Influence of coke on the aromatization of 3-carene in the vapour phase over zeolites

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Received 5 April 2000; revised 31 July 2000

Conversions of 3-carene to cymenes over NaI\(_{13}\)X, NaY and NaZSM-5 are less than over NaH\(_{13}\)X (29% proton exchange), NaHY (33% proton exchange) and NaHZSM-5 (35% proton exchange). In the presence of oxygen, at its different partial pressures, the formation of cymenes increases significantly with increase in time on stream, indicating the formations of some species in the coke during the reaction which enhances the activity of the catalysts. To identify the species that cause enhancement of the activity, zeolite NaHY (catalyst B) has been doped with different amounts of NaOH and the reactions have been carried out over them at 350°C, at a contact time of 1.0 h (contact time is expressed as the reciprocal of \(W_{\text{HSV}}\), the weight hourly space velocity representing the weight of 3-carene passed over 1 g of catalyst per hour). The coke deposited has been examined by IR, ESR and XRD. Formation of quinone type of carbonyl group, responsible for the enhanced activity of the zeolites is observed. The participation of the quinone group in the dehydrogenation process is confirmed by extracting the coke after the reaction and the same reaction is carried out over the extracted coke both in the presence and in the absence of oxygen under the same experimental conditions. The quinone group is present in an atmosphere of oxygen but is absent if there is no oxygen.

All catalytic reactions of organic compounds are accompanied by the deposition of carbonaceous materials called coke which affects the activity of the catalysts. Menon reported\(^2\) that coke formed during the oxydehydrogenation of ethylbenzene acts as true catalytic active sites. For the same reaction, the carbonaceous materials formed over \(\text{Al}_2\text{O}_3\) were identified as the actual catalytic active sites.\(^3,5\) Carbonaceous deposits formed during the oxidative dehydrogenation of ethyl benzene, attacked by \(\text{O}_2\) have been shown to produce active coke containing carbonyl oxygen.\(^6\) Boehm and Knozinger observed\(^7\) that oxygen reacts with carbon at high temperature to yield the functional groups such as carbonyl, lactone, carboxyphenol, hydroquinone and aldehyde. Other reactions catalysed by coke include cumene cracking, butene isomerization and ammoxidation of toluene.\(^8,11\) With a view to identify the species present in the coke, initially, the effect of partial pressures of oxygen over NaH\(_{13}\)X, NaHY and NaHZSM-5 was studied. Subsequently the coke formed over NaHY (Catalyst B) and NaHY doped with different amounts of NaOH was examined by IR, ESR and XRD. The coke was extracted and used for the aromatization 3-carene with time on stream.

3-Carene is a bicyclic, mono-olefinic monoterpene, occurring in Indian turpentine to the extent of about 60% along with alpha- and beta-pinenes. The Indian turpentine is rendered poor in keeping quality, since its major component 3-carene undergoes aerial oxidation with remarkable ease\(^12,13\) and resinifies rapidly on exposure to air. Attempts were made to render it more stable and more useful from industrial viewpoint by converting it into a mixture of \(p\)-, and \(m\)-cymenes which could be used for the preparation of fine chemicals.\(^14-18\) The objective of this investigation is to convert 3-carene into a mixture of cymenes over zeolites and also to identify active species in the coke.

Materials and Methods

Preparation of catalysts

As-synthesized NaI\(_{13}\)X, NaY and NaZSM-5 obtained from NCL Pune, were calcined at 350°C for 8 h in a muffle furnace. All zeolites were partially converted into H-form by ion-exchange using 1 M \(\text{NH}_4\text{NO}_3\) solution (20 ml/g catalyst) at 95°C for 1 h and then dried at 110°C for 3 h and finally calcined at 500°C for 6 h to remove \(\text{NH}_3\).

Isolation of 3-carene

3-Carene (b.p.171°C) was isolated from alpha-pinene (b.p.157°C) and beta-pinene (b.p.169°C) by fractionation of Indian turpentine using a 150 cm fractionating column packed with glass beads equivalent to 18 theoretical plates at 10 mm of \(\text{Hg}\).
pressure. Its purity was checked by G.C. (99.5%). n-Butylamine (b.p.78°C) was purified before use.

Characterization of catalysts

Analysis of crystallinity by X-ray studies (Philips X-ray diffractometer, PW 1059) reveals that NaH13X, NaHY and NaHZSM-5 were 100% crystalline. The surface area measured by BET method are 614, 593 and 398 m²/g respectively. The total acidity and strength of acid sites were determined by potentiometric method for all catalysts using n-butylamine. The total acidity of NaH13X, NaHY and NaHZSM-5 were 0.89, 0.76 and 0.46 meq/g respectively and these zeolites are designated as A30, B30 and C30 respectively. The weak, medium and strong acid sites are 0.30, 0.29 and 0.30 meq/g for A30. The corresponding values for B30 are 0.27, 0.21 and 0.28 meq/g.

Catalytic reactor system

The vapour phase catalytic transformations of 3-carene was done in a fixed bed flow type reactor made up of quartz, the inner diameter and length of which were 10 mm and 30 cm respectively. The catalyst was placed at the mid-position of the reactor which was kept inside a tubular furnace, controlled by a digital temperature controller-cum-indicator. The temperature was measured by a chromel-alumel thermcouple placed in the centre of the catalyst bed. The reactant was fed into the reactor by a syringe infusion pump that could be operated at different flow rates.

Analysis of the products

The liquid products were collected in a trap kept in ice and the gaseous products were collected by the downward displacement of brine solution. The products collected for the first 15 minutes were discarded and analysis was made only of the products collected after the attainment of steady state. The liquid products were identified and estimated in a (Hewlett, Packard, 5890 A) gas chromatograph using FID. A two metre column of 5% bentone-34 and 5% DIPD on chromosorb-120 was used. Gaseous products were analysed by Orsat gas analyser.

Regeneration of the catalyst

After each run the reactor was flushed with nitrogen to remove the adsorbed molecules and are regenerated at 500°C by passing a current of CO₂-free air for 5 h. This procedure was found to restore its original activity.
Results and Discussion

The conversion of 3-carene over sodium forms of the zeolites are less than its conversion over proton exchanged forms. The zeolites Na13X, NaY and NaZSM-5 are exchanged for protons to different levels by ion exchange as described earlier. Out of various levels the optimum activity is shown at 29, 33 and 35% proton exchange by Na13X, NaY and NaZSM-5 respectively for the aromatization of 3-carene to cymenes. Various reactions involved during the transformations of 3-carene are shown in the reaction Scheme 1.

Influence of oxygen on TOS

Using NaH13X (A30), NaHY (B30) and NaHZSM-5 (C30), the influence of time on stream (TOS) on the aromatization of 3-carene to cymenes in the presence of O2 at its partial pressures of 0.15, 0.26 and 0.35 atm and also in its absence was investigated at 350 °C and the results are plotted in a, b and c of Fig.1 respectively. In the absence of O2 the formation of cymene decreases with TOS. However, in the presence of O2 at a partial pressure of 0.15 atm the formation of cymenes registers a significant increase (the increase is different for different catalyst systems) up to 4 h beyond which there is a slight decrease. Further increase in partial pressure of O2 decreases the formation of cymenes due to dilution. However, the formation of cymenes in the presence of oxygen is definitely higher compared to its formation in the absence of O2. The higher cymene formation in the presence of oxygen reveals the fact that coke formed during the reaction may contain some species which enhances the activity of the catalysts.

Influence of NaOH doping

To identify the nature and the condition under which the active species are formed, it is decided to carry out the reactions at various acidities of the zeolite. For this purpose the zeolite NaHY (catalyst B30) was doped with 1.0, 2.0, 3.5 and 5.0% NaOH and their surface areas and acidities were determined and given in Table 1. Doping decreases the surface area and the acidity of the catalysts. The total acidity of B30 and B30 doped with 1% NaOH are 0.76 and

![Figure 1](image-url)

**Table 1**—Surface area and acid sites distribution of zeolite B30: Effect of sodium hydroxide

<table>
<thead>
<tr>
<th>NaOH loading wt%</th>
<th>BET area m²/g</th>
<th>Acidity</th>
<th>Total acidity meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak sites meq/g</td>
<td>Medium sites meq/g</td>
<td>Strong sites meq/g</td>
</tr>
<tr>
<td>0.00</td>
<td>0.27</td>
<td>0.21</td>
<td>0.28</td>
</tr>
<tr>
<td>1.00</td>
<td>0.26</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>2.00</td>
<td>0.24</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>3.50</td>
<td>0.20</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>5.00</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3-Carene was aromatized over B30 at 350°C in the absence of O₂ for a period of 1 h, and its acidity was determined without regeneration of the catalyst and the values of weak, medium and strong sites are 0.20, 0.11 and 0.03 meq/g respectively. After regeneration the corresponding values are 0.25, 0.20 and 0.24 meq/g. The data indicate a reduction of all acid sites. But the reduction is more for strong sites. On regeneration, more than 90% of the original acidity of medium and weak acid sites were regained. Strong acidity regained only to the extent of 86%. From the results it can be inferred that coke deposition is more over strong acid sites, which diminishes its activity.

Over catalyst B30 impregnated with 1.0, 2.0 and 3.5% NaOH, the formation of cymenes increases with increase in TOS (Table 2). This is due to the preferential neutralization of strong and medium acid sites (cf Table 1). If they are not neutralised, they catalyse the side reactions such as disproportionation involving hydrogen transfer among the menthadienes to form menthones and cracking reactions leading to the formation of toluene. Since these undesired side reactions are suppressed, the formation of cymenes increases (cf Table 2). In addition, the coke formed over these catalysts also enhances the activity of the catalysts causing an increase in the formation of cymenes. The decrease with 5.0% NaOH impregnation (Table 2), shows that the acid sites present are not strong enough for the initial isomerization of 3-carene to menthadienes which are subsequently dehydrogenated to cymenes.

Analysis of coked catalysts

IR spectra of doped catalysts, after using them for the transformations of 3-carene in the presence and absence of oxygen are presented in I and II of Fig. 2 respectively. The intensity of the characteristic coke peak at 1585 cm⁻¹ both in the presence and absence of oxygen decrease with increase in the concentration of dopant. In the presence of oxygen, an additional peak appears at 1660 cm⁻¹ up to 3.5% NaOH loading, which is assigned to quinone type carbonyl group. The same is not formed for 5.0% NaOH doping.
ESR analysis of coked catalysts

Aromatization of 3-carene over B30 doped with 1.0% NaOH was carried out for 1, 3 and 5 h separately in the presence and absence of O₂ and the ESR spectra of the spent catalysts were recorded and given in a and b of Fig. 3 respectively. In the presence of oxygen, the linewidth of ESR decreases several-folds on increasing the reaction time from 1 h to 5 h, indicating an increase in the concentration of carbon radicals with increase in coke formation. It is reported that free radicals associated with broken carbon-carbon bonds in the coke are responsible for the dehydrogenation of ethylbenzene. In the present investigation, the decrease in the formation of cymenes with TOS over B30 doped with 5.0% NaOH (cf Table 2), indicates that the carbonyl group formed in the coke, and not the carbon radicals present in the coke is responsible for the enhanced formation of cymenes.

Extraction of coke

The reaction was carried out for 5 h over B30 doped with 1.0% NaOH in the presence of oxygen and the coke formed was extracted using concentrated KOH solution according to the methods of Haldman and Botty. The solid material obtained was dried at 90°C for 5 h. The IR spectrum of extracted coke is given in Fig. 4a. The peak at 1660 cm⁻¹ shows the presence of quinone type of carbonyl group. Adsorption of ammonia at room temperature shows the absence of NH₃ chemisorption. This proves the absence of groups like carbonyl or lactone.

Reaction of 3-carene over extracted coke

The transformations of 3-carene over the extracted coke was done in the absence and presence of oxygen at its partial pressure of 0.12 atm at 350°C and the results are presented in Tables 3 and 4 respectively. From the data in the Tables, it is clear, that the overall conversion of 3-carene either in the absence of oxygen or in its presence follows the same trend. In the absence of oxygen, menthenes are found in all

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Transformations of 3-carene over coke extracted from zeolite B30 doped with 1.0% sodium hydroxide: In the absence of oxygen</th>
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</thead>
<tbody>
<tr>
<td>Time min</td>
<td>Conversion wt%</td>
</tr>
<tr>
<td>00-30</td>
<td>45.2</td>
</tr>
<tr>
<td>31-60</td>
<td>40.9</td>
</tr>
<tr>
<td>61-90</td>
<td>36.8</td>
</tr>
<tr>
<td>91-120</td>
<td>30.3</td>
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</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Transformations of 3-carene over coke extracted from zeolite B30 doped with 1.0% sodium hydroxide: In the presence of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time min</td>
<td>Conversion wt%</td>
</tr>
<tr>
<td>00-30</td>
<td>44.7</td>
</tr>
<tr>
<td>31-60</td>
<td>42.0</td>
</tr>
<tr>
<td>61-90</td>
<td>39.8</td>
</tr>
<tr>
<td>91-120</td>
<td>37.5</td>
</tr>
</tbody>
</table>
fractions (cf Table 3) and the formation of cymenes is reduced from 26.5% during 0-30 min to 17.7% during 90-120 min. However, in the presence of oxygen, there is no significant variation in the formation of menthadienes and cymenes with TOS (vide Table 4). In the absence of oxygen the labile hydrogen of the hydroquinone present in coke, reduces a part of the menthadienes to menthenes at lower TOS. At higher TOS this reaction is less significant, resulting in the appearance of cymenes, which are not dehydrogenated to cymenes. As a result, the cymene content is reduced.

Presence of water in the catalysates

The catalysates from B30 and B30 doped with 1.0, 2.0 and 3.5% NaOH in the presence of oxygen, contain water, especially, at the end of second hour. This indicates that oxygen of the quinone group from coke, abstract hydrogen from the reactant molecule 3-carene, to form hydroquinone. The labile hydrogen of hydroquinone reacts with oxygen from the feed to form water. Water was absent from the catalysate from B30 doped with 5.0% NaOH and also in the absence of oxygen in all the cases. This observation confirms the participation of quinone group in the dehydrogenation process which is responsible for the enhanced formation of cymene in the presence of oxygen.

The IR spectra of the extracted coke after usage in the presence of oxygen (Fig. 4b), in the absence of oxygen (Fig. 4c) and after regeneration (Fig. 4d) are given. The peak at 1660 cm\(^{-1}\), assigned to quinone carbonyl group is retained only when the reaction is carried out in the presence of oxygen. In the absence of oxygen, the quinone might have abstracted hydrogen from the reactant hydrocarbon and become a hydroquinone, which does not show absorption at 1660 cm\(^{-1}\). It is reported that quinone group containing polymer when treated with limonene at 350°C shows no absorption at 1660 cm\(^{-1}\) but absorption for the quinone group is regained on treatment with oxygen (cf Fig 4d).

Ratio of (p/m) (p-cymene/m-cymene)

The p/m ratio over A30, B30 and C30 at the end of 1 h are 1.0, 0.9 and 6.9 respectively which changes to constant values of 1.6, 1.4 and 1.3 at the end of 7th hour. Over A30 and B30 the strong acid sites present initially are 0.30 and 0.28 meq/g (cf page 4) respectively which may isomerize a part p-cymene to m-cymene resulting in a lower p/m ratio. A similar isomerization of p-cymene to m-cymene and p-xylene to m-xylene were reported. During the course of the reaction, these strong acid sites may get deactivated by coke deposition. As a result, the concentration of p-cymene in the product is not affected resulting in higher p/m ratio. In the case of C30 the drastic decrease from 6.9 to 1.3 is due to the formation of two dimensional pregraphitic coke on the channel mouth, (as evidenced by XRD), inhibiting the entry of reactant molecule inside the pores. The values over B30 and B30 doped with 1.0, 2.0, 3.5 and 5.0% NaOH are 0.9, 1.2, 1.8, 2.0 and 2.1 respectively which changes to 1.4, 1.5, 1.8, 2.0 and 2.1 respectively. B30 and B30 doped with 1.0% NaOH may contain some strong sites which get deactivated during the reaction thereby, resulting an increase in p/m value, whereas B30 doped with 2.0, 3.5 and 5.0% NaOH do not have any strong acid sites (cf Table 1) and hence no variation.

Acknowledgement

One of the authors, V K thanks the AICTE for the award of Emeritus Fellowship.

References