Catalysis of C-alkylation of phenol using V_2O_5-La_2O_3 system

S Sugunan* & N K Renuka
Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India

Received 13 December 1999; revised 24 July 2000

Vapour phase methylation of phenol is carried out over La_2O_3 supported vanadia systems of various composition. The structural features and physico chemical characterisation of the catalysts are investigated. Orthovanadates are formed in addition to surface vanadyl species on the metal oxide support. No V_2O_5 crystallites are detected. The acid base properties of the oxides are studied by Hammett indicator method and decomposition of cyclohexanol. The data are correlated with the catalytic activity and selectivity of the products. Ring alkylation is found to be predominant over these catalysts.

Supported vanadia are active components of practical catalysts for ammoxidation reactions, oxidation of hydrocarbons, selective catalytic reduction etc. due to their attractive catalytic features. Dispersion of vanadia on the catalyst surface depends strongly on acid base properties of the support and its vanadium content. At low % of vanadia, a finely dispersed layer is observed which includes mono oxo species and two dimensional vanadium oxide clusters. If the composition exceeds a particular value, crystalline vanadia formation is reported along with poly vanadates. Preferential formation of orthovanadates on highly basic catalysts has been reported by Corma et al. With more acidic supports V_2O_5 crystallites are formed.

Phenol alkylation is an important reaction from the industrial point of view. Both O- and C-alkylated products are formed during alkylation which include anisole, o-cresol and 2,6-xylenol. Formation of trimethyl phenol is also reported. Anisole is an additive in gasoline, o-cresol is an intermediate for the preparation of herbicides and insecticides and 2,6-xylenol is used in the manufacture of paints. Selectivity of the products in this reaction is found to depend on the acid base property of the catalyst. Enhancement of C-alkylated products by strong acidic sites have been reported by Balsama et al. On the other hand, Benzouhouna et al. have claimed that strongly acidic catalysts favour O-alkylation. Tanabe has reported that ortho alkylation product selectivity increases with basicity of the catalyst employed. Nature of the products formed is governed by the orientation of phenoxy anion while adsorbed on the catalyst surface. If it is a highly basic catalyst, interaction of the electron cloud of the benzene ring with the surface will be negligible and the ring will be almost perpendicular resulting in O-alkylated products. In this paper, we report the surface properties of La_2O_3-V_2O_5 system. The characterisation of La_2O_3-V_2O_5 catalysts are performed by means of FTIR, XRD, EDX and measurement of surface area and pore volume. The acid base property of the system is studied by Hammett indicator method and cyclohexanol decomposition. The data have been correlated with the catalytic activity of these oxides towards phenol alkylation as a test reaction.

Experimental

Catalyst preparation

Wet impregnation method was adopted for preparing supported catalysts. A solution of NH_4VO_3 in oxalic acid was stirred with the support material, which in turn was prepared via hydroxide method by precipitation from its nitrate solution. The resulting mass was evaporated in a water bath, kept at 110 °C overnight and calcined at 450 °C for 6 h. All the catalysts were sieved to a mesh size < 100 microns and activated at 500 °C before each experiment. Catalysts are denoted by their wt % of vanadia; L3, L7, L11 and L15 for 3, 7, 11 and 15 wt% of V_2O_5.

Characterisation

The chemical composition was determined by Energy Dispersive X-ray analysis (Stereoscan 440 Cambridge, UK). XRD of the samples were measured by a Ni filtered Cu Kα radiation using a DNAX-C Rigaku X-ray diffractometer. Shimadzu FTIR-8101 instrument was used to record IR spectra of the supported samples by KBr disk method. The specific surface area of the catalysts were determined by BET method by nitrogen adsorption using a Micromeritics Flowprep-060 instrument. Mercury porosimeter (Quanachrome, Auto scan-92 porosimetry, USA) was used for measuring pore volume.

Titrimetric method using Hammett indicators was used to measure the acid base property of the cata-
of vanadia decreases the surface area. This may be due to agglomerisation of the particles. Further addition increases the surface area of the supported system. Pore volume also show a corresponding variation.

IR spectra of the samples calcined at 500°C gave the following observations. None of these showed the significant band of crystalline vanadia which appears at 1020 cm⁻¹. Band due to amorphous vanadia was observed at 1060 cm⁻¹. Absence of a band at 1000-950 cm⁻¹ region indicated the absence of polyvanadate formation on the surface. The broad band localised at 900-700 cm⁻¹ was attributed to orthovanadate species.

Basicity data are also presented in Table 1. The catalyst systems responded only to dimethyl yellow, methyl red and bromothymol blue. Basicity decreases up to 6.34% of vanadia and then increases with further vanadia addition. Cyclohexanol decomposition data also support this observation (Table 2). It has already been accepted that acidity is proportional to rate of dehydration and dehydrogenation rate is proportional to both acidity and basicity. Dehydration is prominent over these catalysts indicating the existence of acid sites sufficiently strong to catalyse dehydration. Cyclohexene formed by dehydrogenation isomerises to methyl cyclopentene which suggests the presence of strong acid sites as pointed out by Pines et al. For the supported catalysts, dehydrogenation rate (acidity) is in the order L7 > L3 > L11 > L15. The acidity generation during vanadia addition is due to surface vanadyl species. The vanadium ion present in the amorphous vanadia acts as Lewis acid site. So surface vanadyl species are supposed to be maximum.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>V₂O₅, %</th>
<th>Basicity (mmol g⁻¹)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pKa ≥ 3.3</td>
<td>pKa ≥ 4.8</td>
<td>pKa ≥ 7.2</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>0.530</td>
<td>0.170</td>
<td>0.097</td>
</tr>
<tr>
<td>L3</td>
<td>2.82</td>
<td>0.384</td>
<td>0.110</td>
<td>0.065</td>
</tr>
<tr>
<td>L7</td>
<td>6.34</td>
<td>0.220</td>
<td>0.101</td>
<td>0.048</td>
</tr>
<tr>
<td>L11</td>
<td>9.32</td>
<td>0.448</td>
<td>0.138</td>
<td>0.067</td>
</tr>
<tr>
<td>L15</td>
<td>13.10</td>
<td>0.570</td>
<td>0.181</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Table 2—Data on rate of cyclohexanol decomposition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate(10⁻¹mol s⁻¹g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dehydration</td>
</tr>
<tr>
<td>L3</td>
<td>19.35</td>
</tr>
<tr>
<td>L7</td>
<td>21.29</td>
</tr>
<tr>
<td>L11</td>
<td>15.70</td>
</tr>
<tr>
<td>L15</td>
<td>14.24</td>
</tr>
</tbody>
</table>
for L7 system. It has been proposed that surface Bronsted acid sites are also there in supported catalysts which are located at bridging M-O-support bond. Basicity decrease is accompanied by a concomitant increase of the acidity of V₂O₅-La₂O₃ system.

The % conversion and selectivity of products in the methylation of phenol are shown in Table 3. Ring alkylation takes place predominantly over these catalysts. C-alkylated product selectivity is more than 70%. This may be due to strong basic sites present on the catalysts as reported by Benzouhaneva et al. La₂O₃-V₂O₅ systems are found to be effective for the synthesis of o-cresol, for which the system was found to have maximum selectivity. Selectivity of ortho products (o-cresol and 2,6-xylene) is in the order L15 > L11 > L3 > L7. This is in accordance with the view of Tanabe et al. that ortho selectivity is proportional to the basicity of the catalyst. This is explained by the mode of adsorption of phenoxide ion. On basic systems the electron cloud of the benzene ring will be repelled by the catalyst surface, giving access for the methyl groups to ortho positions. So ortho selectivity will be maximum for more basic catalysts.

Higher alkylated phenols are obtained for systems with higher percentage of vanadia. o-Cresol formed undergoes further methylation to give 2,6-xylene and trimethyl phenol (TMP). But there is no considerable increase in selectivity of 2,6-xylene and TMP as reported on Sm₃O₃-V₂O₅ system. Trimethyl phenol formation in the case of higher vanadia loaded catalysts is due to the generation of acidic sites on the surface. The interaction of acid sites and the benzene ring will bend the phenoxide ion towards the catalyst surface. So it will be easy for an adsorbed alkylating group for migration to other positions also generating higher alkyl phenols. Trimethyl phenol selectivity doesn’t show a drastic change with acid base properties. The selectivity is maximum for L7 which is supposed to be the most acidic one among the catalyst series. Selectivity of anisole formed depends upon the acidity of the system. As the acidity increases anisole selectivity also increases as evident from the higher anisole selectivity of L7.

Anisole formed can undergo 2° reactions in two different pathways. It can undergo a bimolecular reaction to give a mixture of phenol and methylanisole or a monomolecular rearrangement to give o-cresol. 2-Methylanisole is not observed indicating that anisole does not undergo a bimolecular reaction as observed on some other systems like MgAl-CHT catalysts in which the products are phenol and methylanisole. Here the decrease in anisole selectivity is accompanied by an increase in o-cresol selectivity as acid base property changes with vanadia addition. This can be understood as a monomolecular rearrangement taking place over these samples.

Acknowledgement

The authors wish to acknowledge the CSIR, New Delhi for the award of SRF to N K R.

References