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Hydrogenation of phenol over supported platinum and palladium catalysts

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Abstract

The vapour phase hydrogenation of phenol over platinum and palladium supported on alumina and zeolite LTL was studied in a vertical fixed-bed high-pressure reactor. The major products of the hydrogenation reaction were cyclohexanone and cyclohexanol with cyclohexene, cyclohexene and benzene as the minor products. The selectivity for the major products was up to 99%, the conversion being influenced by temperature, feed rate and the partial pressure of hydrogen. Platinum catalysts were found to be better for the production of cyclohexanol while palladium catalysts favoured cyclohexanone production. The platinum catalysts also showed twice as much overall conversion as the palladium catalysts.

Keywords: alumina; hydrogenation; palladium; phenol; platinum; zeolite LTL

INTRODUCTION

Supported metal catalysts have been widely used for hydrogenation and dehydrogenation reactions. Supports ensure better dispersion and stability of the metals in addition to influencing their catalytic properties through electronic interactions [1]. The hydrogenation of phenol and substituted phenols have been carried out over group VIII metals either as "blacks" or as supported catalysts [2-8]. Hydrogenation of phenol produces two important compounds, viz., cyclohexanone and cyclohexanol, both of which are utilized in the manufacture of a large number of industrial products. Cyclohexanone is a key material in the production of nylons for the synthetic fibre and tyre industries [2].

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The products of phenol hydrogenation depend on the type of catalyst and the reaction conditions [3,7]. The yield of cyclohexanone generally increases with increasing temperature [4,7]. It has been shown that phenol can be directly converted to cyclohexanol without going through the intermediate production of cyclohexanone, but phenol reacts very slowly with cyclohexanol converting it to cyclohexanone. Smith and Stump [5] gave the following mechanism for the hydrogenation of phenol over an Adams platinum catalyst and a 5% rhodium–alumina catalyst:

\[
\text{Phenol} \quad 2\text{H}_2 \rightarrow \text{Cyclohexanone}
\]

The tautomerisation of cyclohexene-1-ol to cyclohexanone takes place readily owing to the greater stability of cyclohexanone. Similar mechanisms have been suggested by Takagi et al. [6,9] for the hydrogenation of cresols over rhodium hydroxide based catalysts.

Hydrogenation of phenols and cresols have been extensively studied in the liquid phase, mostly at high pressures over Raney nickel and Adams platinum catalysts. Metals like iridium, palladium, rhodium and ruthenium have also been used in the liquid-phase catalysis of the reaction. Hydrogenation in the vapour phase has not been widely reported although a few results for nickel supported on cerium oxide [7,10] and platinum on alumina [11] are known. The present investigation deals with the hydrogenation of phenol in the vapour phase over platinum and palladium catalysts supported on nonacidic alumina and a basic zeolite LTL.
EXPERIMENTAL

Catalysts

The platinum-alumina catalysts were prepared by adding the required amounts of a standard solution of chloroplatinic acid to γ-alumina extrudates obtained from alumina hydrate (Catapal B, Sarabhai Merck) by extrusion with 2% acetic acid, followed by drying and calcining at 753 K for 3 h. The catalysts were again dried and calcined at 753 K for a further 3 h. The chloride ions were next removed by extraction with a hot ammonia (1 M) solution thrice. The catalysts were then impregnated with a solution of sodium carbonate and further calcined at 753 K for 6 h. The same procedure was followed for the preparation of palladium-alumina catalysts using standard palladium chloride solution.

Zeolite LTL was synthesized by following published procedures [12]. 35.84 g KOH, 6.20 g Al(OH)₃ and 140.00 g water were mixed and boiled to dissolve the Al(OH)₃. The original volume of the solution was restored by adding water and then cooled. 49.76 g of SiO₂ (fumed) was added slowly with constant stirring. The gel so produced was kept in an oven at 413 K for 40 h. It was filtered, washed and dried. The zeolite LTL was identified by its X-ray diffraction (XRD) pattern, sorption capacity (for benzene) and chemical analysis.

Platinum and palladium metals were loaded on the zeolite by ion-exchange methods using tetratriamine platinum and palladium nitrate salt solutions, respectively. The loaded catalysts were calcined at 753 K for 6 h and made into pellets and crushed into 12-14 mesh particles.

The catalysts used are designated as: PtA, 0.6% platinum-alumina with 3% sodium; PtZ, 1% platinum-zeolite LTL; PdA, 1% palladium-alumina with 3% sodium; and PdZ, 1% palladium-zeolite LTL. The catalysts were reduced in flowing hydrogen at 753 K (PtA and PtZ) and 573 K (PdA and PdZ) for 3 h prior to a run. After each run, the catalysts were regenerated by oxidizing the coke deposits in a current of air at 753 K and later were flushed by a flow of nitrogen for at least half an hour.

Reagents

Analar grade phenol (BDH India, distilled at atmospheric pressure, b.p. 455 K) mixed with analar methanol in 90:10 (wt./wt.) ratio was used instead of pure phenol in all the hydrogenation experiments. This made the feeding of the reactants simple. The hydrogen used (Industrial Oxygen Limited, Pune) was passed to the reactor through a filter, keeping the ratio of feed-to-hydrogen at 1:3 (mole ratio).
Apparatus

The hydrogenation reaction was carried out in a fixed-bed, vertical flow, high-pressure reactor. The pressure in the system was controlled by a digital controller (Geomechanique, France).

The products were analysed by gas chromatography (HP 5880A and Shimadzu GC R1A) using 50 m x 0.5 mm phenyl silicone gum and 2-m carbowax columns.

RESULTS AND DISCUSSION

The major products obtained when phenol and hydrogen were passed over platinum and palladium catalysts supported on alumina and zeolite LTL were cyclohexanol and cyclohexanone. Benzene, cyclohexane and cyclohexene were also formed in small amounts in the reaction. The catalysts supported on zeolite LTL yielded a number of other products in very small amounts; these were not identified. Products of methanol (diluent, 10 wt.-% in the feed) conversion, if any, were not detected.

The distribution pattern of products for a typical run of the reaction at 523 K at a total pressure of 1 MPa is given in Table 1. The different behaviour of platinum and palladium catalysts with respect to yield of various products can be clearly seen in this table. Cyclohexanol is the main product with an appre-

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>PdA</th>
<th>PdZ</th>
<th>PtA</th>
<th>PtZ</th>
<th>PdA</th>
<th>PdZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow-rate (mol g⁻¹ h⁻¹)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Total conversion (%/total amount of products)</td>
<td>97</td>
<td>88.7</td>
<td>45</td>
<td>44.3</td>
<td>42.9</td>
<td>41.8</td>
</tr>
<tr>
<td>Product distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>87.2</td>
<td>78.4</td>
<td>5.1</td>
<td>8.9</td>
<td>8.4</td>
<td>8</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>7.7</td>
<td>6</td>
<td>39.5</td>
<td>32.7</td>
<td>32.2</td>
<td>32</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.9</td>
<td>0.81</td>
<td>0.2</td>
<td>0.4</td>
<td>0.31</td>
<td>0.2</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.7</td>
<td>0.31</td>
<td>0.13</td>
<td>0.15</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.57</td>
<td>0.07</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>3.1</td>
<td>-</td>
<td>2.11</td>
<td>1.8</td>
<td>1.54</td>
</tr>
<tr>
<td>Cyclohexanone/cyclohexanol</td>
<td>0.09</td>
<td>0.08</td>
<td>7.74</td>
<td>3.67</td>
<td>3.8</td>
<td>4</td>
</tr>
<tr>
<td>Selectivity</td>
<td>97.8</td>
<td>95.2</td>
<td>99.1</td>
<td>93.9</td>
<td>94.7</td>
<td>95.6</td>
</tr>
</tbody>
</table>

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ciable amount of cyclohexanone in the cases of PtA and PtZ, while the pattern
is reversed in the case of PdA and PdZ.

The effect of temperature was investigated by studying the reaction at four
different temperatures: 473, 498, 523 and 548 K with a constant pressure of 0.3
MPa (PtA and PtZ) and 1 MPa (PdA and PdZ) and a constant feed flow-rate
of 0.05 mol g⁻¹ h⁻¹. The results are shown in Figs. 1 and 2, respectively for the
platinum and palladium catalysts. It can be seen that the total conversion as
well as the yields of the main products, cyclohexanol and cyclohexanone, de¬
creased with increasing temperature. For the platinum catalysts, the yield of
cyclohexanol decreased more rapidly than that of cyclohexanone which is re¬
lected by the slow increase in the cyclohexanone/cyclohexanol ratio (Fig. 1).
In the case of the palladium catalysts, cyclohexanone was the major product
and the cyclohexanone/cyclohexanol ratio showed a much more pronounced
increase between 473 and 498 K for PdA (Fig. 2). For all the catalysts, the
yield of minor products did not change much with increasing temperature. The
results, however, indicate a relative enrichment of cyclohexanone over cyclo¬
hexanol with increasing temperature.

The yield of major products is also influenced by changes in the pressure
(Figs. 3 and 4). For the platinum catalysts (temperature 523 K, feed rate 0.05
mol g⁻¹ h⁻¹, hydrogen/phenol mole ratio 3:1), an increase in hydrogen pres¬
sure yielded more cyclohexanol, which is to be expected due to the presence of
a large excess of hydrogen. Cyclohexanone showed a corresponding decrease
(Fig. 3). This is further reflected in the nearly exponential decrease of cyclo¬
hexanone/cyclohexanol ratio with a pressure in the range 0.1 to 1.0 MPa. The
palladium catalysts, however, showed significantly different results (Fig. 4)
under a similar set of conditions. Total conversion showed an almost linear
increase in the pressure range 0.5 to 2.0 MPa. Initially, the yield of cyclohex¬
anone was much greater than that of cyclohexanol which almost stagnated.
With an increase in pressure, the production of cyclohexanol increased tre¬
mendously while that of cyclohexanone fell after going through a peak. For the
palladium catalysts, 1.0 MPa pressure of hydrogen seemed to be ideal for the
production of cyclohexanone.

The following sequence of reactions are suggested for the vapour-phase hy¬
drogenation of phenol:

\[
\text{O}_4 \xrightarrow{\text{hydrogenolysis}} \text{Benzeno} \xrightarrow{\text{dehydration}} \text{Cyclohexene} \\
\text{Phenol} \xrightarrow{\text{hydrogenation}} \text{Cyclohexanol} \xrightarrow{\text{dehydration}} \text{Cyclohexanone}
\]
Fig. 1. The effects of temperature on the yield of principal products for the platinum catalysts. (Feed rate: 0.05 mol g⁻¹ h⁻¹, pressure: 0.3 MPa, hydrogen/phenol mole ratio: 3/1.)

which, in essence, is similar to those proposed for the liquid-phase hydrogenation [5,6,9]. The increase in the cyclohexanone/cyclohexanol ratio, with temperature indicates that the dehydrogenation reaction is favoured by a high temperature, resulting in the production of more cyclohexanone. Partial hy-
drogenolysis is also responsible for the production of benzene as a byproduct, whose yield was found to increase with increasing temperature.

The increase in the cyclohexanol yield and the corresponding decrease in
Fig. 3. The effects of pressure on the yield of principal products for the platinum catalysts. (Temperature: 523 K, feed rate: 0.05 mol g$^{-1}$ h$^{-1}$, hydrogen/phenol mole ratio: 3/1.)

the cyclohexanone/cyclohexanol ratio with an increase in hydrogen pressure is obviously due to the greater availability of hydrogen. The increased yield of benzene with increasing hydrogen pressure is a clear pointer to its production through the hydrogenolysis of phenol.

An increase in the flow-rate of the feed (keeping the phenol/hydrogen ratio
Fig. 4. The effects of pressure on the yield of principal products for the palladium catalysts. (Temperature: 523 K, feed rate: 0.05 mol g\(^{-1}\) h\(^{-1}\), hydrogen/phenol ratio: 3/1.)
constant) decreased the conversion of phenol (Table 1). The yields of all products declined with decreasing contact time, but the cyclohexanone/cyclohexanol ratio increased slightly. This indicates that cyclohexanone is the intermediate in the hydrogenation of phenol to cyclohexanol.

The conversion of phenol and the selectivities towards cyclohexanone and cyclohexanol are found to be greater in the case of alumina-supported catalysts than in the case of zeolite-supported catalysts, perhaps due to the smaller number of side reactions in the case of alumina (Table 1).

CONCLUSIONS

The vapour-phase hydrogenation of phenol seems to be very much dependent on the metal used. The conversion of phenol over platinum supported on alumina and zeolite LTL is more than twice (about 89% and 97%, respectively) that compared to the respective palladium catalysts (about 42% and 45% for alumina and zeolite LTL supports, respectively) under the same conditions of pressure and temperature for fresh catalysts (Table 1). The cyclohexanone/cyclohexanol ratio is also always lower in the case of the platinum catalysts than in the case of palladium catalysts under the same set of conditions. Rylander [13,14] has shown that when palladium is used as the catalyst, a high yield of cyclohexanone is obtained which agrees with the findings of our present study. According to Rylander, palladium has a high double bond isomerization activity and can readily isomerize cyclohexanol to cyclohexanone. Takagi et al. [15], however, do not subscribe to this view. The present work conclusively proves that platinum is a much better catalyst than palladium for the hydrogenation of phenol in the vapour phase.

This work illustrates how differently two very similar metals, palladium and platinum, behave towards the hydrogenation of phenol. On the basis of percentage d-character of the metallic bond (Pd: 46, Pt: 44), palladium in a crystalline state or in a compound is expected to show the greater catalytic activity [16]. However, this activity depends on a number of factors including temperature and pressure, and the rates of adsorption and desorption of the reactants and the products on the catalyst surface. In hydrogenation reactions, the activity of palladium is likely to be limited by its ability to dissolve hydrogen atoms, thus maintaining a low concentration of them on the surface [17]. Platinum, on the other hand, dissociates molecular hydrogen easily and has a much larger concentration of hydrogen atoms on the surface.

Sintering may also be responsible for the differing pattern of behaviour of palladium and platinum. It is known [18] that dispersed particles of palladium are more sensitive to the hydrogen reduction temperature than those of platinum. Calcining temperatures may also have some effect. Sintering reduces the surface area of the catalysts more in the case of palladium than platinum and the catalytic activity is likely to be modified correspondingly.
Strong metal support interactions (SMSI) may also play some sort of role. Levin et al. [19] have shown the order of charge transfer among the group VIII metals to be Pt > Pd > Rh > Ru, the magnitude determining the extent of activation of the molecules on the surface. Much more work needs to be done in order to draw some conclusion as to the possible cause of the differences in behaviour of palladium and platinum. Similarly, the role of the support has to be evaluated to see if the catalysts behave bifunctionally.

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REFERENCES

Synthetic Zeolites : An Overview

A. K. Talukdar¹, A. K. Misra², and K. G. Bhattacharyya*.

Abstract:

The methods of preparation, identification, surface characterization and study of catalytic properties of the synthetic zeolites have been reviewed with special emphasis on the high-silica zeolites. The review covers important publications mainly from 1984 to mid-1989. It is suggested that much more work is needed to completely understand the complex characteristics of a zeolite surface and to correlate them to the catalytic activity. 46 references.

Key words: Zeolites, Catalysis, Synthetic zeolites.

Classification: Physical Chemistry (Surface Chemistry and Catalysis)

Introduction:

Synthetic zeolites are one of the largest groups of catalysts. The principal user is the petroleum and the petro-chemical industries. More than 90 per cent of all catalytic cracking reactions, yielding hundreds of useful hydrocarbons are now done over zeolites. The natural zeolites have long been replaced with the synthetic ones which can be tailor-made to suit specific requirements. The selectivity and the activity of the synthetic zeolites do not change much with time and temperature. These man-made zeolites are also immensely suitable for a number of other industrially important reactions, such as isomerisation, hydrogenation, oxidation, polymerisation, selective reforming, alkylation, etc.

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A zeolite may be described as a hydrated aluminosilicate or more appropriately as a silicoaluminate, having a definite crystal pattern and of the empirical formula:

$$M_{2/n}Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

where $x \geq 2$ and $n$ is the valence of the metal, $M$. The complex structure is characterised by a rigid, three-dimensional framework of $SiO_4$ and $AlO_4$ tetrahedra mutually cross-linked by sharing of the oxygen atoms. The unit negative charge of the $AlO_4$ tetrahedra is balanced by a suitable cation. This cation can be partially or totally exchanged with other cations. The spaces between the tetrahedra are normally occupied by water molecules. The main feature of the zeolite structure is the existence of a large number of small cavities, interconnected by a number of still smaller channels and pores. These combine to give a very large surface area to the zeolites making them very effective solid catalysts. A large number of both strong and weak acidic sites can be produced on the zeolite surface through various processes making them the most sought-after solid acid catalysts. The structure and properties of the zeolites have been thoroughly discussed by Breck (1974) and Barrer (1978, 1982).

Zeolite Synthesis:

Synthetic zeolites have been first put to extensive commercial use by the Mobil Oil Corporation, USA and most of the methods of synthesis of different zeolites appear as patents by Mobil scientists. The synthesis essentially consists of a nucleation-controlled process occurring from molecularly inhomogeneous, alkaline aqueous gels at temperatures between 80 and 300°C. The composition of the reaction mixture is defined by a set of molar ratios (Lechert, 1984):

$$SiO_2/Al_2O_3 \cdot H_2O/\cdot SiO_2 \cdot OH^-/\cdot SiO_2 \cdot M^+/\cdot SiO_2$$

where $M^+$ is commonly Na$^+$ ion, but can also be other alkali-, alkaline earth or ammonium ions. In recent years the highly shape selective ZSM-type zeolites have been prepared by addition of quaternary ammonium salts, amines or other polar substances. The composition is thus determined also by the molar ratio:

$$R_4N^+/SiO_2.$$
composition of the zeolite have been discussed by Rollmann (1984) and a summary is given in Table 1.

Table 1. Reaction Mixture Composition Parameters and their Primary Influence on Zeolite Synthesis.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Primary Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>Framework composition</td>
</tr>
<tr>
<td>H₂O/SiO₂</td>
<td>Rate, Crystallization mechanism</td>
</tr>
<tr>
<td>OH⁻/SiO₂</td>
<td>Silicate molecular weight and OH⁻ concentration</td>
</tr>
<tr>
<td>Na⁺/SiO₂</td>
<td>Structure, Cation distribution</td>
</tr>
<tr>
<td>R₂N⁺/SiO₂</td>
<td>Framework aluminium content</td>
</tr>
</tbody>
</table>

Barrer (1985) has divided the zeolites into several categories depending upon the SiO₂/Al₂O₃ ratio. The two most important categories are the aluminous zeolites (Si/Al ratio between 1 and 5) and the siliceous zeolites (Si/Al ratio greater than 12). The synthesis conditions for the two are different. In this overview, we will be discussing mostly the siliceous zeolites of which ZSM-5 (SiO₂/Al₂O₃ ratio 5 to infinity) is a typical example.

Commercially available silicon and aluminium source materials may be used for the synthesis of the zeolites. These include sodium silicate, silica gel, silica sol, sodium aluminate, aluminium sulphate, aluminium turnings, alumina, etc. Clays can also be used as the source material (e.g. Haden and Dzierzanowski 1972 and Drag et al. 1985). Successful synthesis always requires addition of organic bases or salts of these bases to the reaction mixture. Often the organic base itself functions as the templating agent in the nucleation process and there is no need for the addition of an inorganic base like NaOH or KOH. A large number of organic compounds are in use but the quaternary ammonium salts like tetrapropyl ammonium hydroxide are the favourites.

The zeolite framework, which crystallizes from a reaction mixture is determined by the composition and the temperature of the mixture. The cation M⁺ has also strong influence. Zdanov (1968) has shown that the alkali-content has a greater influence on the kind of zeolites.
than the Si\textsubscript{3}O\textsubscript{7} /Al\textsubscript{2}O\textsubscript{3} ratio. On the other hand, Rollmann (1980) has observed that the addition of an organic templating agent helps in obtaining a new zeolite structure or a zeolite with a significantly new chemical composition or with different crystal parameters or in increasing the crystallisation rate.

The zeolite crystallisation takes several days. Arganer and Landolt (1972) have shown that the crystallisation of ZSM-5 may take 5 to 10 days depending upon nucleation conditions. Plank, Rosinski and Rubin (1977) have reported the crystallisation of ZSM-35 in 17 to 62 days again depending on the reactants and other conditions. Vallyocsik (1984) has reported the formation of ZSM-23 in 5 days. The zeolite HZSM-5 was synthesized similarly by Chen et al. (1978).

Szostak (1988) has described in details the methods of synthesis and identification of molecular sieve zeolites. Ernst et al. (1987) have described the synthesis of a ZSM-20 zeolite. Zeolite L was prepared in presence of copper by Verduijn (1988).

Zeolite Characterisation:

X-ray diffraction is the most convenient method for identification of the zeolites. The diffraction pattern for a synthesized species is compared with that of an authentic zeolite sample having identical composition and similar crystal size. Elemental analysis, study of sorption and cation exchange properties supplement the diffraction studies.

The principal parameters which characterize a zeolite are, according to Barthomeuf (1984),

i) the Al content or the Si/Al ratio;
ii) the cation content and the nature of the cations, and
iii) the surface acidity, the nature and amount of strong and weak acid sites and their behaviour with temperature.

An increase in Si/Al ratio improves greatly the thermal or hydrothermal stability of the zeolite (McDaniel and Maher, 1976). Uytterhoeven et al. (1968) have shown that a lower Al content (higher Si/Al ratio) always means a lower density of hydroxyl groups with longer separations between them and therefore, the probability of dehydroxylation and defect-generation will be less. A higher Si/Al
ratio generally makes the zeolite catalytically very active, but there is always an optimum Si/Al ratio beyond which catalytic activity again shows a decreasing trend. For example, the zeolite ZSM-5 containing 10 to 10,000 ppm Al is known to have maximum activity for intermediate Al content.

The replacement of monovalent ions of the zeolite by polyvalent ions imparts very favourable properties. The polyvalent cations create acidic centers by undergoing hydrolysis:

\[ M^{n+} + x\text{H}_2\text{O} \rightarrow M(O\text{H})^x \]

Introduction of rare-earth cations to the zeolite framework also produces higher activity; good thermal stability and low probability of deactivation. In general, the activity of the zeolites increases as the sodium content is decreased. Handreck and Smith (1989) have recently studied the nature of exchange sites on the surface of Al-ZSM-5 zeolite.

Characterization of zeolite acidity is done with spectroscopic and analytical methods. Infra red measurements are useful in hydroxyl group characterization and measuring Bronsted and Lewis acidity. Ward (1976) has very elaborately discussed the application of infra red spectroscopy for zeolite characterization. Acidity strengths and concentrations are commonly determined with respect to pyridine and ammonia adsorption, while 2, 6 dimethyl pyridine is used to estimate Bronsted acidity as steric hindrance prevents its coordination with Lewis acid sites.

The Bronsted acid strength in zeolites can also be evaluated from the IR frequency shift of hydroxyl groups upon interaction with hydrogen bond acceptor molecules such as benzene. A comparative infra red study of zeolite acidity by using ammonia, methyamine and n-butylamine has been reported by Ghosh and Curthoys (1984).

Other methods such as UV, NMR, ESR, DTA, Chromatography, etc., are also used by various workers to characterize zeolite acidity. Direct titration with butylamine and colour indicators is also in practice but although this method allows an easy estimation of acid site concen-
tration and strength, it cannot yield information on the nature of the acid sites.

The Brønsted or protonic acid centers in zeolites are generated in several ways, e.g.,
(i) By thermal decomposition of ammonium from of the zeolite:

\[
\begin{align*}
\text{Si} \quad & \quad \text{Al} \quad & \quad \text{Si} \\
\text{H}^+ & \quad \text{H}_2\text{O} & \quad \text{Si} \quad & \quad \text{Al} \quad & \quad \text{Si} \\
\end{align*}
\]

However, during heating some dehydroxylation may also take place and then, Lewis acid sites are produced:

\[
\begin{align*}
\text{Si} \quad & \quad \text{Al} \quad & \quad \text{Si} \\
\text{H}_2\text{O} & \quad \text{Si} \quad & \quad \text{Al} \quad & \quad \text{Si} \\
\end{align*}
\]

(ii) Polyvalent ions may ionise water producing Brønsted acid sites as already discussed.
(iii) Transition metal cations in zeolites may be reduced by hydrogen with the formation of hydrogen-zeolites. For example, Brønsted acidity in \( \text{Cu}^{2+}Y \) zeolite can be generated in this way:

\[
\begin{align*}
2 \text{Cu}^{2+} + \text{H}_2 & \rightarrow 2 \text{Cu}^+ + 2\text{H}^+ \\
2 \text{Cu}^+ + \text{H}_2 & \rightarrow 2 \text{Cu}^0 + 2\text{H}^+
\end{align*}
\]

Carbon monoxide and hydrocarbons are also used for reduction.
(iv) Exposure of the zeolite to halide compounds at room temperature or to carbon dioxide at 150—400°C also generates Brønsted acid sites.
The overall acidity of a zeolite depends on pretreatment temperature and both Brønsted (\(-\text{OH}\)) and Lewis (\(-\text{Al}\)) sites can be present simultaneously at high temperatures. The acid strength of these sites depend on their location and environment. Infra red measurements indeed can detect several types of hydroxyl groups in a single zeolite.

The potential number of acid sites in a zeolite is equal to the number of Al atoms per any reference unit. However, the actual number available for catalytic activity is still smaller as this depends on several factors like degree of crystallinity, amount of dehydroxylation, partial neutralization with cations or bases, accessibility of the sites, the acid strength of such sites, etc.

The Si/Al ratio and the short and long range ordering of the Si and Al atoms also affect the acid strength. The use of \(^{29}\text{Si} \) NMR and \(^{27}\text{Al} \) NMR in recent times has made it possible to know the exact location of the Si and Al atoms in the zeolite framework. This and other measurements including theoretical calculations have helped in determining the relative acid strength distribution in a zeolite. Kiricsi and Forster (1988) have used UV-Visible and IR spectroscopy to characterize a HZSM-5 surface from propene adsorption. XPS and ESR data have been used to study X- and Y-zeolites by Goldfarb et al. (1988). A large number of physical methods have been investigated for zeolite characterization by Shpiro et al. (1988). Spaciousness index has also been used (Weitkamp et al., 1989) to find out the effective pore width in the zeolites. Far infra red measurements have been utilised successfully (Godber et al., 1989) to probe into the cation site occupancies and their distributions in a zeolite framework.

Despite all these work, the overall picture of a zeolite is still very much complex and much more work will be needed to completely understand the structural characteristics of the zeolites.

Catalysis by Zeolites

Poutsma (1976) has shown that any reaction, which involves a carbonium ion intermediate, can be catalyzed by a zeolite. The mechanism of catalytic action is not different from catalysis by an
acidic oxide. However, the very open structure of a zeolite makes the larger part of $\text{AlO}_4$ and $\text{SiO}_4$ tetrahedra accessible to the adsorbed molecules. The three-dimensional network has cavities and channels where the reactant molecules can undergo transformations. Most of the surface of a zeolite is in fact inside the crystal and the cavity wall properties are strongly dependent upon the framework constituting atoms.

Fundamental discoveries in the use of zeolites in hydrocarbon catalysis were made in the 50's primarily in the laboratories of Union Carbide, Mobil Corporation and Esso Research and Engineering Company. A commercial zeolite Y isomerization catalyst introduced by Union Carbide in 1959 was the first of a series of molecular sieve based catalysts for the petroleum industry. Since then zeolite catalysts have found innumerable applications in industry.

Perhaps, of all the reactions studied in the laboratory on zeolite catalyst, cumene cracking has received the widest attention as a model reaction for evaluating the catalytic efficiency of the zeolites. Wojciechowski and his group have very exhaustively studied the kinetics and the mechanism of this reaction over a large number of synthetic zeolites. Corma and Wojciechowski (1979) have studied cumene cracking over HY and LaY zeolites at 360, 430 and 500 C with the conclusion that the nature of active sites is the same in both the catalysts and that the HY has a higher activity than the LaY. This is attributed to the higher number of Bronsted sites in the HY than in the LaY. For the same reason, the HY is deactivated rapidly. Later, Corma and Wojciechowski (1982) proposed a detailed mechanism of cumene cracking and explained the formation of various products. This mechanism was examined thoroughly by Pines (1982). Fukase and Wojciechowski (1986) have studied the same reaction over HZSM-5 catalyst at 430 C, showing propylene, n-propyl benzene and coke as the principal primary products accompanied by a large number of secondary products of which olefins constitute the major part. The differences in products for HZSM-5, HY and LaY zeolites are attributed to the pore structure of HZSM-5 and the corresponding shape selectivity. A similar but somewhat less exhaustive study was earlier done by Katsanos and Kotinopoulos (1985) on HY and LaY zeolites.
Bielanski and Malecka (1986) have identified benzene and propylene to be the main products of cumene cracking over NaH-Y and NaH-ZSM-5 zeolites. According to these authors, side reactions producing a large number of secondary products, are favoured by strong acid sites. The shape selectivity of ZSM-5 is responsible for partial conversion of propylene to butenes and pentenes.

In cracking of n-paraffins over zeolites, the length of the hydrocarbon chain is always a determining factor. The longer the chain, the smaller is the activation energy required for cracking and the more is the percentage conversion.

Corma et al. (1982) studied the kinetics of n-heptane cracking, isomerization and disproportionation over CrHNaY zeolites at 400-470 °C. They concluded that although a wide range of acid sites with different strengths could be detected on the zeolite surface by titration method, only a small fraction of these sites were involved in the cracking reaction. The rate-controlling step according to them is not the formation of the carbonium ion, but the C-C bond breaking. The same group of authors (1984) studied n-heptane cracking on ultrastable HY zeolites.

The kinetics of catalytic cracking of n-paraffins on HY zeolites were studied by Abbot and Wojciechowski (1987). By assuming simple first-order Langmuir adsorption, a rate expression of the form,

\[ \frac{dX}{dt} = \frac{A}{1-X} + B(1-X) \]

where \( A \) and \( B \) are constants and \( X \) is the fractional conversion of the paraffin (\( t \) is the feed contact time) is obtained. They also showed that the cracking reaction was strongly inhibited by product olefins. The influence of acidity and pore structure of a HZSM-5 zeolite on n-heptane cracking was studied earlier by Corma et al. (1985), showing that HZSM-5 and ultrastable HY zeolites behave differently in cracking reactions. It is shown that this difference is due to the fact that although ultrastable HY has a higher number of acid sites, the HZSM-5 has a higher proportion of stronger acid sites. While the ultrastable HY is three times more active for n-heptane cracking compared to the HZSM-5, it also decays eight times faster than the HZSM-5. The rates of cracking
of n-heptane on Ni-, Zn—and H-ZSM-5 incorporated with a silica binder are found to be

Ni-ZSM-5 > Zn-ZSM-5 > H-ZSM-5

by Riley and Anthony (1986). The HZSM-5 is already known for its superb activity, lower ageing rate and better steam stability for cracking reactions compared to most other zeolites (Wang et al., 1979).

Another reaction, which has been receiving wide interest is the conversion of methanol to hydrocarbons over zeolites. Roy et al. (1987) have shown that the product pattern on methanol conversion varies very greatly depending upon the type of zeolite, e.g. ZSM-5 gives 85% methane, while H-13X gives 46% ethene as the main product.

Transformation of lower hydrocarbons to aromatics over zeolites has also received considerable attention. Thus, while studying the conversion of propane into aromatic hydrocarbons over HZSM-5 and Ga-ZSM-5, Kitagawa et al. (1986) observed that introduction of Ga to ZSM-5 greatly improved the selective formation of aromatics as well as total conversion. Sirokman et al. (1986) also observed similar influence of Ga in conversion of pentane to aromatics. Ono et al. (1988) have also shown that either Zn or Ga in ZSM-5 appreciably increases the yield and selectivity of aromatics on methanol conversion. Sano and his coworkers (1987) have similarly observed that introduction of Fe into the ZSM-5 network increases the yield of ethane and propane on hydroconversion of benzene. Incorporation of metal ions thus considerably improve the catalytic properties of the zeolites.

Conclusion:

Synthesis of newer and newer varieties of zeolites, characterization of their surfaces and probe into their use for catalyzing a huge number of reactions, involving transformations of hydrocarbons have presented a fascinating and ever-expanding field of research. The synthesis itself is very simple with the possibility of preparing a large number of different zeolites by varying the synthesis conditions. All available spectroscopic and other tools
have been utilised for surface characterization of the zeolites. No single method can give all the necessary informations. The actual mechanism of catalytic action by these catalysts is still a matter of research. Attempts to correlate catalytic activity to the surface acidity, both Bronsted and Lewis, have not been entirely successful. Much work is still needed to have a complete understanding of the activity and selectivity of the zeolites.

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Characterization of Zeolite Linde Type L with XRD and Other Techniques

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Abstract

The crystallinity and purity of zeolites, Linde type L (LTL), which were synthesized from $8K_2O$, $1A_12O_3$, $20SiO_2$, $200H_2O$ system by standard method, were examined by different physical techniques such as X-ray powder diffraction, infra-red spectroscopy, scanning electron microscopy, etc. Thermal stability was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). All these techniques along with chemical analysis and adsorption studies proved the formation of pure and fully crystallised zeolite LTL.

Introduction

The aluminosilicate framework of zeolite LTL, which belongs to the class of intermediate silica large pore zeolites, is based on polyhedral cages formed by five six-membered and six four-membered rings. The main channels consisting of alternate cancrinite (or E) cages and hexagonal prisms form columns that run parallel to c-axis. Each column is isolated from all neighbouring ones. The main channel is circumscribed by 12-membered rings. The field of application of LTL zeolites is considerably broadened by its structural peculiarities and its high thermal stability and acid resistant properties. The aim of the present work is to study the purity and crystallinity of the synthesized zeolite LTL by XRD and other physical methods.
Experimental

Zeolite of Linde type L (LTL) was synthesized from an initial oxide mole composition of the gel of $8K_2O: 1A1_2O_3: 20SiO_2: 200H_2O$. The reaction mixture was prepared by dissolving 3.1g of aluminium trihydrate in a boiling alkali solution prepared by dissolving 17.92g of KOH in 70ml of water. 24.88g of fumed silica was added slowly to this solution with vigorous stirring till the gel was homogeneous. The gel was sealed in an autoclave and kept in an air oven at 413K under unstirred condition for 40 hrs. The solid product obtained after filtration was washed with distilled water till the pH of the effluent was in between 9-11. The product was then dried in an air oven at 393K for 4 hrs.

X-ray powder diffraction pattern of the sample was obtained on Rigaku D/MaX-III VC diffractometer using Ni-filtered CuKα (λ = 1.540Å) radiations. Stereoscan-150 (Cambridge) scanning electron microscope was used for morphology study. IR-spectrum of the sample was recorded with a Perkin-Elmer 221 spectrometer using KCN as an internal standard. TG/DTA was recorded simultaneously on an automatic derivatograph NETSCH, model STA 490. Preheated and finely powdered α-alumina was used as a reference material. The sorption properties for different probe sorbates were measured gravimetrically in a conventional high vacuum adsorption system using McBain balance, after the sample was degassed prior to the measurement, at 673 K for 4 hrs. at $P=1.3 \times 10^{-6}$ bar. Then it was cooled in vacuum to 298 K. The amount adsorbed at equilibrium at $P/P^0=0.5$ was recorded. The chemical analysis was obtained on dry basis by gravimetric method using atomic absorption spectroscopy and flame photometry.

Results and Discussion

As the X-ray powder diffraction pattern is the fingerprint of the individual zeolite structure, it provides information about the degree of crystallinity and the phase purity. Fig. 1a shows the x-ray powder diffraction pattern of the zeolite phase obtained. The d-spacing values and the relative intensities derived from the pattern were found to be similar to those reported$^4$ for the LTL zeolite. It was also observed that after prolonged hydrothermal treatment (more than 40 hrs.), the
Impurity peaks due to zeolite W (Merlionite) starts appearing at the cost of LTL phase. This suggests that maximum crystallinity of the zeolite LTL phase could be obtained by limiting the synthesis to 40 hrs. at 413 K. The contribution, if any, due to amorphous phase was examined by SEM. Fig. 1b shows the SEM photograph of the LTL phase. Well-defined crystallites with nearly spherical disc-like shapes of size ranging from 0.5 to 1.5 μm were found with no contribution due to impurity or amorphous phase. Framework IR spectrum (400-1200 cm⁻¹) for the LTL phase is shown in Fig. 1c. A shoulder band around 440 cm⁻¹, characteristic of pore opening, is seen to be fully developed in the spectrum. A doublet at 770 and 720 and a triplet at 1020, 1090 and 1150 cm⁻¹ were also observed suggesting fully crystalline nature of the obtained LTL phase. From the chemical analysis, the unit cell composition of the LTL zeolite was calculated on anhydrous basis. The unit cell composition can be represented as K₀.₀₁ [(Al₂O₃) 8.₉₉ (SiO₂) 2₇.₀₁⁻]. The equilibrium sorption capacities for water and benzene were found respectively to be 17.52 molecules and 2.81 molecules per unit cell. These values also show the absence of any occluded amorphous material.

Thermoanalytical curves are often used to characterize the thermal properties of the zeolites. The temperature of the maximum of the high temperature exotherm is taken as a criterion for the thermal stability of the zeolite lattice. Fig. 1d shows the TG/DTA curves of the LTL phase, (prepared at 423 K and 40 hrs.). DTA curve does not show any exotherm upto 1273 K indicating zeolitic lattice stability at least upto 1273 K. The dehydration proceeds in a single stage, which is confirmed by a broad endotherm between 308 to 538 K at a peak minimum at 433 K. The TG curve shows 12.1% weight loss due to zeolitic water present in the sample.

Conclusion

The experimental data demonstrates that zeolite LTL can be obtained at highly pure, crystalline state by hydro-thermal synthesis at 413 K and 4 hours. If, however, the synthesis period exceeds 40 hours, the impure phase due to zeolite W begins to replace zeolite LTL.
Fig. 1a. XRD PATTERN OF ZEOLITE LINDE TYPE L
[0] synthesized, [X] standard.

Fig. 1b. XRD PATTERN OF ZEOLITE LINDE TYPE L

Fig. 1c. IR SPECTRA OF ZEOLITE LINDE TYPE L

WAVE NUMBER CM$^{-1}$
Fig. 1a. TGA of zeolite Linde type (ii).
results also show the utility of such analytical techniques as XRD, SEM, IR, DTA/ TGA and sorption studies for characterization of the zeolites whose importance in the field of catalysis needs no emphasis.

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