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Evidence for strong metal–support interaction (SMSI) in Rh/TiO_2 system

V. Vishwanathan and S. Narayanan

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Rh(1 wt%)/TiO_2 samples were prepared by both incipient wetness and ion-exchange methods and were characterised by temperature programmed desorption (TPD), electron spin resonance (ESR), mass spectrometry (MS) and hydrogen chemisorption. The incipient wetness sample was found to be more favourable for the onset of SMSI state. The reduction of Ti^{4+} to Ti^{3+} during hydrogen spillover or due to the lattice oxygen (O^{2-}) deficiency seemed to be responsible for the SMSI state. A mechanistic pathway is proposed to explain the onset of SMSI behaviour.

Keywords: Rh/TiO_2; SMSI state; incipient/ion-exchange methods; lattice oxygen (O^{2-}) deficiency; catalyst characterisation

1. Introduction

The interaction between metal and support depends to a large extent upon the reducibility of the support. When a reducible oxide, such as TiO_2 is used as a support for the transition metal, there is a possibility of strong metal–support interaction (SMSI) [1,2]. As a result, the ability to adsorb hydrogen and carbon monoxide decreases while adsorption of nitrogen increases [3–5]. Different postulates have been put forward to explain this SMSI behaviour [6–10]. The presence of –OH groups on the support plays an important role in metal–support interactions [11]. The reducibility of the support due to hydrogen spillover or due to high temperature evacuation inducing migration of TiO_x species over the metal has also been reported [6,12]. The interface formed during SMSI state depends on the method of preparation and activation conditions. In this communication, we present experimental evidences to show how the catalyst preparation conditions along with other pretreatment procedures would influence the interaction between metal and support in the Rh/TiO_2 system.

2. Experimental

Rh(1 wt%)/TiO_2 catalyst samples were prepared by incipient wetness (IW) and by ion-exchange (IE) methods. The support TiO_2 used was of a commercial origin (Tioxide International Ltd., UK; pore volume = 0.3 cm^3 g^{-1}, surface area = 70 m^2 g^{-1}). The incipient wetness sample of Rh/TiO_2 was prepared by impregnating TiO_2 with an aqueous solution of $RhCl_3 \cdot 3H_2O$, dried overnight and calcined in air at 623 K for 3 h. In the case of the ion-exchange sample, about 3 g of TiO_2 was refluxed at 373 K for 20 h in 70 cm^3 of solution of known concentration of $RhCl_3 \cdot 3H_2O$ in NH_4OH at pH = 11. After 20 h of refluxing, the mixture was filtered hot, dried at 423 K and then calcined in air at 623 K for 3 h.

Temperature programmed desorption experiments were carried out in conjunction with a proportional temperature controller at a fixed heating rate. Adsorption (H_2 and N_2) measurements were performed at room temperature in a constant volume high vacuum apparatus on the catalyst reduced at low temperature (LTR, 523 K) and at high temperature (HTR, 773 K) in a hydrogen flow (0.226 mol h^{-1}). The details of experimental measurements for ESR and mass spectrometry have been reported elsewhere [5,12].

3. Results and discussion

The influence of preparation method plays an important role on the onset of SMSI behaviour. The TPD profile of water with respect to temperature is shown in

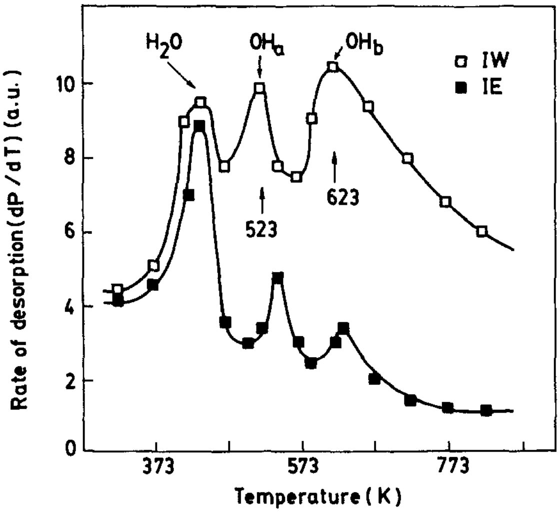


Fig. 1. TPD profile of water with respect to temperature.

fig. 1 observed from the calcined samples of Rh/TiO_2 prepared from incipient wetness and ion-exchange methods.

Both IW and IE profiles show three distinct regions from where water desorbs from the surface of Rh/TiO_2. The first peak below 473 K suggests the desorption of molecular water while the other two peaks, one at 523 K and the other at 623 K, correspond to two types of OH groups bound strongly to the surface of the support. The support TiO_2 (anatase) alone has been reported to show a similar pattern as that of Rh/TiO_2 [13]. Infrared studies have reported [14] the presence of two kinds of OH bonds, namely at 3715 and 3670 cm^{-1} on a high surface area TiO_2 support. This is further confirmed by ^1H NMR study on TiO_2 surface [15]. It is possible that one type of hydroxyl (OH_a) is bound to co-ordinately saturated Ti^{4+} ions while the second type (OH_b) is bound to lattice O^{2-} ions via H-bonding. This is an agreement with the model proposed by Boehm [16]. The two types of hydroxyls differ in their strength of basicity, OH_a being less than OH_b [17]. The quantitative difference in the amount of desorbed water from the two samples (IE and IW) suggests that more free OH groups are available on IW samples than on IE samples. It is true that because of ion-exchange, the Rh ion is bound to the surface OH groups and has fewer OH groups for desorption.

To test the validity of SMSI behaviour on the two types of samples, hydrogen adsorption measurements were studied at room temperature. The amount of adsorbed hydrogen measured on reduced Rh/TiO_2 samples at room temperature under LTR and HTR conditions is shown in fig. 2. Both the IE and IW samples show nearly equal uptake at LTR conditions. However, when reduced at HTR, IW

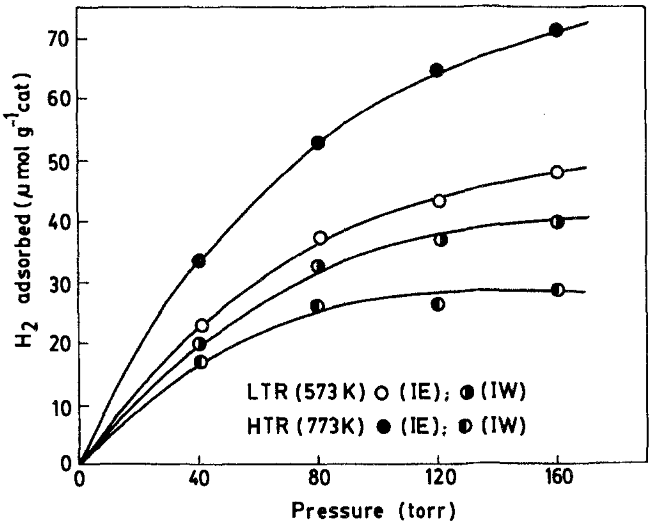


Fig. 2. Hydrogen adsorption on reduced Rh/TiO_2 at room temperature under LTR and HTR conditions.

only shows a decrease in hydrogen uptake while IE shows an increase. The drop in the hydrogen uptake in the IW sample suggests the onset of SMSI state and supports further the assumption that Rh metal sites are covered with TiO_x moieties arising due to the reduction of support.

The influence of calcination prior to reduction on Rh/TiO_2 samples prepared from IW sample is shown in table 1. Hydrogen adsorption measurements were used [18] to calculate the metal area, dispersion and crystallite size of Rh metal particles. The behaviour of calcined and uncalcined samples is quite the opposite. The hydrogen uptake of the sample whether it is under LTR or HTR condition, increases with increase in reduction time for the uncalcined samples. The decrease in the chemisorption capacity for hydrogen as a result of HTR of supported metal catalysts is indicative of the SMSI state in these systems.

In the case of uncalcined sample, with increasing time of reduction, the support species is also simultaneously reduced (as evidenced from the presence of Ti^{3+} species) and migrates over the metallic Rh particles. The blocking of the available sites, as a result of this migration, thus decreases the chemisorption of hydrogen with reduction time. The migration appears to be facile in the case of uncalcined samples subjected to HTR treatment as revealed by the greater initial decrease in chemisorption capacity with reduction time. While in the case of calcined samples, the increase in adsorption capacity with reduction time shows that the reduction to active metallic particles increases with reduction time and this results in an increase in the active adsorption centres. Under HTR condition, this rate is low because of the difficulty involved in the reduction of the active metal oxide obtained as a result of calcination.

The blockage of Rh particles by TiO_x moieties is explained by the decoration

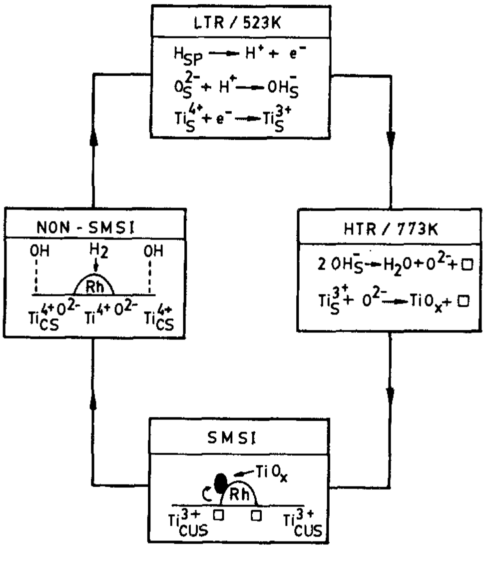
Table 1
Adsorption data on Rh(1 wt%)/TiO_2 catalysts in relation to the SMSI effect

Pretreatment	Reduction temp. (K)	Reduction time (h)	Uptake (μmol g^{-1} cat)	Dispersion (H/Rh)	Metal area (m^2 $g(Rh)^{-1}$)	Crystallite size (nm)
uncalcined	LTR	3	20	0.41	182	2.65
	(523)	8	15	0.31	136	3.54
		15	14	0.30	127	3.80
	HTR	3	19	0.39	172	2.80
	(773)	8	7	0.14	63	7.65
		15	5	0.10	45	10.71
calcined	LTR	3	18	0.37	163	2.96
	(523)	8	31	0.64	281	1.72
		15	32	0.66	290	1.66
	HTR	3	6	0.12	54	8.93
	(773)	8	13	0.27	118	4.08
		15	21	0.43	190	2.54

model in the literature [19]. Scheme 1 explains the mechanistic pathway involved in the reduction from non-SMSI state to SMSI and back to non-SMSI state. In the case of the IW sample, the loss of –OH groups changes co-ordinately saturated Ti^{4+} species into co-ordinately unsaturated Ti^{3+} species (Ti^{3+}_{cus}). The transformation of Ti^{4+}_{cs} to Ti^{3+}_{cus} and the presence of anion vacancies created by lattice oxygen deficiency at HTR condition are responsible for the onset of SMSI behaviour. In contrast, the increase in hydrogen uptake with IE sample at HTR condition is due to the absence of any coverage of TiO_x species over Rh sites. From these observations, it may be inferred that SMSI state is induced for the sample prepared by incipient wetness method and not by ion-exchange.

The reduction of Ti^{4+} to Ti^{3+} and the presence of lattice oxygen deficiency as the origin of SMSI in the Rh/TiO_2 system are shown in fig. 3. The samples of Rh/TiO_2 reduced at various temperatures gave rise to two ESR signals [5]. The signal progressively increased in intensity with increase in reduction temperature. At the same time, there is a desorption of oxygen arising due to loss of lattice oxygen from the oxide surface. Desorption of oxygen was significant only beyond 623 K, as analysed by an on-line mass spectrometer, and thereafter increased with temperature.

The adsorption of H_2 and N_2 molecules with increase in reduction temperature is also shown in fig. 3. The decrease in H_2 adsorption on the pre-reduced samples between 473 and 773 K confirms that the system under consideration attains a SMSI state after HTR condition. The amount of N_2 adsorbed is less significant upto 573 K, but beyond this temperature there is a sharp rise in nitrogen adsorp-



Scheme 1. Mechanistic pathway involved in the reduction from non-SMSI state to SMSI and back to non-SMSI state.

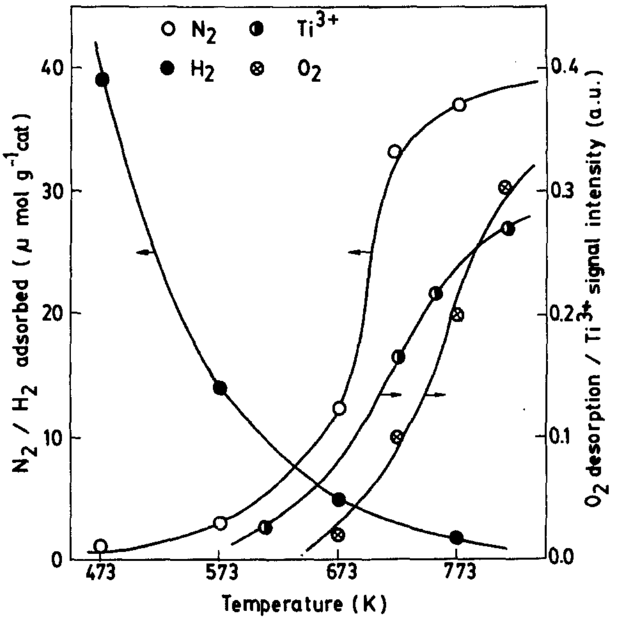


Fig. 3. Adsorption of N_2/H_2 and desorption of O_2/Ti^{3+} signal intensity with respect to temperature.

tion. This coincides with the increase in the signal intensity of Ti^{3+} at 573 K. This suggests the possibility of a direct interaction between Ti^{3+} and the nitrogen molecule. This property when considered along with our earlier work on the sequential adsorption of hydrogen on the preadsorbed surface of Rh/TiO_2 surfaces [20] would make an SMSI catalyst as a potential electron donor.

4. Conclusion

Our observations show that the method of preparation of Rh/TiO_2 samples affects the surface chemistry of the catalysts. For example, Rh/TiO_2 prepared by the incipient wetness method possesses more surface hydroxyls before reduction compared to the samples prepared by ion-exchange. This along with severe activation treatments such as removal of surface OH groups and creation of lattice oxygen vacancies either due to hydrogen spillover or high temperature evacuation would lead finally to the onset of SMSI behaviour.

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