

NITROGEN CHEMISORPTION SUPPRESSION IN THE STRONG METAL SUPPORT
INTERACTION STATE OF Co/TiO₂ CATALYST

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Table 2 Experimental data and calculated values of Q for F.C.C. metals

Metal	K (GPa) (1, 2)	G (GPa) (1, 2)	$\Omega \times 10^{30}$, (m ³) (3)	Q observed, (Kcal/mol) (3)	Q calculated, (Kcal/mol)
Al	78.89	25.00	16.5	34.50	35.51
Ca	18.26	7.38	43.4	38.50	27.39
Ni	190.00	76.00	10.9	67.86	70.97
Cu	133.50	46.40	11.8	50.40	46.84
Pd	184.39	45.00	14.7	63.30	56.89
Ag	99.69	30.30	17.0	45.20	44.26
Pb	40.40	5.59	30.3	25.65	14.74
Ce	19.80	12.00	34.3	36.60	35.09
Pt	275.70	52.82	15.1	66.47	68.80
Au	171.00	26.00	16.9	41.70	38.24
Th	54.00	30.80	32.9	71.60	86.24

W and Ta but relatively poor for metals like Li and Rb. The average difference between the calculated values and experimentally observed values is 19%. Table 2 presents the data and the calculated values of the activation energy for F.C.C. metals. The fit seems to be very good for all elements excepting Pb and Ca. The mean deviation between the calculated and experimentally observed values is 12%.

A look at the empirical equation makes it clear that A and B should be identified as dilational strain and shear strain terms. It is then interesting to note that during diffusion dilational strains are introduced locally in B.C.C. structure, while in F.C.C. structure, primarily shear strains are introduced. Apparently, the B.C.C. structure being open allows the migration of atoms by momentary local expansion and contraction of the adjacent regions. The shear strain is relatively insignificant. F.C.C. structure being closely packed does not permit contraction of adjacent regions. The atomic diffusion, then, involves local shear.

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NITROGEN CHEMISORPTION SUPPRESSION IN THE STRONG METAL SUPPORT INTERACTION STATE OF Co/TiO₂ CATALYST

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THE suppression of chemisorption capacity for CO and hydrogen and the increase in CO hydrogenation activity induced in group VIII metals supported on oxides like TiO₂¹, MgO², Nb₂O₅³, SiO₂ and Al₂O₃⁴, as a result of high temperature (≥ 773 K) reduction (HTR) in hydrogen has been considered to be due to strong metal-support interaction (SMSI)⁵. Earlier studies were confined only to the probe molecules of hydrogen and CO^{6,7}. This has greatly limited the scope of identifying the cause of SMSI behaviour. In this communication, the possibility of using nitrogen as probe species for the SMSI behaviour of Co/TiO₂ system is considered. Reports are available on the characterization of SMSI state of Ni, Ru, Rh, Pd and Pt supported on oxides like TiO₂⁹. Similar studies on Fe and Ir are limited¹⁰ and practically no report is available on supported cobalt systems.

Fifteen per cent cobalt on titanium dioxide was prepared by adding the required amount of aqueous solution of cobalt nitrate to freshly prepared TiO₂ (by the hydrolysis of TiCl₄) powder and dried at 110°C (incipient wetness method) with constant stirring. About 1 g of this sample was reduced at 673 K (LTR) or at 803 K (HTR) in a flow of hydrogen for 3 hr. Adsorption was measured with an accuracy of ± 0.01 ml in a conventional volumetric unit at room temperature at a pressure of 200 torr for 12 hr. CO was hydrogenated at 583 K using a mixture of CO:H₂

= 1:4 at 200 torr pressure. After exposure to CO, either in adsorption or in reaction measurements or after exposure to nitrogen, the surface was regenerated by soaking the sample in hydrogen at 760 torr at 623 K for 15 hr followed by evacuation at 673 K for 4 hr. In the case of hydrogen chemisorption experiments, the surface was regenerated by evacuating at 673 K for 4 hr.

The chemisorption data collected on the model system are given in table 1. It is seen that the chemisorption of all the three probe molecules is suppressed as a result of high temperature reduction. The extent of chemisorption of hydrogen and nitrogen was quite small due to the activated nature of adsorption but are highly reproducible. To ascertain that the catalyst attained the SMSI state as a result of HTR, typical results were obtained for the CO hydrogenation on this model system and are given in figure 1. It is seen that the system after HTR shows increased CO hydrogenation activity though the attainment of steady state activity seems to involve more or less the same time whether the system is in SMSI state or not, and the catalyst in the SMSI state shows approximately the same steady state rate compared to the catalyst obtained after LTR. This observation rules out the possibility of sintering as the cause for the suppression in chemisorption capacity. Tanaka *et al*¹¹ propose that chemisorption of CO could be dissociative on the SMSI system and hence could account for the suppression of chemisorption capacity. Takatani and Chung¹² propose a tilted configuration for the chemisorbed CO (with a loss peak at 1850 cm⁻¹) with simultaneous adsorption of carbon and oxygen of CO on the metal sites as well as on the support sites. The suppression in the chemisorption of nitrogen could be either due to the dissociation of the molecule or due to the precursor state wherein both the atoms are attached to the surface. This form of activation of nitrogen may favour facile subsequent hydrogenation to form ammonia. However, ammonia formation at 303 K and at a pressure of 1 atm of hydrogen was not observed. It is probable that hydrogenation of nitrogen could be

Table 1 Comparison on SMSI and non-SMSI states of Co/TiO₂ catalyst.

Reduction temperature (K)	Gas adsorbed at room temperature (mol/g)		
	Hydrogen ($\times 10^{-6}$)	CO ($\times 10^{-5}$)	Nitrogen ($\times 10^{-6}$)
673	1.34	1.74	3.12
803	0.0	1.12	0.45

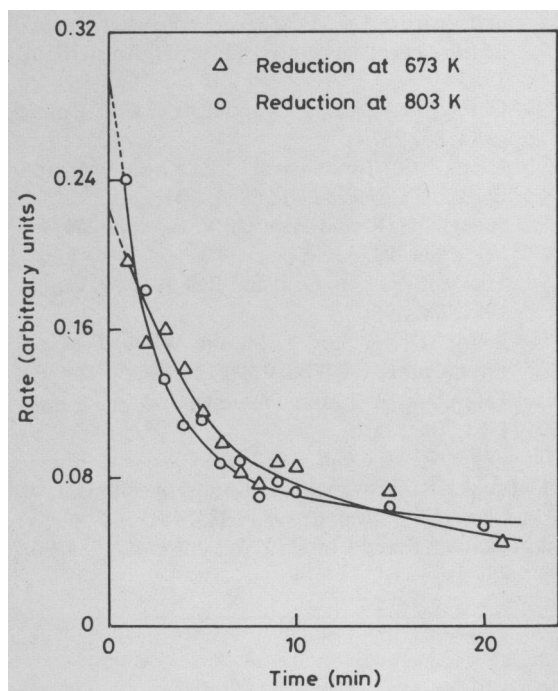


Figure 1. CO hydrogenation rate as a function of time on 15/Co/TiO₂ catalyst after LTR and after HTR.

achieved at considerably reduced pressure and temperature on the SMSI state of the catalysts.

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LIGNOCAINE HYDROCHLORIDE AS A HIGHLY SELECTIVE EXTRACTANT FOR SPECTRO-PHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH THIOCYANATE

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A NUMBER of reagents reported for extraction photometric determination of molybdenum have been reviewed¹⁻³. During our investigation it was found that the sensitivity and stability of the molybdenum-thiocyanate complex could be enhanced by adding lignocaine hydrochloride (LH) to form a new ion-association complex which could be extracted into an organic solvent. The proposed method offers the advantages of rapidity, reproducibility, stability and high sensitivity without the need for heating and dependence of colour intensity upon a number of factors such as volume of aqueous phase, coefficient of expansion of isopentyl alcohol, concentration of iron and tin (II) chloride.

A stock solution of molybdenum (VI) was prepared from AR grade ammonium molybdate tetrahydrate in doubly-distilled water containing a few drops of ammonia, and standardised gravimetrically using 8 hydroxy quinoline⁴. The stock solution was further

diluted to give a standard solution containing 20 μg Mo (VI)/ml.

A 10% aqueous solution of potassium thiocyanate (AR) was prepared. A 5% aqueous solution of ascorbic acid was prepared.

A 2% aqueous solution of LH (ASTRA-IDL) in water was used. Beckman model DB spectrophotometer with 1 cm matched silica cells was used for absorbance measurements.

Recommended procedure: An aliquot of the stock solution containing 1–30 μg of molybdenum(VI), 10 M hydrochloric acid (3 ml), 5% ascorbic acid (2 ml) and 10% potassium thiocyanate (5 ml) solutions were taken in a 150 ml separatory funnel and diluted to 15 ml with doubly-distilled water. The contents in the separatory funnel were mixed and left at room temperature for 15 min. To this was added LH solution (2%, 3 ml) followed by 5 ml of chloroform and the mixture equilibrated for 3 min. The deep orange red chloroform layer was separated and the aqueous solution extracted twice with chloroform (2 \times 5 ml). The chloroform extracts were combined and made upto 10 ml with chloroform, dried (anhyd. Na_2SO_4) and its absorbance measured at 465 nm against a corresponding reagent blank prepared under similar conditions.

Molybdenum (V) formed by the reduction of molybdenum (VI) with ascorbic acid combines with potassium thiocyanate to form a red molybdenum (V) thiocyanate complex in 0.9–3 M hydrochloric acid solution. On adding LH solution an orange-red ion-association complex is formed at the same range of hydrochloric acid concentration. The mixed complex can be extracted into chloroform while binary molybdenum (V)-thiocyanate complex is not extracted.

Molybdenum (V)-thiocyanate complex in 1.5 M hydrochloric acid concentration has an absorption maximum at 465 nm showing a bathochromic shift of 20 nm. The reagent blank in chloroform does not show any absorption either at 445 nm or at 465 nm. All subsequent measurements were made at 465 nm.

Effect of experimental variables: Various water immiscible organic solvents such as benzene, toluene, carbon tetrachloride and chloroform were examined for extracting the ion-association complex. The ϵ values for molybdenum complex in various solvents are, chloroform; 2.12×10^4 ; carbon tetrachloride 4.40×10^2 ; toluene, 1×10^3 ; benzene, $1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Hence chloroform was selected for further studies. A double extraction was