Study on the deactivation of the MCM-22 catalyst in liquid phase cyclopentene hydration

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Abstract

The deactivation of MCM-22 zeolite was found to occur gradually during the direct hydration of cyclopentene to cyclopentanol in the liquid phase. When the catalyst was re-used in the next batch hydration cycle, the reaction rate reached only half of original value. The high selectivity to cyclopentanol was retained even the re-used catalyst was employed in the hydration reaction. The deactivation of MCM-22 zeolite is caused by carbonaceous deposit settled down in catalyst pores. Crystallinity and structure of zeolite did not change either during the zeolite exposition in hydration cycle or during the catalyst reactivation at 823 K. The zeolite fast deactivation is caused by cyclopentadiene, which is impurity contained in commercial starting raw material, but the significant catalytic activity decrease was also observed, when the cyclopentene free of dienic impurities was used as a raw material. Therefore, carbonaceous deposit settled down in catalyst pores had to be generated although by acid catalysed reaction of olefinic cyclopentene. Only partial restoration of catalyst activity is possible, when MCM-22 is reactivated either using calcination under temperature programme 1 K.min⁻¹/823 K/+8 hours or using hydrogen peroxide as oxygenation agent.

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Key words: Cyclopentene direct hydration; MCM-22 deactivation; MCM-22 reactivation
1. Introduction

Cyclopentene is an attractive chemical commodity conventionally produced by the partial hydrogenation of cyclopentadiene. Cyclopentene finds use in the production of polypentanamers, which are the easily vulcanised elastomers applied in the rubber industry as a component of commercial blends. Cyclopentene can be also used as a copolymer in production of cyclic olefin copolymers with ethylene [1]. Promising is the use of cyclopentene as a starting material in production of consecutive cyclic C5 derivatives.

An important cyclic C5 derivative is cyclopentanone, which is used as a starting material in the production of chemical specialities such as perfume components (jasmine type), drug substances (e.g. cyclopenthiazide), and pesticides (pencycurone) [1]. Cyclopentanone is conventionally produced by the decarboxylation of adipic acid esters over ZnO at temperature above 673 K [2]. In new processes of cyclopentanone production, the cyclopentene is used as a cheaper raw material. One of the more considerable new processes is a two-step process created by the petrochemical company Nippon Zeon [3]. In this process, cyclopentene is directly hydrated into cyclopentanol, which is then dehydrated (oxidised) into cyclopentanone. The most critical step to success of this process is the cyclopentene direct hydration, which is the topic of our study.

Cyclopentene direct hydration is a reversible exothermic reaction catalysed by solid acid catalysts. Reaction equilibrium is significantly shifted towards the reactants: at 393 K and water ratio equal to 5/1 the cyclopentene equilibrium conversion is only 4 % [4]. The reaction system consists of two phases; one is the organic phase and the other water phase. Cyclopentanol, product of the hydration reaction, is presented in both phases. Cyclopentanol is hardly isolated from water phase by rectification, due to the fact that cyclopentanol creates the azeotrope with water. Predominating byproducts generated in cyclopentene direct hydration reaction are dicyclopentylether and cyclopentylcyclopentene. The highly selective solid acid catalyst is the MCM-22 zeolite with selectivity to cyclopentanol up to 99 %.

Zeolite catalysts are known to often undergo fast deactivation. Deactivation of a zeolite catalyst was also observed when ZSM-5 was used several times in the batch cyclohexene hydration [5]. In our study we examined the extent of MCM-22 deactivation in the batch cyclopentene hydration. We also investigated possibilities of MCM-22 reactivation.

2. Experimental

2.1. Catalyst

Na⁺ form of zeolite MCM-22 was prepared [6] using a method published by Corma et al. [7]. Catalyst was transferred into NH₄⁺ form using the conventional ion-exchange method: A calcined catalyst sample was treated with 0.5 M NH₄NO₃ solution (100 ml of solution to 1 g of catalyst sample) for 4 hours at 293 K four times under vigorous stirring. The ion exchanged catalyst sample was filtered, washed with distillate water, and dried. Catalyst was activated by calcination at temperature of 823 K for 6 hours.

2.2. Materials

The cyclopentene was obtained commercially (98.6 wt. %; Fluka). Predominating impurities contained in commercial cyclopentene were cyclopentane (0.66 wt. %) and cyclopentadiene (0.63 wt. %). When cyclopentene contains more than several tenths of cyclopentadiene, it is difficult to decrease cyclopentadiene content to tenth of ppm by cyclopentene rectification, especially when cyclopentene
rectification is carried out batch-wise. Therefore, the cyclopentadiene content in commercial cyclopentene was decreased by the partial hydrogenation and consequent atmospheric rectification.

The cyclopentene partial hydrogenation was carried out batch-wise in a 200 ml stainless autoclave. The reaction was carried out by heating reactor under vigorous stirring at temperature of 293 K and under pressure of 0.7 MPa. As catalyst we used commercial Pd/Al$_2$O$_3$ (0.56 % Pd, Cherox 40-00). Detail description of the cyclopentadiene partial hydrogenation is given in our previous work [1].

Partially hydrogenated cyclopentene was rectified using distillation column with efficiency equal to 18 theoretical plates. Rectification was carried out batch-wise under atmosphere pressure. Cyclopentene refined with partial hydrogenation and rectification contained cyclopentadiene in order of units of ppm. Cyclopentane content was 3.37 wt. %.

2.3. Hydration experiments

Hydration experiments were carried out batch-wise in a 300 ml stainless autoclave. We chose such reaction conditions so the results are comparable with those published by Nuntasri et al. (cyclopentene equilibrium conversion, selectivity to cyclopentanol) [4]. For a typical run, the molar ratio of water/cyclopentene was 5/1 and weight ratio water/cyclopentene/catalyst was 45/34/1.8. To ensure sufficient reaction rate, the hydration experiments were carried out at temperature of 393 K. At this temperature it was possible to reach the cyclopentene equilibrium conversion in real time (24 hours). To avoid unwanted cyclopentene oxidation by air oxygen, the cyclopentene hydration was performed under nitrogen atmosphere. Samples of the reaction mixture could not be collected during the hydration experiments because of technical problem connected with the two phase reaction mixture. After the hydration experiment, the reaction product was centrifuged in order to separate organic phase and water phase. A sample of each phase was analysed by gas chromatography. In the case of experiments in which the catalyst was reused in the next batch hydration cycle, the catalyst was separated from the water phase by decantation and the proper quantity of catalyst was transferred into autoclave.

2.4. Analytical methods and experimental data evaluation

We used gas chromatography for quantitative estimation of the reaction mixture composition. Under this chromatograph SCHIMADZU GC-17A equipped with the flame ionised detector (FID) and weakly polar column DB-5 (length 30 m, diameter 0.32 mm) was used. Weight of detected substances $m_i$ was calculated from (1),

$$m_i = m_{std} \cdot k_i \cdot A_i / A_{std}$$  \hspace{1cm} (1)

where $m_{std}$ is weight of internal standard, $k_i$ is calibration factor of detected substance, $A_i$ is area of chromatographic peak of detected substance and $A_{std}$ is area of chromatographic peak of internal standard. As an internal standard the 1-butanol was used. Calibration factor $k_i$ of substances were calculated from (2),

$$k_i = \frac{m_i \cdot A_{std} \cdot k_{std}}{A_i \cdot m_{std}} \hspace{1cm} k_{std} = 1$$  \hspace{1cm} (2)

where $k_{std}$ is calibration factor of internal standard (equal to one). Calibration factors of determined substances were calculated from chromatographic analysis of calibration solutions.
3. Results and discussion

In first set of hydration experiments we used unrefined commercial cyclopentene. For our purpose it was important to estimate cyclopentene equilibrium conversion, because a value comparable to literature was needed. At temperature of 393 K and molar ratio water/cyclopentene equal to 5/1 the cyclopentene conversion reached 3.83 mol. % after 72 hours (enough time to reach cyclopentene equilibrium conversion). Selectivity to cyclopentanol was more than 99 mol. %. Value of the cyclopentene conversion and selectivity to cyclopentanol was in an agreement with Nuntasri results [4], and approaches equilibrium conversion.

In order to estimate if the catalyst deactivation occurs in cyclopentene hydration we used test, where the catalyst was re-used in the next hydration cycle (Table 1). In this test, the hydration time was 24 h, this time still enough long to reach cyclopentene equilibrium conversion. In second hydration cycle observed the catalyst activity decreased, the cyclopentene conversion reached only a half of the original value. The high selectivity to cyclopentanol was retained. In order to restore MCM-22 catalytic activity we tried to reactive catalyst by air oxidation (calcination):

After the second hydration cycle, the catalyst was separated from the reaction mixture and dried at temperature of 363 K. Catalyst calcination was carried out under temperature programme 1 K.min⁻¹/823 K/8 hours. Reactivated catalyst was employed in next hydration cycle. Because of catalyst weight loss during the catalyst postreaction treatment, we had to revise the starting amount of water and cyclopentanol to retain the weight ratio of water/cyclopentanol/catalyst equal to 45/34/1.8. As shown in Table 1, the catalyst activity was only partially restored by catalyst calcination; cyclopentene conversion reached only 60 % of the original value.

Table 1. Cyclopentene batch-wise hydration over MCM-22 at temperature of 393 K and water/cyclopentene ratio equal to 45/34

<table>
<thead>
<tr>
<th>Catalytic cycle</th>
<th>Catalyst use degree</th>
<th>XCPEN [mol. %]</th>
<th>SCPOL [mol. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fresh</td>
<td>3.83</td>
<td>99.69</td>
</tr>
<tr>
<td>2.</td>
<td>1x used</td>
<td>1.83</td>
<td>99.39</td>
</tr>
<tr>
<td>3.</td>
<td>Reactivated¹</td>
<td>2.26</td>
<td>99.73</td>
</tr>
</tbody>
</table>

24 hour; 1.8 g of catalyst; 0.63 wt. % of cyclopentadiene in starting cyclopentene

If there was a loss of the finest fraction of catalyst (finest catalyst particles) during the catalyst post reaction treatment, the decrease of catalyst activity could be explained by changes in the catalyst particle size distribution. Smaller catalyst particles exhibit better area/volume ratio than bigger catalyst particles, thus they are more active. We used laser diffractometry to characterise fresh catalyst samples and samples of catalyst which have been several times exposed to the hydration cycle and reactivated by calcination. Since the laser spectra of both catalysts were the same (Fig. 1A and Fig. 1B), it can be concluded that the particle size distribution of both zeolites also is the same. Therefore, the decrease of catalyst activity must be caused by the catalyst deactivation during the hydration cycle.

We also used roentgen diffractometry (XRD) to characterise fresh catalyst samples and exposed catalyst samples. XRD spectra of both catalysts were the same (Fig. 2), thus changes of zeolite crystallinity and structure do not occur during reaction or catalyst reactivation. We can confirm, the dealumination of the catalyst also does not occur, because according to the Holmberg et al. work, the dealumination of the catalyst will cause changes in zeolite XRD spectrum [8]. Therefore, the catalyst deactivation must be caused by carbonaceous deposits in the catalyst pore. This is proven with changes in catalyst colour: The
fresh catalyst was clearly white and the catalyst exposed in hydration cycle was darker shade, shade of yellow and brown, indicating carbonaceous deposits (Fig. 3).

Carbonaceous deposit could be generated by acid catalysed reactions of cyclopentene, but they could be generated by acid catalysed reactions of cyclopentadiene, which was contained in starting raw material (unrefined commercial cyclopentene). Dienic substances are generally known to easily undergo oligomerisation reactions resulting in heavy products (carbonaceous deposit), which can cause gradual catalyst deactivation. It can be found in the Japan patent that in order to avoid fast catalyst deactivation during the cyclopentene direct hydration process over zeolit ZSM-5 it is strongly recommended to use cyclopentene which contains 10 – 20 ppm of cyclopentadiene [9].

Fig. 1. MCM-22 catalyst particles size distribution detected using laser diffractometry: (A) fresh catalyst; (B) catalyst three times used in hydration cycle and two times reactivated using calcination at 823 K

Fig. 2. XRD spectra of MCM-22 catalyst: (“before”) fresh catalyst; (“after”) catalyst three times used in hydration cycle and two times reactivated using calcination at 823 K
The extent of MCM-22 deactivation was examined using hydration experiments, where reaction time was 8 hours (Table 2). The cyclopentene equilibrium conversion is not reached at this time, the reaction is still controlled by kinetics, and therefore it is possible to observe changes on catalyst activity caused by catalyst deactivation. Changes of catalyst activity were indicated by cyclopentene conversion decrease at the end of the hydration cycle (8 hours). In order to examine if it is possible to prevent MCM-22 deactivation by hydrating the cyclopentene free of dienic impurities, set of MCM-22 deactivation test were conducted with cyclopentene, which contained units ppm of cyclopentadiene.

In the first hydration cycle, the cyclopentene conversion reached 2.35 mol. % after 8 hours. After the fourth hydration cycle, the cyclopentene conversion decreased to 1.45 mol. %. We also observed a decrease of hydration selectivity of cyclopentanol. When the catalyst was used four times, selectivity to cyclopentanol decreased to 92.88 mol. % from its original value of 97.21 mol. % Hydration selectivity decrease probably occurs during product processing where by products are generated, when part of the water phase that oxidized in air needed to be recycled with the catalyst to avoid great catalyst losses.

When the unrefined cyclopentene was hydrated, after first catalyst re-use (Table 1) the cyclopentene conversion decreased to 48 % of original value. When hydrating cyclopentene free of dienic impurities after first catalyst re-use the cyclopentene conversion decreased to 82 % of original value. It can be concluded, that use of starting material free of dienic impurities is beneficial to catalysts deactivation although the catalyst deactivation during the catalyst re-use in the next hydration cycle also appears when cyclopentene free of dienic impurities is used as a starting material.

After four reaction cycles, the catalyst was reactivated with calcination at the same conditions as described previously. The reactivated catalyst was then weighted. Using the fresh catalyst and reactivated catalyst weight difference, we calculated catalyst weight loss in four particular hydration cycles. Reactivated catalyst was then used in the next hydration cycle (cycle 5 in Table 2). For this hydration cycle we, modified starting amount of water and cyclopentanol in order to retain the weight ratio of water/cyclopentanol/catalyst = 45/34/1.8. After 8 hours of reaction with reactivated catalyst a cyclopentene conversion was only 1.41 mol. %, the catalyst activity was not restored completely.

We also tried to reactive catalyst by wet oxidation using hydrogen peroxide, which is described in the previous paper [10]. After the reactivation, the catalyst suspension pH was 2.65. Low pH was caused by carboxylic acids, which are produced by carbonaceous deposit oxidation. Reactivated catalyst was washed
with distillate water to pH 7, dried, and used in cyclopentene hydration (cycle 7 in Table 2). Activity of catalyst fell down dramatically, the cyclopentene conversion reached only 0.46 mol. %.

Table 2. Cyclopentene batch-wise hydration over MCM-22 at temperature of 393 K and water/cyclopentene ration equal to 45/34

<table>
<thead>
<tr>
<th>Catalytic cycle</th>
<th>Catalyst use degree</th>
<th>X_{CPEN} [mol. %]</th>
<th>X_{CPOL} [mol. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fresh</td>
<td>2.35</td>
<td>97.21</td>
</tr>
<tr>
<td>2.</td>
<td>1x used</td>
<td>1.93a</td>
<td>95.42</td>
</tr>
<tr>
<td>3.</td>
<td>2x used</td>
<td>1.52a</td>
<td>92.08</td>
</tr>
<tr>
<td>4.</td>
<td>3x used</td>
<td>1.45a</td>
<td>92.88</td>
</tr>
<tr>
<td>5.</td>
<td>Reactivatedb</td>
<td>1.41</td>
<td>93.33</td>
</tr>
<tr>
<td>6.</td>
<td>Used</td>
<td>1.04a</td>
<td>91.74</td>
</tr>
<tr>
<td>7.</td>
<td>Reactivatedc</td>
<td>0.46a</td>
<td>85.82</td>
</tr>
</tbody>
</table>

8 hours; 1.8 g of catalyst; 10 ppm of cyclopentadiene in starting cyclopentene

*a Corrections on catalyst weight loss

*b Catalyst reactivated by calcination at temperature programme 1 K.min⁻¹/823 K/9 h

*c Catalyst reactivated by hydrogen peroxide at 353 K

4. Conclusions

The fast deactivation of MCM-22 in cyclopentene hydration is partially caused by cyclopentadiene, which is an impurity contained in commercial cyclopentene. But the significant catalyst deactivation was also observed, when cyclopentene free of dienic impurities was used as a starting material in the hydration reaction. Carbonaceous deposit is apparently generated by acid catalysed reaction of olefinic cyclopentene. High selectivity to cyclopentanol was retained even when the re-used catalyst was applied in hydration reaction. Catalytic activity of MCM-22 zeolite cannot be restored either by catalyst reactivation using air oxidation (calcination) at 823 K or by catalyst reactivation by wet hydrogen peroxide oxidation.

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References


