Preparation of mixed oxide supports by homogeneous precipitation method

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Preparation of catalytically important TiO₂-Al₂O₃, TiO₂-SiO₂, TiO₂-ZrO₂, TiO₂-SiO₂-ZrO₂ and SiO₂-ZrO₂ mixed oxides by coprecipitation method using urea as hydrolysing agent is described. These mixed oxides are X-ray amorphous and exhibit high N₂ BET surface areas.

The support material in heterogeneous catalysts acts as a vehicle for the active phase or active component. The support also exercises several functions, among the most important of which is to maximise the surface area of the active phase by providing a large specific surface area. The typical support materials which are frequently encountered in heterogeneous catalysis are Al₂O₃, SiO₂, TiO₂, ZrO₂ and Al₂O₃-SiO₂, etc. Each support possesses some advantages and disadvantages with respect to a particular active component and the reaction to be catalyzed. The beneficial functions of every individual support can be exploited fully by using them in combination, which constitute yet another important class of heterogeneous catalyst supports whose characteristics and preparative procedures are not studied fully. In this paper, we describe the preparation of various mixed oxide supports namely TiO₂- Al₂O₃, TiO₂-SiO₂, TiO₂-ZrO₂, TiO₂-SiO₂-ZrO₂ and SiO₂-ZrO₂ by the technique of precipitation from homogeneous solutions using urea as hydrolysing agent. These binary oxides are also very useful as solid acid catalysts for alkylation and dehydration reactions.

Experimental procedure

Materials—The materials used are titanium tetrachloride (Fluka, AR grade), sodium aluminate (Loba Chemie, AR grade), sodium silicate (Loba Chemie, AR grade), zirconium oxychloride (Fluka, AR grade), urea (Loba Chemie, AR grade), and ammonium nitrate (Loba Chemie, AR grade).

Preparation of mixed oxides—The requisite quantities of the metal salts to yield the desired molar ratios of the oxides were dissolved separately in deionized water and mixed together. An excess amount of urea solid with metal to urea molar ratio of 1:2.5 was also added. The resulting mixture solution was heated slowly to 90-95°C on a hot plate with vigorous stirring. The pH of the solution was monitored at different intervals of time. No change in the pH of the solution was observed until the temperature of the solution reaches 90-95°C. At this temperature the pH of the solution increased slowly in the beginning from 3.5-4.5 and then rapidly with increase in time of heating attaining a final value between 7-8. Heating was further continued at this pH for 3-4 h in order to complete the precipitation of respective metal oxides. The resulting precipitates were filtered, washed with deionized water until no chloride ions could be detected with Ag⁺ in the filtrate. The resulting cake was then dried at 110°C for 12h. To remove sodium ions in the case of TiO₂-Al₂O₃, TiO₂-SiO₂ and TiO₂-SiO₂-ZrO₂ preparations, the oven dried precipitates were again washed with ammonium nitrate (0.01 M) solution for several hours and washed further with deionized water. Thus obtained precipitates were once again dried at 110°C for 12h and finally calcined at 500°C for 6h in an open air furnace.

Surface area measurements—The BET surface areas were determined on a previously described standard static volumetric high vacuum set up. Before the measurements samples were evacuated (1 × 10⁻⁶ torr) for several hours at 110°C temperature. Specific surface areas were measured by adsorption of nitrogen at −195°C assuming 0.162 nm² as the area of cross-section of N₂ molecule.

X-Ray diffraction measurements—The X-ray powder diffraction patterns have been recorded on a Philips PW 1051 diffractometer by using Ni-filtered CuKα radiation.

Electron microscopy—SEM investigations were made on a Hitachi Model S-520 scanning electron microscope at an applied voltage of 10 kV.

Results and discussion—The X-ray powder diffraction patterns of various samples calcined at 500°C are shown in Fig. 1. All the mixed oxide supports obtained are in amorphous state. No characteristic XRD lines due to crystalline phases

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Fig. 1—X-Ray diffraction patterns of various mixed oxides calcined at 500°C: (a) SiO₂-ZrO₂, (b) TiO₂-SiO₂-ZrO₂, (c) TiO₂-ZrO₂, (d) TiO₂-SiO₂, (e) TiO₂-Al₂O₃.

<table>
<thead>
<tr>
<th>Mixed oxide</th>
<th>Composition, N₂ BET surface area, m²g⁻¹</th>
<th>molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-Al₂O₃</td>
<td></td>
<td>1:1</td>
</tr>
<tr>
<td>TiO₂-SiO₂</td>
<td></td>
<td>1:1</td>
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<tr>
<td>TiO₂-ZrO₂</td>
<td></td>
<td>1:1</td>
</tr>
<tr>
<td>TiO₂-SiO₂-ZrO₂</td>
<td></td>
<td>1:1:1</td>
</tr>
<tr>
<td>SiO₂-ZrO₂</td>
<td></td>
<td>1:1</td>
</tr>
</tbody>
</table>

of individual oxides or compounds between them are observed. Only broad diffraction patterns can be seen in some cases. Representative electron micrographs of the four samples are shown in Fig. 2. The SEM micrographs also demonstrate evidently the amorphous nature of these mixed oxide supports. This is, of course, a positive indication for any support material that can be utilized for impregnating or depositing any active component on its surface. The N₂ BET surface areas of various mixed oxides are shown in Table 1. As can be noted, reasonably high surface areas are obtained for all the support materials prepared. When these mixed oxides were subjected to high temperature thermal treatments from 600 to 800°C, a gradual improvement in the crystallinity of these materials was observed. In the case of TiO₂ containing mixed oxides no XRD lines due to anatase or rutile phases of TiO₂ were noted at 500°C calcination. However, after high temperature treatments both phases with varying intensities were observed. A gradual loss in the BET surface areas was also noted after thermal treatments beyond 500°C. These investigations clearly indicate that the mixed oxides prepared as per the procedure described in the experimental section are quite thermally stable upto 500°C calcination temperature and are uniform throughout the bulk.

The technique of precipitation from homogeneous solutions using urea as hydrolyzing agent makes it possible to prepare a homogeneous precipitate which has a constantly identical composition as well as properties with good reproducibility. Urea aqueous solution when heated to 90-95°C decomposes into carbon dioxide and ammonia. Since, it is highly soluble in water and its rate of decomposition into NH₃ and CO₂ is dependent upon the temperature and duration of heating, a good control of the pH of the solution is possible. This method has been utilized earlier to make high surface area gamma aluminas, SnO₂, TiO₂-SiO₂, and other catalytically important oxides. The present study once again demonstrates that the technique of homogeneous precipitation using urea as hydrolyzing agent is a promising method for making a catalytically important mixed oxides with desired compositions and high surface areas.

Acknowledgement—Thanks are due to University Grants Commission, New Delhi, for the award of Junior Research Fellowship to one of the authors (EPR).
References