Indian Journal of Chemistry
Vol. 38A, January 1999, pp.56-60

Acid - base properties of binary oxide catalysts of alumina - rare earth oxides

Jayasree, J
St.Xavier's College, Thumba, Thiruvananthapuram 695 586, India

Received 5 August 1998, revised 5 October 1998

Binary oxides of aluminium with rare earths like Pr, Nd, Sm and Eu have been prepared by coprecipitation using NH$_3$ from corresponding nitrates. Surface characteristics and acid-base properties have been determined by DTA, SEM, ESCA, MAS$^2$AINMR, IR and titrimetric methods. Electronegativity of the rare earth oxide influences the acidity and basicity of the binary oxide. Both Brønsted and Lewis acid sites are observed on catalyst surface. Higher number of Lewis acid sites are observed on AI$_2$P$_2$J-Nd$_2$P$_2$J surface.

Rare earth oxides are often used as catalysts and catalyst supports$^{9,10}$. Ionic radii and electronegativity values of rare earths are almost similar. It is generally thought that the catalytic behaviour of rare earth oxides are similar when prepared similarly. Large variations in catalytic properties are observed when rare earth oxides are mixed with Al$_2$O$_3$ and coprecipitated$^{11,12}$. The morphology and acid-base properties of catalysts are found to be different. The present work has been undertaken to investigate the surface properties, morphology and acid-base properties of the catalysts.

Materials and Methods

Al(NO$_3$)$_3$.9H$_2$O used was of AR grade and supplied by E. Merck (India) Ltd. Rare earth oxides used were 99.9% pure supplied by Indian Rare Earths (India) Ltd.

The hydroxides of binary oxides were coprecipitated from the mixed nitrate solution using 25% NH$_3$. The precipitates were aged for 20h, washed with water and filtered. The hydroxides were dried at 130°C for 24h and calcined in air at 400°C for 5h. Chemical analysis of the catalysts were done by precipitating rare earth as oxalate and ignited to oxide by standard procedure.$^1$ From the weight of rare earth oxide, the weight of alumina in the catalyst was determined.

Surface areas of the catalysts were measured by N$_2$ adsorption at 77K and applying BET method on a Quantisorb Jr. surface area analyser. DTA measurements were carried out in a Shimadzu TD 50H instrument. ESCA studies were carried out on an ESCA-3MK 11 electron spectrometer-(VG scientific, UK). Scanning electron micrographs were taken on Jeol 35C SEM. MAS$^3$AINMR of catalyst samples were taken on Brucker MSL 300 at 78.2 MHz.

Acidity of catalyst samples were determined by titrating benzene solution of n-butyl amine with catalyst samples in benzene$^{8,9}$. Purified and dried samples of benzene and n-butyl amine were used for acidity determination. The catalyst samples were calcined at 400°C for 5h. At the end of calcination, samples were cooled by passing dry air over it. As soon as sample was cooled to 200°C, it was transferred to airtight vessel and stored in a desiccator until it was titrated. Approximately 1g of catalyst sample was transferred to screw cap bottle and correct weight was determined. 10 ml dry benzene and appropriate number of millimoles of n-butyl amine was added into the catalyst. The tightly capped samples were equilibrated in a rotator, for 12h at room temperature. The catalyst suspension was divided to five portions and tested with Hammett indicators. By increasing n-butyl amine content, the stage at which n-butyl amine has been added to neutralize catalyst acidity for the particular indicator was determined. The Hammett indicators used are Neutral red (+6.8), $\alpha$-naphthyl red (+4), methyl yellow (+3.3), (4-phenyl azo) diphenyl amine (+1.5), dicinnamal acetone (-3), benzal acetophenone (-5.6) and anthraquinone (-8.2). Basicity of catalysts were determined by titrating catalyst in cyclohexane with benzoic acid. Indicators like 2,4,6- trinitroaniline (12.2), 2, 4-dinitroaniline (15.0), 4-nitroaniline (18.4) were used for basicity determination.

For differentiating the nature of the acid sites chemisorption of pyridine has been employed. The infrared spectrum was taken on a Perkin-Elmer 882 spectrometer. The samples were evacuated and exposed to pyridine for 10 minutes followed by outgassing at room temperature and at 200°C for 1h. The outgassed catalyst samples were cooled to room temperature and spectra were obtained on KBr pellet.

Results and Discussion

The single oxides used in the present study indicated partial crystalline nature but binary oxides are amorphous$^{10}$. The composition of all catalysts, acidity and basicity values are given in Table 1. The acidity of rare earth oxides ranged from
Table 1 - Acidity and basicity of various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid amounts in mmol/m² at various acid strength</th>
<th>Basicity in mmol/m² at different basic strength</th>
<th>Chemical estimation value (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+6.8</td>
<td>+4</td>
<td>+3.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.115</td>
<td>0.115</td>
<td>0.103</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>0.0431</td>
<td>0.021</td>
<td>0.011</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.071</td>
<td>0.001</td>
<td>0.023</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>0.031</td>
<td>0.056</td>
<td>0.013</td>
</tr>
<tr>
<td>Al₂O₃-Sm₂O₃</td>
<td>0.107</td>
<td>0.509</td>
<td>0.012</td>
</tr>
<tr>
<td>Al₂O₃-Sm₂O₃</td>
<td>0.092</td>
<td>0.437</td>
<td>0.029</td>
</tr>
<tr>
<td>Al₂O₃-Eu₂O₃</td>
<td>0.113</td>
<td>0.499</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table 2 - Surface area and binding energy values of different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area m²/g</th>
<th>Binding energy (eV) Al (2p)</th>
<th>O(1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-Sm₂O₃</td>
<td>97.4</td>
<td>73</td>
<td>532</td>
</tr>
<tr>
<td>Al₂O₃-Pr₂O₁₁</td>
<td>42.5</td>
<td>73.7</td>
<td>536.2</td>
</tr>
<tr>
<td>Al₂O₃-Nd₂O₃</td>
<td>121.5</td>
<td>74.5</td>
<td>532.3</td>
</tr>
<tr>
<td>Al₂O₃-Eu₂O₃</td>
<td>101.2</td>
<td>74</td>
<td>536</td>
</tr>
</tbody>
</table>

Fig 1 - DTA diagram of the catalysts; 1. Al(OH)₃; 2. Al₂O₃-Pr₂O₁₁; 3. Al₂O₃-Nd₂O₃; 4. Al₂O₃-Sm₂O₃; and 5 Al₂O₃-Eu₂O₃.

Not be estimated due to the greenish black colour of the catalyst. Two single oxides having acid sites when combined generate new acid sites with higher strength. Generation of new acid sites may be due to charge imbalance on M₁-O-M₂ bonds in the binary oxide. Addition of rare earth oxides with low electronegativity to Al₂O₃ leads to a weakening of acid sites on Al₂O₃ and generation of more basic sites which are associated with oxygen species coordinated to rare earth cations. Single oxides used in the present study did not possess basic sites. Basicity values of binary oxides ranged from H⁺ +12.2 to +15. New basic sites are created on the binary oxide since the electronegativity of rare earth oxides - alumina surface phase is in between the values for rare earth oxide and alumina.

Hydrated Al(OH)₃ showed an initial weight loss of 5% at 84°C and 15% loss at 285°C followed by a gradual decomposition to oxide over a temperature range of 800°C. From the DTA diagram in Fig. 1 it is clear that rare earth oxides show a general tendency to bring down the final decomposition temperature of binary oxides to about 520°C. Al₂O₃ - Eu₂O₃, Al₂O₃ - Sm₂O₃ and Al₂O₃ - Pr₂O₁₁ showed 50% weight loss below 300°C. A different thermal decomposition pattern was observed for Al₂O₃ - Nd₂O₃. A slow removal of hydroxyl groups accounts for the large surface area and basicity of the catalyst. The behaviour of hydroxyl groups on the oxide surface largely depends on the composition of the oxide and the local environment. The acid/base character of such surface hydroxyls depend on the extent of dehydration.

Morphological features of the catalysts are given in Fig. 2. Al₂O₃ - Eu₂O₃ and Al₂O₃ - Sm₂O₃ showed large particle size.
and an intermediate value for surface area. \( \text{Al}_2\O_3 - \text{Pr}_\text{O}_{11} \) showed an agglomerated structure with minimum pores on its surface. \( \text{Al}_2\O_3 - \text{Nd}_\text{O}_{11} \) appeared as a partial gel with slow evolution of water which results in a network structure.

Al(2p) and O(1s) binding energies of the different catalysts are given in Table 2. Al(2p) binding energy varied from 73.2 eV to 74.5 eV and O(1s) binding energy varied in the range of 532 to 536.2 eV. A moderate increase in the binding energy values of Al(2p) and O(1s) explains the presence of mixed Al-O and Al-OH groups on the catalysts\textsuperscript{13,15}.

The MAS\textsuperscript{27}AlNMR of the catalysts are given in Fig.3. Two signals are observed for all catalysts one around 0 ppm corresponds to aluminium atom in the octahedral coordination and the peak around 60 ppm is due to aluminium atom in the tetrahedral coordination\textsuperscript{15}. In the case of \( \text{Al}_2\O_3 - \text{Sm}_\text{O}_{11} \), the percentage area of signal at 62 ppm is less indicating 30% of aluminium atoms in tetrahedral coordination. For \( \text{Al}_2\O_3 - \text{Nd}_\text{O}_{11} \), both signals at 4.3 ppm and 56 ppm are having equal intensity showing the equal distribution of aluminium atoms in tetrahedral and octahedral coordinations. The more Lewis acidity of \( \text{Al}_2\O_3 - \text{Nd}_\text{O}_{11} \) is due to aluminium atoms in low coordination state.\textsuperscript{16} Two signals around 56.8 ppm and 2.8 ppm are seen in the case of \( \text{Al}_2\O_3 - \text{Eu}_\text{O}_{11} \) with more Al atom in octahedral coordination. \( \text{Al}_2\O_3 - \text{Pr}_\text{O}_{11} \) showed two signals around 50 ppm and 4.4 ppm with 40% aluminium atoms in tetrahedral coordination.

Infrared spectrum of the catalysts were taken in the region 1400 - 1700 cm\textsuperscript{-1} by evacuating the pyridine containing catalyst samples at room temperature and at 200°C. The background spectra of the catalysts were recorded in a normal
manner. Catalysts showed 2 bands in the region 1582 and 1534 cm\(^{-1}\) and two other bands at 1456 and 1490 cm\(^{-1}\). Absorption bands seen around 1582 and 1456 cm\(^{-1}\) were assigned to be due to coordinately bonded pyridine at Lewis acid sites\(^\text{20,21}\). Two absorption bands around 1534 and 1490 cm\(^{-1}\) were assigned to be due to pyridinium ions on Brønsted acid sites\(^\text{20}\).

The following absorption bands around 1534, 1490, 1581 and 1456 cm\(^{-1}\) were observed for Al\(_2\)O\(_3\) - Sm\(_2\)O\(_3\). The spectra at two different temperatures are illustrated in Fig.4a. When catalyst is evacuated at high temperature there is not much variation in the band intensities. Al\(_2\)O\(_3\) - Nd\(_2\)O\(_3\) showed two intense absorptions around 1581 and 1456 cm\(^{-1}\) showing the presence of strong Lewis acid centres on the surface (Fig.4b). On evacuation at high temperature the intensity of these bands increases. Two absorptions corresponding to 1534 and 1490 cm\(^{-1}\) were also observed on Al\(_2\)O\(_3\) - Nd\(_2\)O\(_3\). These absorptions are due to pyridinium ions formed on Brønsted acid sites. On evacuation at 200°C, the intensity of these bands decrease showing a reduction in the number of Brønsted acid sites on catalyst surface.

In the case of Al\(_2\)O\(_3\) - Eu\(_2\)O\(_3\) the absorption bands in the region 1534 and 1490 cm\(^{-1}\) are more intense than absorptions in the region 1581 and 1461 cm\(^{-1}\). The pyridine absorption spectrum is given in Fig.4c. The intense absorption bands at 1534 and 1490 cm\(^{-1}\) are due to the Brønsted acidity of the
catalyst. When catalyst is evacuated at 200°C the intensity of absorptions due to Lewis acid sites increases. The pyridine absorption spectrum of Al₆O₁₈ - Pr₆O₁₂ is given in Fig.4d. The absorption bands at 1534 and 1456 cm⁻¹ are of low intensity while absorption at 1581 cm⁻¹ is absent. With increase of evacuation temperature, the absorption shows small variations in intensity.

To conclude surface area, acidity and basicity of catalysts are largely influenced by thermal decomposition and morphology of the catalysts. New acidic and basic sites are created on catalyst surface by coprecipitation. Catalyst with more aluminium atom in tetrahedral coordination showed more Lewis acid sites on the surface.

References