
20. M.K. Bahl, S.C. Tsai and Y.W. Chung, Phys. Rev., B21, 1344(1980).
21. M.A. Vannice and C.Sudhakar, J.Phys.Chem., 88, 2429(1984).
22. D.N. Belton, Y.M. Sun and J.M. White, J.Am.Chem.Soc., 106, 3059(1984).
23. H.R. Sadeghi and V.E. Henrich, J.Catal., 87, 279(1984).
24. M. Tsukada, H. Adachi and C. Satoko, Prog.Surf.Sci., 14, 113(1983), J.Phys.Soc.Jpn., 47, 1610(1979).
25. P.Lagarde, T.Murata, G.Vlaic, E. Freund, H. Dexpert and J.P. Bournonville, J.Catal., 84, 333(1983).
26. G.C. Bond and R. Burch, in: Specialist Periodical Report Catalysis Vol.6(1982) Royal Society of Chemistry, p.27.
27. R.T. Baker, Studies in Surface Science .17, 37(1982).
28. R. Burch and A.R. Flambard, J.Catal., 78, 389(1982).
29. M.A. Vannice and C.Sudhakar, J.Phys.Chem., 88, 2429(1984).
30. J.M. Driessen, E.K. Poels, J.P. Hindermann and V.Ponec, J.Catal., 82, 26(1983).
31. Y.W. Chung, W.J. Lo and G.A. Somorjai, Surf.Sci., 64, 588(1977).