Infrared Spectroscopic Study of Acidity of Amorphous Silica-Alumina

A K BANDOPADHYAY* SISIR Kr ROY & G S MURTY
Central Fuel Research Institute, P.O. FRI-828 108, Dhanbad
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Surface acid sites of amorphous silica-alumina catalysts have been characterized by infrared spectroscopy using three different probe molecules: pyridine, ammonia and carbon monoxide. The study reveals that quantitative estimate of acidity depends on the method of preparation of the catalyst as well as on the probe molecule used.

Acidic sites are generally regarded as the active centres on certain oxides, which catalyse many reactions involving hydrocarbons, e.g., polymerization, isomerization, alkylation and cracking. These processes generally involve carbonium ion mechanism and silica-alumina catalysts are quite active for these processes due to the acidic nature of the mixed oxide, where a trivalent aluminium has replaced a tetravalent silicon in the silica lattice.

The acid sites on oxide surfaces are of two types: Lewis and Bronsted. Lewis acid sites are capable of accepting electrons from the adsorbate molecules and Bronsted acid sites can donate a proton to the adsorbate molecule. These two sites are generally considered to be interdependent. On dehydrated surface, the major contribution to acidity is from Lewis sites only. Addition of a small amount of water to such a surface will convert the Lewis sites to Bronsted sites, which donate protons to adsorbate molecules resulting in the formation of carbonium ions.

Infrared spectroscopy can be used to distinguish between Bronsted and Lewis sites when adsorbing basic molecules like ammonia, pyridine, piperidine, 2,6-lutidine, etc., which may act as both proton acceptors and electron donors, are used as probes. These molecules have characteristic absorptions in the infrared spectra, both in the coordinately bonded and protonated forms. Positions of the IR bands together with integrated molar extinction coefficients of the respective bands available in existing literature, lead to determination of concentration of both types of acid sites. The object of this paper is to report the effect of different probe molecules on measurement of acidity. Further, the change in acidity of silica-alumina as a result of preparation with different pore regulating agents is also highlighted.

Materials and Methods

Preparation of catalysts

All the four silica-alumina samples used in the present work were prepared with the same composition, i.e., with silica: alumina ratio = 88:12. Sample A was prepared without using any pore regulating agent by gelation technique from sodium silicate and aluminium sulphate solutions. Samples B, C and D were prepared by coprecipitation method from the same solutions in presence of the pore regulating agents tetramethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium bromide, respectively. After gelation, the gels were aged, filtered and washed with distilled water. The gels were further base-exchanged with ammonium chloride solution. The base-exchanged gels were then slowly heated, first in the air-oven at 120°C and finally in the muffle furnace at 450°C. The surface area of the catalyst was determined by argon adsorption.

IR spectral measurements

The catalysts prepared as explained above were examined in the form of thin wafers (10-15 mg/cm²) obtained by applying high pressure on the powders of the catalysts. The spectra of the adsorbed species on the catalysts were recorded on an IR-75 Specord spectrophotometer using a special designed cell shown in Fig. 1. The body of the cell was made of molybdenum glass with heating device at one end (A) and IR transmitting windows (CaF₂) on the other end (B). Passage (C) was meant for evacuation, injection of gas and insertion of wafers.

At first, each wafer was calcined at 500°C for 2 hr inside the cell, kept under evacuation. After calcination the cell was cooled to room temperature and the spectrum of the catalyst was re-
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Table 1 — Lewis and Bronsted Acid Sites Measured Using Three Types of Probe Molecules

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lewis sites (µMol/g)</th>
<th>Bronsted sites (µMol/g)</th>
<th>Lewis sites (µMol/m²)</th>
<th>Bronsted sites (µMol/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₅NH₂</td>
<td>NH₃</td>
<td>CO</td>
<td>C₆H₅NH₂</td>
</tr>
<tr>
<td>A.</td>
<td>110</td>
<td>420</td>
<td>26</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>(1) 86</td>
<td></td>
<td>(2) 51</td>
<td></td>
</tr>
<tr>
<td>B.</td>
<td>47</td>
<td>200</td>
<td>15</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>(1) 19</td>
<td></td>
<td>(2) 18</td>
<td></td>
</tr>
<tr>
<td>C.</td>
<td>85</td>
<td>305</td>
<td>22</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>(1) 38</td>
<td></td>
<td>(2) 32</td>
<td></td>
</tr>
<tr>
<td>D.</td>
<td>30</td>
<td>163</td>
<td>17</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>(1) 18</td>
<td></td>
<td>(2) 12</td>
<td></td>
</tr>
</tbody>
</table>

corded. Pyridine, adsorbed on zeolite, was then allowed to be adsorbed by the catalyst for sometime. After this, desorption was carried out under evacuation at 150°C. The spectrum of the chemisorbed species formed on the catalyst surface was then recorded at room temperature. Similar procedures were adopted for ammonia except that desorption was carried out at 100°C. For CO, the portion B of the cell was modified in such a way as to record spectra at liquid nitrogen temperature. The spectra were also taken at liquid nitrogen temperature for all the catalysts.

Beer-Lambert law in integrated form was applied for the determination of concentration of sites. The integral intensity of an absorption band is related to concentration of adsorbed species through the following relation,

\[ B = \log \left( \frac{T_0}{T} \right) dv = A_0 \cdot C \cdot \rho \cdot 10^{-3} \]

where \( T_0, T \) are the transmittances at frequency \( v \) of the catalyst before and after adsorption, \( C \) the concentration in µmol/g, \( \rho \) the thickness of the wafer in mg/cm² and \( A_0 \) the integral adsorption coefficient in cm·µmol⁻¹. The values of \( A_0 \) for pyridine, ammonia and CO were taken from literature.

Results and Discussion

Probe molecules interact with acid sites and form complexes. Pyridine forms complexes PyH⁺ with Bronsted sites and Al:Py with Lewis centres; the frequencies of absorption of the adsorbed species formed are 1540 and 1450 cm⁻¹ respectively. The Lewis (L) and Bronsted (B) centres for catalyst C are shown in Fig. 2(3). Similarly, ammonia forms complexes NH₃⁺ with Bronsted and Al:NH₃ with Lewis centres which absorb at 1620 and 1460 cm⁻¹ respectively [Fig. 2(4)]. The concentrations of sites measured from pyridine and ammonia adsorption are given in Table 1.

Lewis and Bronsted sites determined from pyridine and ammonia are found to be different for

![Infrared cell for studying acidity of catalysts](image)
each of the four catalysts studied here. In fact, the concentrations of both the sites (L and B) as measured from ammonia adsorption are much higher than those measured from pyridine adsorption. This can be explained on the basis of the fact that ammonia, being a strong base and relatively a small molecule (kinetic diameter 2.62 Å), has access to practically all the acid sites. This points to the fact that in porous materials the quantitative estimate of the acidity depends on the size of the probe molecules used. The selection of probe molecule is important while correlating catalytic activity with acidity.

Zaki et al. have demonstrated the usefulness of CO as a surface probe for the characterization of aprotic sites on metal oxide surfaces. The adsorption bond to Lewis acid centres is a σ-donor bond which leads to positive frequency shifts of the carbonyl stretching mode relative to the gas phase frequency of the free molecule (2143 cm⁻¹). Fig. 2(5) shows that there are two types of Lewis sites L(1) and L(2) respectively, the concentrations of which are included in Table 1. Fig. 2(2) shows three different types of Bronsted sites, B(1), B(2) and B(3) at 3660, 3560 and 3480 cm⁻¹ respectively. Thus, this selective surface probe is able to throw more light on the nature of surface sites than pyridine and ammonia can. The characterization of surfaces by a number of probes has the advantage of knowing surface sites in a more detailed way. Fig. 2(1) indicates two types of OH groups on dehydrated surface of silica-alumina, one at 3750 cm⁻¹ due to isolated surface SiOH groups and the other, a bonded one, at a lower frequency ~ 3600 cm⁻¹.

It can be seen from Table 1 that surface area as well as acidity of silica-alumina has changed when templating agents like tetramethylammonium hydroxide, etc., are used. This is due to the action of strongly basic quaternary ammonium compounds on the acid centres of silica-alumina. It is observed that the acidity is maximum for the sample C which has been prepared with tetrapropylammonium hydroxide as pore regulating agent. It is interesting to note that tetrapropylammonium cation is the preferred templating agent for the preparation of ZSM-5, the new generation shape-selective molecular sieve. Table 1 also shows that although catalysts B and D have practically the same surface area, the acidities determined by pyridine and ammonia are different. This indicates that templating agents affect the distribution of surface acid sites. It may be presumed that the variation in acidity is due to the difference in charge densities of tetramethyl and tetrabutyl groups.

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