Surface analysis of supported platinum catalysts—encapsulation model for metal-support interaction: An XPS study

R Malathi, P Madhusudhan Rao, B Viswanathan & R P Viswanath
Department of Chemistry, Indian Institute of Technology, Chennai 600 036, India
Received 14 January 1998; accepted 29 June 1998

The surface properties of supported platinum catalysts have been investigated using hydrogen chemisorption and XPS. A mixed oxide system, Pt/TiO$_2$-Al$_2$O$_3$ has been compared with titania-supported systems. A metal-support interaction after high temperature reduction (HTR) has been observed in these systems. The chemisorption measurements indicate a weak suppression in hydrogen uptake after HTR for the mixed oxide system. The encapsulation of the metal particles by the reduced support after reduction at 773K has been elucidated based on the difference in the binding energies between oxygen atom and the support metal. This has been found to be more marked for TiO$_2$ prepared from gel and for mixed oxide samples than for the commercial TiO$_2$. The role of the SMSI state in catalytic activity towards reduction of cinnamaldehyde has also been investigated.

Supported metal catalysts have been used extensively in heterogeneous catalysis. Many investigations have been inspired by the possibility that an interaction between the metal crystallite and the support can alter the chemisorptive properties of the catalyst. Evidence for this concept has been provided by Sinfelt et al.\textsuperscript{1} Earlier, Schwab\textsuperscript{2} and Solymosi and Szabo\textsuperscript{3,4} have attempted to investigate metal-support interactions induced by supporting the metal with reducible transition metal oxides. This effect has been studied using noble metals supported on TiO$_2$, Al$_2$O$_3$, SiO$_2$ and other oxides. The interaction of the noble metals with TiO$_2$ support has been deduced from H$_2$ and CO chemisorption measurements at room temperature by Tauster and Fung\textsuperscript{5} and it has been shown that these systems exhibit the so called “strong metal-support interaction” (SMSI).

The various reasons attributed to metal-support interaction, especially SMSI state, are (i) an ordered or arranged dispersion of the metal in a particular geometry, (ii) topology, (iii) the formation of compounds, (iv) phase transformation of the support as well as (v) electron transfer from support to metal\textsuperscript{6,7}. Madhusudhan Rao et al.\textsuperscript{8}, have postulated the formation of a ternary oxide phase and its subsequent re-organization under reduction at 773 K in hydrogen as the cause for the induction of SMSI state in the Fe/TiO$_2$ system. The aim of this paper is to examine this postulate, especially with respect to Pt/TiO$_2$ system, which is known to exhibit pronounced SMSI characteristics, employing TiO$_2$ support (prepared in a similar manner to that reported by Madhusudhan Rao\textsuperscript{9}) and to compare these results with those obtained from a mixed oxide support (TiO$_2$-Al$_2$O$_3$).

Mixed oxide supports have been employed and their role in inducing SMSI state has been examined in the past. McVicker and Ziemacki\textsuperscript{10} considered the effect of TiO$_2$-Al$_2$O$_3$ support for group VIII metals and reported on the basis of hydrogen chemisorption measurements that the effect is in between that of TiO$_2$ (an SMSI support) and of Al$_2$O$_3$ (considered to be a non-SMSI support). Other reports available with mixed oxides of TiO$_2$-Al$_2$O$_3$, Nb$_2$O$_5$-SiO$_2$ and TiO$_2$-SiO$_2$\textsuperscript{11-14} have addressed to the question of the relative dispersions of the two oxides as well as to the question of the chemical state of the supports.

The objective of the present investigation includes the study of the mixed oxides in comparison to simple oxides by different characterization techniques, especially X-ray Photo Electron Spectroscopy (XPS). Platinum was supported on titania (commercial), titania (gel) and a mixed oxide containing 22% titania and 78% alumina. The catalysts were characterized by X-ray diffraction (XRD), hydrogen chemisorption measurements, sorptometry (BET surface area) and XPS techniques.
Experimental Procedure

The platinum supported on titania catalysts were prepared by the conventional wet impregnation method using an aqueous solution of chloroplatinic acid. The loading of platinum was 5%(w/w) which was estimated quantitatively by spectrophotometric analysis using the stannous chloride method. A commercially available titania (Baker, UK, 99% pure anatase) designated as TiO2(C) and a laboratory prepared titania gel, prepared by the hydrolysis of titanium tetrachloride, indicated as TiO2(G), were used as simple oxide supports. A mixed oxide support, TiO2-Al2O3, indicated as T-A was prepared for comparison.

The mixed oxide was prepared by the co-hydrolysis of titanium isopropoxide and aluminium isopropoxide in isopropanol solution. The mixture was stirred continuously for one hour at room temperature in dry N2 to avoid contact with moisture and prevent hydrolysis. The solution was then added dropwise to distilled water (total volume of the solution being 300 mL) to form the precipitate which was then aged for one hour. The precipitate was filtered and washed 5 times with hot distilled water. The product was dried for 16 h at 383 K, then calcined in air at 573 K for 2 h followed by final calcination at 773 K for 2 h. A composition of 78% Al2O3 and 22% TiO2 was estimated quantitatively by gravimetric analysis of aluminium by the oxine method. In all the cases, the catalysts were reduced in hydrogen flow after purification of the gas by copper and moisture traps. The flow rate of hydrogen was 30 mL/min. The reduction was carried out at two different temperatures namely, 573 K for low temperature reduction (LTR) and 773 K for high temperature reduction (HTR). The reduction time was maintained at 24 h at the respective temperatures. The characterization of these samples were carried out using these freshly reduced samples.

The X-ray diffractograms of all the freshly reduced catalysts were recorded using a Rigaku Miniflex diffractometer using Co-Kα radiation.

The measurements of BET surface area of the samples were carried out by adsorbing nitrogen at 77 K using a Carlo Erba Sorptometer(1800). The samples were degassed at 393 K prior to all the experiments.

The room temperature hydrogen chemisorption measurements were carried out in a conventional all glass static vacuum system. The volume of hydrogen adsorbed by the catalyst was determined in the system after evacuating the catalyst for 6 h at a pressure of 10⁻⁶ Torr at 573 and 773 K (LTR and HTR), respectively. It is assumed that each metal atom (Pt) adsorbs one hydrogen atom and hence the ratio, H/Pt, is taken to be one as reported in the literature. The particle size was calculated using the expression, \[ d_s (\text{nm}) = \frac{108}{\%D}, \] where \( D \) is the dispersion given by

\[ D = \frac{\text{Number of surface metal atoms}}{\text{Total number of metal atoms}}. \]

The X-ray photoelectron (XP) spectrum was recorded using ESCALAB MARK II of VG Scientific (UK) Limited. This instrument consists of a twin anode (Al/Mg anode). In this, Mg anode was selected (1253.6 eV) because of low line-width [0.8 eV at full width half maximum (FWHM)]. Charging effects were corrected by adjusting the main C1s peak to 285.0 eV binding energy. The pressure in the analytical chamber during measurements was nearly 1x10⁻⁹ Torr for recording the XP spectra. The samples were taken in the form of pellets. O1s, C1s, Pt4f, Ti2p and Al2s, Al2p regions were scanned.

Preliminary investigation of the activity of these catalysts were studied by the liquid phase hydrogenation of cinnamaldehyde. The hydrogenation was carried out in liquid phase using ethanol as the solvent. The kinetics of the reaction was monitored on a time-on stream basis for 5 h at intervals of 30 min in each case.

Results and Discussion

The hydrogen chemisorption results have been used for calculating the hydrogen adsorption capacity, metal particle size and dispersion and are given in Table 1. The BET surface area is also exhibited in Table 1.

It is observed from XRD that the titania supported samples exhibit the pure anatase form in all the cases. Thus, anatase to rutile transformation is not predominant even after high temperature reduction (773 K) of the catalyst. This indicates that the phase transformation of the support need not be the cause for SMSI state nor for the migration of the support on the metal particles. It has been postulated that the metal dispersion will...
be governed by the procedures employed for the preparation of the support and dissolution of the metal precursors in the support. This latter phenomenon can be expected to be limited in the case of mixed oxide support as compared to titania support. The individual oxide phases could be identified from the XRD of mixed oxide. The systems which resist dissolution of metal precursors into the support phase should show higher dispersion of the metal on the support as compared to systems which are amenable for the dissolution of metal precursor into the support phase, namely TiO₂(G).

The hydrogen chemisorption measurements show that platinum supported on titania samples exhibit the characteristic SMSI behaviour, i.e., complete suppression of hydrogen uptake after HTR. But the mixed oxide catalyst exhibits only a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature of reduction, K</th>
<th>H₂ uptake, μmol/gcat</th>
<th>Dispersion (%)</th>
<th>BET surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pt / TiO₂ (C)</td>
<td>573</td>
<td>4.4</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>773</td>
<td>0.0</td>
<td>—</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>5% Pt / TiO₂ (G)</td>
<td>573</td>
<td>7.5</td>
<td>6</td>
<td>100</td>
</tr>
<tr>
<td>773</td>
<td>0.0</td>
<td>—</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>5% Pt / T-A</td>
<td>573</td>
<td>5.3</td>
<td>4</td>
<td>211</td>
</tr>
<tr>
<td>773</td>
<td>3.9</td>
<td>3</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

Table 1—Hydrogen chemisorption and surface area results of supported platinum samples

Fig.1—XP spectra of Ti²p regions for platinum supported samples reduced at (a) 573K and (b) 773 K.

Fig.2—XP spectra of Pt⁴f regions for platinum supported samples reduced at (a) 573K and (b) 773 K.
moderate suppression even after HTR probably due to the presence of \(\gamma\)-Al\(_2\)O\(_3\) which has been proved earlier to be a non-interacting support\(^{21}\). Moreover, the pretreatment conditions used for the support seem to have little effect on chemisorption behaviour except for the fact that the dispersion of platinum is higher for the gel and mixed oxide systems. This is due to the surface area of the mixed oxide being higher than that of the gel which in turn is higher than that of the commercial catalyst as shown in Table 1.

Figs 1 and 2 show the XPS patterns of the Pt\(4f\) and Ti\(2p\) levels, for all the catalysts reduced at 573 K (LTR) and 773 K (HTR) respectively. The surface concentration was calculated using the equation

\[
\frac{N_1}{N_2} = \frac{A_1 \sigma_2}{A_2 \sigma_1} \sqrt{\frac{K.E_1}{K.E_2}} \tag{1}
\]

where \(N_1\) and \(N_2\) are the surface concentrations of elements 1 and 2 while \(A_1\) and \(A_2\) are area under the peaks of 1 and 2, \(\sigma_1\) and \(\sigma_2\) are the photoionisation cross-sections of the levels probed for these elements and \(K.E_1\) and \(K.E_2\) are the kinetic energy values corresponding to the peaks of the elements 1 and 2, respectively. The kinetic energy was obtained from the conventional equation,

\[
K.E_i = E - B.E_i \tag{2}
\]

where \(E\) is the energy of the MgK\(\alpha\) source.

Fritsch and Legare\(^{24}\) have proposed, on the basis of their observations, a new feature in terms of changes in the valence band spectrum of alumina on platinum depositions and its manifestation in the OKVV Auger transition. According to their proposal the interaction between the metal and the substrate involves the oxygen atoms. This proposal should be examined in the context of the fact that, for SMSI state, there is considerable reduction of the support as shown\(^{25}\) by the presence of Ti\(^{3+}\) or Ti\(^{4+}\) species (when TiO\(_2\) support has been used). Moreover, the reduced species is located in the outermost region on the surface with the metal particles\(^{26}\). The point of contention here is, whether the rehybridisation of the metal orbitals and the oxide ion orbitals, as proposed by Fritsch and Legare, is connected with such defect species or whether it corresponds to the core hole generated in the oxide ion of an idealized oxide matrix (a situation more favorable with Al\(_2\)O\(_3\) support).

Since it is difficult to find, at present, specific answers to these questions, an attempt has been made to obtain partial answers from the XPS study of the three catalyst systems. The XP spectra of Ti\(2p\) and Pt\(4f\) for these supported systems after reduction at 573 and 773 K are given in Figs 1 and 2. The relevant data extracted from these figures are given in Table 2. The following observations can be made from these data:

(i) The extent of reduction of the support is least for TiO\(_2\)(C) while a considerable extent of reduction is discernible in the case of TiO\(_2\)(G) as well as the mixed oxide support. The separation in binding energy between O1s level and the Ti\(2p\) levels has been determined\(^{27}\) and the data are given in Table 2. This difference in binding energy values should be about 71.00 eV for TiO\(_2\) while it is 73.4 eV for Ti\(_2\)O\(_3\), 75.0 eV for TiO and 77.0 eV for metallic Ti from the literature values. The data given in Table 2 show that it is around 71.0 eV for Pt/TiO\(_2\) systems reduced at 573 K while it increased when these systems were reduced at 773 K. The increase was more for TiO\(_2\)(G) sample showing that reduction of Ti\(^{4+}\) is more marked on this support. In the mixed oxide system, the magnitude of this separation cannot be used as the criterion, since O1s level could have arisen from the oxide ions of alumina support as well. However, it is seen that this separation increases with increase in reduction temperature showing that reduction of Ti\(^{4+}\) could have taken place in this sample as well. In all the cases, the binding energy of Ti\((2p)\) was found to be around 458 ± 0.5 eV, as shown in Table 2\(^{28-30}\).

(ii) The extent of dispersion of the metal decreased as a result of high temperature reduction for the TiO\(_2\)(G) and mixed oxide supported systems (a result deduced from the values of Pt/Ti ratio given in Table 2).

(iii) Munuera et al.\(^{31}\) have devised a method for deducing the encapsulation of the metal particles by the reduced support. This is based on the observation of increase in the values of \(h_i/h_b\), where \(h_i\) is the height of the peak due to emission from the metal core level and \(h_b\), that of the background at higher binding energy with respect
Table 2—XPS results of all the supported platinum samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature of reduction K</th>
<th>Binding energy, eV [FWHM]</th>
<th>Ratios</th>
<th>Difference in B.E. Between O and Ti eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O(1s)</td>
<td>Pt(4f)</td>
<td>Al(2s)</td>
</tr>
<tr>
<td>5% Pt / TiO₂(C)</td>
<td>573</td>
<td>529.66</td>
<td>76.52</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>[2.26]</td>
<td>[2.0]</td>
<td>[1.91]</td>
</tr>
<tr>
<td>5% Pt / TiO₂(G)</td>
<td>573</td>
<td>529.55</td>
<td>75.58</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>[2.26]</td>
<td>[2.1]</td>
<td>[1.91]</td>
</tr>
<tr>
<td>5% Pt / T - A</td>
<td>573</td>
<td>530.86</td>
<td>75.50</td>
<td>121.43</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>[2.62]</td>
<td>[2.4]</td>
<td>[2.86]</td>
</tr>
</tbody>
</table>

(iv) The FWHM of O1s peak for TiO₂(G) is quite broad (2.1eV) thus showing that oxide ions are in more than one environment. It is proposed that the metal particles are incorporated into the reduced support matrix and the oxygen orbitals are rehybridised so as to coordinate with platinum particles as well as with reduced Ti species. This situation may also hold good in the case of mixed oxide support. However, this could not be unambiguously established since there are already multiple types of oxide ions, namely, oxide ions of alumina and titania in addition to oxide species that coordinate to the metallic particles. This result is also corroborated with the binding energy value of Pt4f state which increases with increase in reduction temperature for TiO₂(G) as well as mixed oxide support. Such an increase is not observed for TiO₂(C) showing incorporation and interaction of platinum orbitals with oxide ion orbitals are the least in this case.

Table 3—Percentage conversions on titania and mixed oxide supported platinum catalysts for cinnamaldehyde hydrogenation.

<table>
<thead>
<tr>
<th>Time min</th>
<th>Temperature of reduction K</th>
<th>5% Pt / TiO₂(G)</th>
<th>5% Pt / TiO₂(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>45 (0)</td>
<td>42 (0)</td>
<td>41 (0)</td>
</tr>
<tr>
<td>120</td>
<td>65 (0)</td>
<td>62 (11)</td>
<td>60 (0)</td>
</tr>
<tr>
<td>180</td>
<td>65 (0)</td>
<td>75 (13)</td>
<td>75 (0)</td>
</tr>
<tr>
<td>240</td>
<td>67 (0)</td>
<td>75 (30)</td>
<td>74 (0)</td>
</tr>
<tr>
<td>300</td>
<td>67 (0)</td>
<td>76 (41)</td>
<td>74 (0)</td>
</tr>
</tbody>
</table>

The values in parentheses indicate the % selectivity towards cinnamyl alcohol.

ear the platinum surface sites will act as a source of electrons which could affect the catalytic activity and selectivity for the hydrogenation of α,β-unsaturated aldehydes. Our preliminary investigations, the results of which are given in Table 3, corroborate the earlier conclusion derived based on the ΔB.E. values.

It is observed from Table 3 that the selectivity towards cinnamyl alcohol is exhibited only in the case of HTR catalysts or in SMSI state and it is greater for platinum on titania(gel) sample than on TiO₂(C).

Conclusions

The results indicate a more pronounced SMSI condition for TiO₂(G) sample than for the mixed oxide system. From the ratio of the intensity of the metal peak to that of the background in XPS, it may be concluded that in the case of TiO₂ supports
the encapsulation of the metal by the support is the cause of reduction in the uptake of hydrogen after HTR treatment. However, such an unambiguous statement is not possible for TiO$_2$-Al$_2$O$_3$ systems from XPS study in view of multiplicity of interactions with different metal species. The high selectivity for cinnamyl alcohol in the case of Pt/TiO$_2$ shows that SMSI state is prevalent in this system.

References