COMPARISON OF RUTHENIUM CATALYSTS SUPPORTED ON BETA AND MORDENITE IN THE HYDROCYCLOALKYLATION OF BENZENE

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Abstract

One way of conversion of benzene into a valuable component of motor fuel is hydrocycloalkylation producing cyclohexylbenzene (CHB) and dicyclohexylbenzene (DCHB). Two catalysts containing 0.2 wt. % of ruthenium were prepared using mordenite (Ru/M) and beta (Ru/B) zeolites as supports. Catalytic tests were carried out in a batch reactor at 175 and 200 °C and hydrogen pressure of 2 MPa at maximum. Cyclohexane was used as a solvent. Better results were obtained with Ru/B catalyst, which corresponds with better accessibility of the interior space. Selectivity to sum of CHB and DCHB varied from 60 down to 40 % at the conversion of benzene 30 and 80 %. Obtained results should motivate further technological investigation of the process.

Key words: hydrocycloalkylation; benzene; cyclohexylbenzene; dicyclohexylbenzene; beta-zeolite; ruthenium; motor fuel

1. Introduction

Due to increasingly stringent legislation, content of aromatics, particularly benzene, which is a proven human carcinogen [1], has started to be strongly limited in motor fuels. The current EU legislation valid from 2005 prescribes the content of benzene in gasoline bellow 1 wt. % and the contents of aromatics lower than 38 wt. %. Moreover, the reduction of the aromatic content in diesel has been found to have a positive effect on the cetane number. Hydrogenation of benzene is a possible way of lowering the content of benzene, but the formed cyclohexane is not a very valuable component of diesel fuels since the molecular weight and boiling point of the product are too low. As a challenge, conversion of benzene to a valuable motor fuel component through partial hydrogenation of benzene accompanied by cycloalkylation has arisen (The term hydrocycloalkylation is applied in the next text). Truffault [2] was the first to report the production of cyclohexylbenzene (CHB) from a nickel catalyzed hydrogenation of benzene in the presence of P₂O₅. Since the time a wide set of patents and papers have been devoted to this process [3-6]. Slaugh and Leonard [4] studied the hydrocycloalkylation of benzene over a range of supported metal catalysts. They suggested a cyclohexane intermediate, but more recent work shows that cyclohexane desorbs very easily [5] and that cyclohexadiene and cyclohexene are more probable intermediate. Such an assumption has been also involved in the work of Fahy, Trimm and Cookson [6] who used zeolite (13X) and other solid acids supporting nickel, platinum and rare metals. The four component catalysts (3 types of metals and an acidic moiety) are rather complicated and it is difficult to explain the role of individual catalytic sites (if possible to identify them). Trim et al. [6] have stated that hydrocycloalkylation is favored above hydrogenation since the pores are large enough to admit benzene. Zeolite acidity is more important in conversion than in

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selectivity and small amounts of platinum on the catalyst were found to facilitate the reduction of nickel and hence to favor hydrocycloalkylation at lower temperatures. Acidity and reactivity are affected by the presence of rare earth oxides. The best explanation involves electron transfer to the metal component to reduce the adsorption strength of benzene, thereby favoring the hydrocycloalkylation rather than hydrogenation. Selectivity to cyclohexylbenzene of about 70% at the conversion rate of about 25% of benzene were reported to be the best ones, and these figures are similar to previously published results [3]. In accordance with the proposed effect of platinum, which has much stronger hydrogenetic capability than nickel [7], or rare metals, a small (ca. 1%) addition of this component presented good yields and selectivity to cyclohexylbenzene at ca. 450 K, a performance which was matched only in the experiments carried out at ca. 670 K in the absence of platinum.

To achieve good yields of cycloalkylated benzenes, zeolites proved to be the best carriers of metals. Metal species together with a suitable tuned pore size and strengths of acidic sites allow the hydrogenation and a subsequent alkylation to proceed in such extents as not to obtain mainly cyclohexane (low alkylation functionality), or not to obtain large proportion of side products carried out from cyclohexene and cyclohexadiene (low hydrogenation functionality). Cookson et al. [8] have reported large series of experiments dealing with the ARODIS process. The product slate from the hydroalkylation stage of ARODIS varies according to the type of used catalyst, the nature of the feedstock, and the process conditions. Considering benzene as a model feedstock, conversions as high as 80-95% can be achieved under conditions considered to be at the higher end of severity for this process, viz. 230°C, 3 MPa and the mass hourly space velocities of around 4 hr⁻¹. Hydrogen consumption is stoichiometric and no light hydrocarbon gas is produced in the reaction. Product selectivity tends to fall in the following ranges: CHB, 60-80%; CH, 10-20%; DCHB, 10-20%. Benzene/cyclohexane separation is required, yielding a benzene-rich fraction, which could be recycled, and a cyclohexane-rich fraction. The end-use of this fraction would depend upon individual refinery circumstances, as well as process economics. In this report [8] details about catalyst are not published, however there are indications that zeolites are the basis for their preparation.

A special focus on the type of zeolites is stressed in the patent of Cheng et al. [9]. Where the preparation of the zeolite MCM 68 including a new organic directing agent which is either N,N,N',N'-tetraalkylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium dication, or N,N,N',N'-tetraalkylbicyclo[2.2.2]-octane-2,3:5,6-dipyrrolidinium dication, or N,N'-Diethyl-exo,exo-bicyclo[2.2.2]octane-2,3:5,6-tetracarboxylic diimide, or others, is reported. The hydrogenation metal is preferably selected from palladium, ruthenium, nickel, cobalt and their mixtures, with the optimum content of about 0.2 wt. %. Other metals, for example tin, improve the activity and selectivity to CHB and DCHB. With an Ru-Sn catalyst (both in 0.3 wt. % content), after 18 hours on stream, the conversion of benzene was 46.5%. The selectivity to cyclohexylbenzene was 41.9% by weight. Byproducts included cyclohexane (54 %), dicyclohexylbenzene (2.7%), and other ,C12' and ,C18' species (about 1.0%).

It is worthwhile to mention that CHB is not valuable only as a component of motor fuels but it can be also used in the production of cyclohexanone and phenol (similar procedure like the cumene process in the production of phenol).

Starting from our experience with the partial hydrogenation of benzene to cyclohexene [10], and study of the influence of acidity and the zeolite type on the hydration of cyclohexene [11], we have been motivated to prepare simpler catalysts containing only one type of acid sites – zeolitic, and one type of hydrogenation sites – dispersed ruthenium, and to test them for the hydrocycloalkylation of benzene. Two kinds of zeolitic supports are compared; mordenite and beta.

2. Experimental

2.1. Catalyst preparation and characterization

Catalysts were prepared using two zeolitic supports: a) mordenite CBV 90A, and b) beta CP 811E-75 supplied by Zeolyst. These materials were characterized by means of adsorption-desorption nitrogen isotherms, XRPD measurements and SEM.

Catalysts were prepared by the following procedure: supports were treated in 1 M water solution of NH₄NO₃. After filtration and drying the material was calcined at 500°C for 3 h. 25.00 g of the zeolite was converted to its ammonia form using 3 wt. % of ammonium water solution. After mixing for about 2 h, 0.15685 g of Ru(NH₃)Cl₃ (supplied by Sigma Aldrich) dissolved in 9 cm³ of distilled water was added and stirred for another 4 h at 60°C. During this period, the color of the suspension changed from pink-yellow to
white. The suspension was filtered and the solid material was dried at 80°C and 20 kPa. Then the material was put into a reactor filled with methanol and exposed to hydrogen at 5 MPa and 150°C for 2 h. The suspension was filtered; the solid material was dried and calcined at 500°C for 4 h. The atomic absorption analysis proved that virtually all amount of ruthenium was deposited onto the zeolite, and the ruthenium content was 0.20 wt. %. The catalyst was characterized in a similar way like the support. Catalysts were denoted as Ru/M and Ru/B for mordenite and beta zeolites, respectively.

2.2. Catalyst testing

The catalyst testing was carried out using a batch reactor system equipped with a stirrer (500 rpm), temperature control and dosing of hydrogen. In a typical experiment 0.5 g of the catalyst, 45 cm³ of cyclohexane and 5 cm³ of benzene were charged into the reactor. After closing the reactor, checking its tightness and heated to the desired temperature (175, or 200°C), hydrogen was added to reactor up to the desired increase of the overall pressure (usually 0.5, or 1 MPa). Then, mixing was turned on and the pressure decrease was monitored. When the pressure decreased by a certain value (e.g. 0.25, or 0.5 MPa) hydrogen was quickly added to the reactor to reach the maximum working pressure. After the time planned for an experiment, the mixing was stopped, the reactor was cooled down to the temperature of about 10°C, opened and the reaction mixture was quickly filtered. Analysis was carried out by GC and GC-MS.

3. Results and discussion

Fig. 1 shows particles of the zeolite beta and mordenite. Compared to beta, better developed crystallites of mordenite are evident.

![Figure 1. SEM image of the zeolite beta (left) and mordenite (right).](image)

The adsorption-desorption nitrogen data have been treated by a wide set of approaches. Results are listed in Table 1. Similarly to our previous experience the best description was obtained with the combination of the BET and DR isotherms. Both, pure and ruthenium-charged zeolites, have similar properties owing to the nature of the type of zeolite. Only a slight decrease in volume of micropores was registered after charging them with ruthenium. However, values for sMe calculated for BET with micropore, DR-BET model and the Kelvin equation imply much higher surface of the mesopores in the beta materials compared to the mordenite materials. It is noticeable that the stronger mesoporous feature of the beta zeolite is caused by the structure of agglomerates formed by small crystallites as indicated by SEM (Fig. 1).

The procedure for preparation of the catalysts was established in such a way to maximize a uniform distribution of metallic ruthenium throughout a catalysts particle. According to our previous experiments ion exchange is necessary to carry out using ammonium form of a zeolite and ammonium complex. The
acidic form of the zeolite causes hydrolysis of the ammonium ruthenium complex and formed large aqua-complexes hardly access the interior space of zeolitic support. Consequently, deposition of ruthenium moieties is mainly on the outer surface of a catalyst particle. In the next, the catalysts are dried and reduced in the methanol under hydrogen and after that calcination to renew acidic sites is performed. If the calcination precedes the reduction, ruthenium moieties can again move to the outer surface. Apprehension from movement of ruthenium species during calcinations showed to be true in the case of beta zeolite (Fig. 2). Diffraction peaks of the calcined material have clearly indicated ruthenium dioxide. In contrast, the mordenite material has not possessed any evidence of ruthenium dioxide after calcination (Fig. 3). This different behavior may be prescribed to the lower beta particles compared to mordenite ones (see Fig. 1) and larger pores of beta zeolite. According literature information \[13\], a wider broadening of diffractions in the case of beta materials shows on much lower crystallinity than the mordenite material. Lower crystallinity and size of particles also imply a higher outer surface (Table 1). Therefore, taking into account all these factors, we applied procedure described in Experimental. Corresponding curves in Figures 2 and 3 document that no change in the morphology of the supports occurred and no ruthenium particles registerable by XRPD (larger than 1 nm) were found.

Table 1. Parameters of supports and the catalyst Ru/B and Ru/M calculated from the nitrogen adsorption-desorption measurements.

<table>
<thead>
<tr>
<th>Method</th>
<th>Param.</th>
<th>( \beta )</th>
<th>0.2 % Ru/B</th>
<th>M</th>
<th>0.2 % Ru/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET with micropores ((V_{\text{mi}}))</td>
<td>( V_{\text{mi}} ) (cm(^3)/g)</td>
<td>0.241</td>
<td>0.183</td>
<td>0.208</td>
<td>0.207</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>14.6</td>
<td>16.5</td>
<td>14.74</td>
<td>15.18</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>0.0024</td>
<td>0.0018</td>
<td>0.0021</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>( s_{\text{me}} ) (m(^2)/g)</td>
<td>190</td>
<td>138.8</td>
<td>63.18</td>
<td>64.49</td>
</tr>
<tr>
<td>Combination of DR and BET: volume of micropores ((V_{DR})) results from the DR part</td>
<td>( V_{DR} ) (cm(^3)/g)</td>
<td>0.273</td>
<td>0.220</td>
<td>0.218</td>
<td>0.218</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5.34</td>
<td>3.29</td>
<td>5.71</td>
<td>5.657</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>1.5E-4</td>
<td>1.2E-4</td>
<td>0.7E-4</td>
<td>0.6E-4</td>
</tr>
<tr>
<td></td>
<td>( s_{\text{me}} ) (m(^2)/g)</td>
<td>145.9</td>
<td>88.0</td>
<td>46.8</td>
<td>45.9</td>
</tr>
<tr>
<td>Surface ((s_{\text{me}})), volume ((V_{me})) and average radius ((r_{me})) of mesopores calculated using the Kelvin's relationship</td>
<td>( s_{\text{me}} ) (m(^2)/g)</td>
<td>216</td>
<td>190.4</td>
<td>99.6</td>
<td>40.2</td>
</tr>
<tr>
<td></td>
<td>( V_{me} ) (cm(^3)/g)</td>
<td>0.60</td>
<td>0.69</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>( r_{me} ) (nm)</td>
<td>5.60</td>
<td>7.26</td>
<td>3.22</td>
<td>4.60</td>
</tr>
</tbody>
</table>

\( C \) – the interaction constant in the BET isotherm, \( d \) – average deviation between measured and calculated data, \( s, V, r \) – surface, volume and radius, respectively (total, micropores or mesopores – depending on the used model).

Hydrocycloalkylation experiments were designed under such conditions as to minimize the effect of heat generated during the hydrogenation process and a consequent local increase in the temperature on the catalyst surface. Data for the hydrogenation of benzene and the subsequent intermediates to cyclohexane are as follows \[10\] (298 K, kJ.mol\(^{-1}\)): benzene (208), 1,3-cyclohexadiene (231) and cyclohexene (120). These indicate that hydrogenation of benzene to cyclohexadiene is endothermic due to the loss of the aromaticity feature.\[14\]. Thus, if the cyclohexadiene is the main reaction intermediate for the formation of CHB, any apprehension of heat generation would be worthless. However, if the hydrogenation to cyclohexene is supposed, generation of heat is rather high, and it is better to work with a diluted reaction mixture. Following a technological rule that, if possible, a good solvent is one of the product components, cyclohexene was chosen. Of course, one has to take into account that cyclohexane can also act as an alkylation, or transalkylation agent, which is demonstrated in paper \[15\].

The reaction mixture from the hydrocycloalkylation of benzene contained more than 15 various components from which cyclohexane, methylpentenes, benzene, cyclohexylbenzene and dicyclohexylbenzene and its isomers, were present in the amount of more than 90 %. Numbers of moles were calculated from analytical data. Conversion and selectivity were calculated while for CHB two moles of the reacted benzene and for DCHB three moles of the reacted benzene were considered. Figures 4-6 report about results obtained from experiments under various conditions.
Figure 2. XRPD patterns of the beta support (beta zeolite), beta after ion-exchange with Ru(NH$_3$)$_6$Cl$_3$ and calcination (0.2 % Ru/B calc.), beta after ion-exchange with Ru(NH$_3$)$_6$Cl$_3$ after reduction and calcination (0.2 % Ru/B red. calc.).

Figure 3. XRPD patterns of the mordenite support (mordenite), mordenite after ion-exchange with Ru(NH$_3$)$_6$Cl$_3$ and calcination (0.2 % Ru/M calc.) and mordenite after ion-exchange with Ru(NH$_3$)$_6$Cl$_3$ after reduction and calcination (0.2 % Ru/M red. calc.).

Figure 4. Selectivity (S) to products listed in the bottom of the Figure and conversion (X- squares) under conditions denoted in individual bars in the sequence (from top): temperature (°C), starting pressure of hydrogen (MPa), time (min) obtained over the Ru/B catalyst. (Labels of x-axis denote experiments).

From Fig. 4 and 5 it is apparent that the Ru/B catalyst is more active and selective than the Ru/M catalyst. The highest conversion in the case of Ru/B was 28 % with cumulative selectivity to cyclohexylbenzene and its isomers and to dicyclohexylbenzene of about 50 %, while over the Ru/M only the conversion of about 20 % at comparable selectivities was reached.

In order to evaluate the alkylation, isomerization and hydrogenation activity, the following 4 reactions have been analyzed:

\[ \text{C}_6\text{H}_6 + \text{cC}_6\text{en} \rightarrow \text{C}_6\text{H}_5-\text{C}_6\text{H}_{11} \]  
(1)

\[ \text{C}_6\text{H}_6 + 2 \text{cC}_6\text{en} \rightarrow \text{C}_6\text{H}_{11}-\text{C}_6\text{H}_2-\text{C}_6\text{H}_{11} \]  
(2)

\[ \text{cC}_6\text{en} \rightarrow \text{MecC}_5 \]  
(3)

\[ \text{cC}_6\text{en} + \text{H}_2 \rightarrow \text{cC}_6\text{H}_{12} \]  
(4)

where cC6en denotes cyclohexene and MecC5 methylcyclopentene.
In Table 2 are listed values of the average reaction rates calculated according to formula:

\[ \zeta_i = \frac{\Delta r_i}{t_{\text{reac}}/m_{\text{cat}}} \]  

where \( \Delta r_i \) is the extent of the reaction \( i \), \( t_{\text{reac}} \) is the reaction time and \( m_{\text{cat}} \) is the mass of the catalyst.

Obviously, catalysts prepared using the zeolite beta are more active in the formation of CHB and DCHB. On the other hand, catalysts of the mordenite type favor isomerization of cyclohexene to methycyclopentene and hydrogenation of cyclohexene to cyclohexane. This observation could be clarified by taking the following two facts into account: a) the surface of mesopores in the case of the beta zeolite is larger than that in mordenite (see Table 1), b) pores of the beta zeolite are larger than in the mordenite. Both these facts ensure better conditions for the reactions (1) and (2) over the Ru/B catalyst.

Table 2. Average reaction rate (\( \zeta_i \)) of reactions 1-4 (reaction time: 60 min, pressure 0.5 MPa)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>T [°C]</th>
<th>Average reaction rate ( \zeta_i ) [mol/(s.g)] x 10^8</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Ru/M</td>
<td>175</td>
<td>9.8 0.32 0.49 25</td>
</tr>
<tr>
<td>13</td>
<td>Ru/M</td>
<td>200</td>
<td>9.0 0.29 0.85 30</td>
</tr>
<tr>
<td>1</td>
<td>Ru/B</td>
<td>175</td>
<td>13 0.76 0.41 16</td>
</tr>
<tr>
<td>5</td>
<td>Ru/B</td>
<td>200</td>
<td>8.1 0.21 0.64 16</td>
</tr>
</tbody>
</table>

Another set of experiments was carried out with cyclohexene and benzene using the catalysts Ru/M and Ru/B in nitrogenous atmosphere. Analysis of the reaction mixture has shown that besides reaction 1-4, the following reactions have to be taken into account:

\[
\begin{align*}
2 \text{cC6en} & \rightarrow \text{C}_9\text{H}_{11}\cdot\text{C}_6\text{H}_6 \\
\text{cC6en} + \text{C}_9\text{H}_{12} & \rightarrow \text{C}_9\text{H}_{11}\cdot\text{C}_6\text{H}_{11} \\
3 \text{cC6en} & \rightarrow \text{C}_9\text{H}_6 + 2 \text{C}_9\text{H}_{12}
\end{align*}
\]

Surprisingly, no DCHB (reaction (2)) was found in these experiments. Results in Table 3 indicate good reactivity of cyclohexene with benzene. Significantly lower was the isomerization extent (reaction 3), from which it is possible to conclude that cyclohexene formed in the hydrogenation of benzene and chemisorped on the catalytic surface is the main reactant in the isomerization. Comparing the reaction rates of (1) in Table 2 and 3 it is possible to state that the alklylation step is rate determining, i.e. hydrogenation capability of the used catalysts is sufficient. From data in Table 3, a significantly stronger alklylation activity of beta comparing to mordenite based catalyst is evident. The stronger alklylation activity of the Ru/B catalyst results from larger pores and accessibility of acid catalytic sites [13].

Following our experience with the alklylation of biphenyl [15], we tested a direct alklylation of benzene with cyclohexene. Conditions were: 0.5 g of the catalyst, 45 cm^3 of cyclohexene, 5 cm^3 of benzene, 1 and 4 h, 175 and 200 °C, nitrogen atmosphere. Neither alklylation, nor other reactions were observed.

Table 3. Average reaction rate (\( \zeta_i \)) of reactions in the alklylation of benzene with cyclohexene (reaction time: 60 min, pressure 0.5 MPa)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>T [°C]</th>
<th>Average reaction rate ( \zeta_i ) [mol/(s.g)] x 10^8</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>Ru/M</td>
<td>175</td>
<td>0.32 0.006 0.91 0.6</td>
</tr>
<tr>
<td>25</td>
<td>Ru/M</td>
<td>200</td>
<td>1.3 0.008 2.7 0.056 1.7</td>
</tr>
<tr>
<td>26</td>
<td>Ru/B</td>
<td>175</td>
<td>4.8 0.097 0.097 0.37 4.1</td>
</tr>
<tr>
<td>27</td>
<td>Ru/B</td>
<td>200</td>
<td>4.5 0.26 14.0 0.35 0.48</td>
</tr>
</tbody>
</table>

In order to see the influence of the reaction mixture dilution, a set of experiments with 0.5 g of catalyst, 47.5 cm^3 of cyclohexene and 2.5 cm^3 of benzene was performed. Results are presented in Figure 6. In this case, according to rules of subsequent reactions, the selectivity to CHB and DCHB decreased with increasing conversion while the formation of MCP increased. In any case, at the conversion rate of 80 %, the selectivity to CHB, DCHB and their isomers of about 40 % was achieved.
However, the proportion of DCHB is relatively large and such a course of the process is not desirable from the technological point of view.

\[ \text{Figure 6. Selectivity (S) to products listed in the bottom of the Figure and conversion (X- squares) under conditions denoted in individual bars in the sequence (from top): temperature (°C), starting pressure of hydrogen (MPa) and time (min), or pressure and time in one line, obtained over Ru/B catalyst. (Labels of x-axis denote experiments). The starting reaction mixture consisted of 47.5 cm}^3 \text{ of cyclohexane and 2.5 cm}^3 \text{ of benzene.} \]

Considering the literature information, as well as our experience \cite{10, 11, 15} we have tried to explain the behavior of the reaction system. (Scheme 1). Benzene (1) is gradually hydrogenated to cyclohexadiene (2) (CHDE), cyclohexene (3) and the final hydrogenation (not hydrogenolytic) product – cyclohexane (4). It is difficult to state which of the reactions, either the reaction of two molecules of cyclohexadiene, or the reaction of activated cyclohexene with benzene is favored in the production of cyclohexylbenzene (5). However, formation of CHB from two molecules of CHDE requires an aromatizing procedure featured with a relatively large reorganization of electron structures of reactants. Therefore, the alkylation of benzene with cyclohexene seems to be more probable. CHB can be alkylated to dicyclohexylbenzene (DCHB) (8). In contrast to other types of catalysts and reaction conditions (higher temperature) \cite{3-6} the reaction of cyclohexane with benzene is only to a low extent. The presence of methylcyclopentene (MCP) (6) in the reaction mixture confirms the well-known fact that cyclohexene isomerizes easily at acidic catalytic sites even at mild temperature \cite{11}. MCP can also enter alkylation reactions yielding either methylcyclopentylenzene (9) or cycloalkylated cyclohexylbenzene. All unsaturated products may be hydrogenated to saturated ones (4, 7, 10, 11, 12), whereas the extent of the reactions is affected by the size of molecules and the pores dimensions of the catalysts.

\[ \text{Scheme 1. Reaction routes in the hydrocycloalkylation of benzene. The asterisk (*) and H}^+ \text{ denote the redox (hydrogenotic) site and acidic (cycloalkylation-isomerization) sites, respectively.} \]
4. Conclusions

It has been experimentally proved that benzene can be hydrocycloalkylated to cyclohexylbenzene and dicyclohexylbenzene at relatively high yields over ruthenium-zeolite catalysts. Yields of about 35% at the conversion of 80% over a ruthenium/beta catalyst at the temperature of about 175-200°C and pressure of hydrogen of about 1 MPa were achieved. Catalysts prepared using the mordenite zeolite gave slightly lower yields than those on beta zeolite, which is in accordance with values of outer surface and the overall better accessibility of acid catalytic sites of the zeolite beta. Higher relative yields of CHB compared to DCHB are obtained at lower conversion. A similar reaction rate using cyclohexene as the alkylating agent in comparison to the rates of the hydrocycloalkylation process suggests that cyclohexene should be the main alkylation moiety. From the technological point of view, the process could be arranged in a similar way like in [8], i.e. that the streams of cyclohexane and benzene are mixed, enter the reactor, then cyclohexane is separated, one part of it is recirculated and the other part is led to further treatment, e.g. to the production of cyclohexanone and adipic acid. The separation of CHA, CHB, DCHB is easy due to high differences in boiling points.

References