HYDRATION OF CYCLOHEXENE CATALYZED BY ZEOLITES*

Milan KUCERA[a], Milan KRALIK[a], Michal MATAS[a], Pavol HUDEC[b] and Milan HRONEC[a]

[a] *Department of Organic Technology,*
Slovak Technical University, 812 37 Bratislava, The Slovak Republic
[b] *Department of Petroleum and Petrochemistry,*
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

Received October 27, 1994
Accepted December 19, 1994

Liquid phase hydration of cyclohexene over faujasite, mordenite and ZSM-5 catalysts at 10 MPa and temperatures 150 – 210 °C in a batch system was studied. Influence of the type and Si/Al ratio of the zeolite on the conversion of cyclohexene and the selectivity to cyclohexanol formation was determined. Performance of the catalyst was also investigated through adsorption measurements of water and cyclohexene. Mordenite with the Si/Al ratio 70 provided the best results. The selectivity to cyclohexanol was 99% at the conversion of cyclohexene 27% at 200 °C after 4 h. All the catalysts were regenerated by calcination at 450 °C.

Hydration of olefins is used for the production of alcohols[1]. Recently, a special interest has been devoted to hydration of cyclohexene to cyclohexanol, the basic component in a caprolactam production. Asahi Chem. Ind.[2] developed production of cyclohexene by a partial hydrogenation of benzene over ruthenium catalysts. This process possesses about 70% selectivity to cyclohexene at about 60% conversion of benzene. Thus, cyclohexene seems to be an easily accessible substrate for the cyclohexanol preparation.

Hydration of cyclohexene proceeds in the presence of both homogeneous and heterogeneous acidic catalysts. Sulfuric, phosphoric acid, or *p*-toluenesulfonic acid, in the presence of additives such as copper(II) acetate, zinc(II) acetate or zinc(II) chloride produces cyclohexanol with 70% selectivity at ca 35% conversion of cyclohexene[3]. This process has, however, a disadvantage in the formation of high molecular by-products which are difficult to remove from a reactor.

The selectivity of cyclohexene hydration depends on the competition between the desired hydration reaction and other reactions, such as oligomerization, addition reactions, etc. producing high molecular products. In order to decrease the extent of undesirable reactions, microporous inorganic or organic catalysts were applied.

---

* Presented at the *XXVIth Czech and Slovak Symposium on Catalysis, Prague, 7 – 8, 1994.*

Hydration of cyclohexene catalyzed by polymers functionalized with perfluorosulfonic acid[4] or strong acid polymer[5] LEWATIT-SPC have been described. At 150 °C, ca 20% conversion was obtained. Anionic resins are selective catalysts. However, their thermal stability is limited to 150 °C, what is not sufficient for a suitable reaction rate of the hydration. This disadvantage can be overcome by using inorganic catalysts, e.g. zeolites, which have acidic catalytic sites on their surface. Natural as well as synthetic zeolites were tested for hydration of olefins[6,7], e.g. hydration over mordenite, faujasite or ferrierite with Si/Al > 20 yielding 20% of cyclohexanol[6].

In this paper, we report on hydration of cyclohexene over modified zeolite catalysts, such as faujasite, mordenite and ZSM-5.

EXPERIMENTAL

Chemicals. Cyclohexene, 99.5% purity, obtained from Duslo Sala (The Slovak Republic) was purified by distillation. The other chemicals (cyclohexanol, ethylenediaminetetraacetic acid, natrium acetate, hydrochloric acid, hydrofluoric acid and ammonium nitrate) were analytical grade purity and were used without further purification.

Catalysts. Activated clay (acidity 0.365 mval/g, nitrogen BET surface 122 m^2/g) was supplied by Istrochem Bratislava. ZSM-5 with different Si/Al ratio and ultrastable Y zeolites were prepared in the Research Institute for Petroleum and Hydrocarbon Gases Bratislava. Mordenite was commercial sample (Norton Chemical Process Product LTD). Properties of the catalysts are summarized in Table I. All the zeolites were used in the acid form.

Dealumination of mordenite was made by the repeated procedures using hydrochloric acid[8] or ethylenediaminetetraacetic acid[9] (EDTA). The dealumination was carried out at boiling point of the reaction mixture. Both methods involved seven steps. In the first method, typically, 90 g of zeolite and 600 cm^3 of water were put into a three-necked flask equipped with a stirrer, a cooler and a dose funnel filled with hydrochloric acid. Concentration of the acid was subsequently 0.05, 0.1, 0.15, 0.2, 0.5, 0.5, 0.5 mol/dm^3, respectively. Each step lasted about 6 h. Filtration, washing and calcination at 450 °C for 4 h were performed after each step. A portion of the prepared sample was used for the

TABLE I
Composition of zeolites

Zeolite	SiO_2	Al_2O_3	CaO	Na_2O	Si/Al ratio
Faujasite	87.1	11.94	0.37	<0.05	12.4
Mordenite	72.09	8.43	0.6	0.18	14.52
ZSM-5/I	93.36	3.98	0.4	<0.05	40.1
ZSM-5/II	94.66	3.67	0.49	<0.05	43.8
ZSM-5/III	92.3	3.56	0.36	<0.05	43.9[a]
ZSM-5/IV	96.17	3.33	0.47	<0.05	48.6
ZSM-5/V	83.9	1.14	0.36	<0.05	124.8

[a] Grains were significantly smaller than grains of ZSM-5/II.

catalyting testing and the rest was treated by the next steps. The second method was similar but the concentration of EDTA was constant and given by the solubility of EDTA, in each step ≈2 g in 1 000 cm^3.

Determination of the Si/Al ratio was based on the analysis of samples for aluminium and silica performed by a "wet" procedure[10].

Adsorption capacity of the catalyst. About 1 g of a dry calcined zeolite was put into the bottle equipped with a cap and weighed. Then the bottle was quickly transferred into a dessicator filled with a dry silica gel, where the beaker with an adsorptive was placed before. The dessicator was placed into an oven with temperature maintained at 50 °C. After 6 h, the bottle with the sample was closed and weighed. (Measurements of adsorption dynamics showed that 6 h is sufficient to reach equilibrium adsorption.)

Catalytic tests. Hydration of cyclohexene was carried out in a stainless steel reactor (120 cm^3) equipped with a magnetic drive stirrer, a pressure gauge, a nitrogen inlet, and an electric heating mantle. The temperature was controlled (±1 °C) using thermocouples located inside the reactor and on the outside wall of the reactor. After charging the reactor with the reaction mixture, it has been pressurized to 5 – 7 MPa with nitrogen, and during 15 min heated to the desired temperature, during which the pressure increased to 10 MPa. (At this pressure all runs were carried out.) A typical reaction mixture consisted of 50 cm^3 of water, 15 cm^3 of cyclohexene and 1 g of the catalyst, except for runs where the effect of the water/cyclohexene mole ratio on the cyclohexene conversion was studied. Preliminary tests showed that the reaction is sensitive to the sequence of the addition of reactants to the catalyst. The catalyst was suspended in cyclohexene followed by addition of water. Experiments were stopped usually after 4 h, since after this period, no significant change of conversion was registered.

Analysis of the reaction mixture. Reaction mixture was extracted (3 × 50 cm^3) with diethyl ether and analyzed by CHROM-5 gas chromatograph using a flame ionization detector. A steel column (4 mm i.d., 2.5 m long) packed with 10% Carbowax 20 M on Chromaton NAW DMCS (0.125 – 0.160 mm) was used. The analysis was performed at 120 °C, nitrogen flow of 20 cm^3/min and temperature of the detector 150 °C.

RESULTS AND DISCUSSION

In order to compare the activity and selectivity of zeolite catalysts for hydration of cyclohexene, an activated clay as the acid catalyst was investigated. Very low selectivity obtained in its presence (Fig. 1) can be explained by a nonuniform wide-narrow

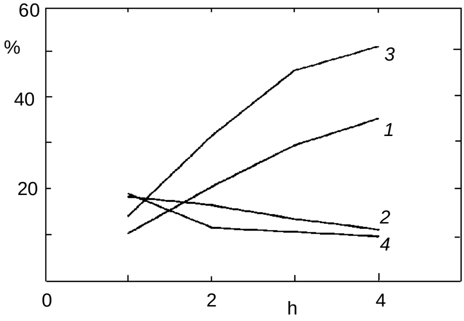

FIG. 1

Conversion of cyclohexene (%) and selectivity (%) to cyclohexanol on activated clay at 10 MPa and various temperature and time (h). *1* Conversion and *2* selectivity at 170 °C, *3* conversion and *4* selectivity at 200 °C porous structure of the catalyst, and probably also by high acid strength resulting from the activation of the clay by concentrated HCl. These properties create conditions for the formation of high molecular weight products.

Faujasite, mordenite and ZSM-5 zeolites were chosen for catalytic tests as they represent wide, middle and narrow porous materials, respectively[11]. This is typical for Faujasite with a high difference between chemical and crystal-chemical modules. This difference of the modules (12.4 and 28.5, respectively) is caused by the presence of extra framework aluminium species insoluble in hydrochloric acid solution used after hydrothermal stabilization of the zeolite. The so treated USY possesses secondary pore structure with wide pores in the range of small mezopores. During hydration of cyclohexene the catalyst is rapidly deactivated, and cyclohexene conversion is low (Figs 2 and 3). This is likely do to the formation of by-products which remain on the catalyst surface.

The advantage of the use of mordenites lies in the relatively simple dealumination procedure and the stability of dealuminated zeolites. The effect of dealumination procedure on the size of zeolite particles was checked by treating with water under the same conditions under which was performed dealumination procedure. Catalytic tests with these materials showed a little increase of cyclohexene conversion (approximately 1% in comparison to the original material). This value is significantly smaller than the conversion changes due to the dealumination procedure. Therefore, it does not need to be taken into account for the evaluation of catalyst activity. The mordenite catalysts prepared by dealumination with HCl yielded cyclohexanol in more than 99% selectivity. The highest conversion of cyclohexene was observed with the mordenite catalysts having the Si/Al ratio about 70 (Fig. 4). The dependence of cyclohexene conversion on

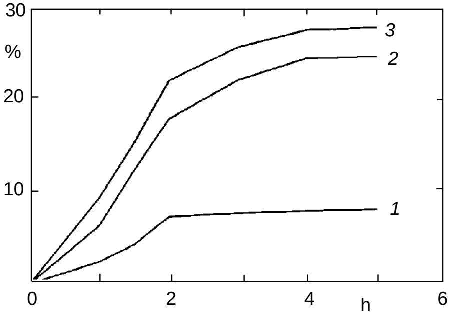

FIG. 2
Conversion of cyclohexene (%) vs time (h) at 200 °C and 10 MPa. *1* Faujasite with Si/Al = 12.4, *2* mordenite dealuminated with HCl – Si/Al = 71, *3* mordenite dealuminated with EDTA – Si/Al = 52

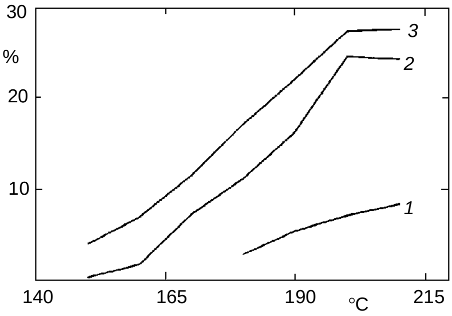

FIG. 3
Conversion of cyclohexene (%) vs temperature (°C). Catalysts and denotation as in Fig. 2

the Si/Al ratio also fairly correlates with the afinity of the catalyst to the reactants, evaluated as an adsorption capacity. Both the maximum of cyclohexene and water adsorbed on mordenite correspond to the maximum of cyclohexene conversion.

In Figs 2, 3 and 5 are summarized the results obtained with mordenites dealuminated by EDTA. It can be seen that the dependence of the maximum of cyclohexene conversion on the Si/Al ratio differs from that for the catalysts dealuminated with HCl. This can be explained by a different mechanism of dealumination procedure. Thus, the dea-

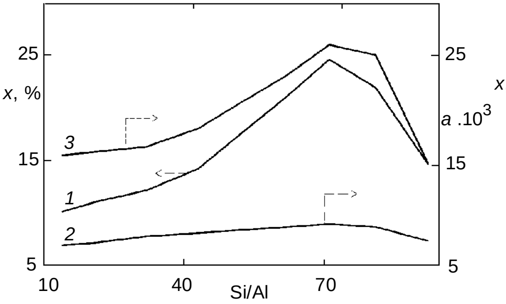

FIG. 4
1 Conversion of cyclohexene (*x*, %) and adsorption of *2* water and *3* cyclohexene (*a*, g/g) vs Si/Al ratio for mordenite dealuminated with HCl; 10 MPa, 200 °C, 4 h; sorption measurements at 50 °C

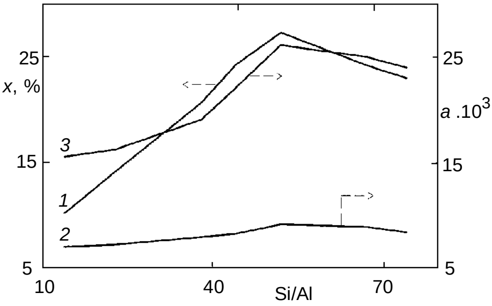

FIG. 5
1 Conversion of cyclohexene (*x*, %) and adsorption of *2* water and *3* cyclohexene (*a*, g/g) vs Si/Al for mordenite dealuminated with EDTA; 10 MPa, 200 °C, 4 h; sorption measurements at 50 °C

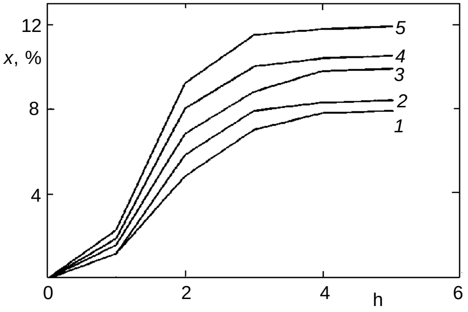

FIG. 6
Conversion of cyclohexene (*x*, %) vs time (h) using ZSM-5 catalysts with the Si/Al ratio *1* 40.1, *2* 43.8, *3* 43.9 (lower crystallinity as the previous one), *4* 48.6, *5* 124.8; 10 MPa, 200 °C

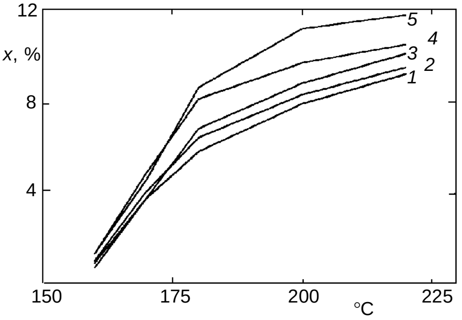

FIG. 7
Conversion of cyclohexene (*x*, %) vs temperature (°C). Catalysts and denotation as in Fig. 6

lumination of the zeolite with a relatively large molecule of EDTA, probably proceeds mainly on the external surface of the zeolite grains. It causes a different concentration of aluminium near to the surface and inside the crystal lattice of the zeolite. Consequently, the EDTA dealuminated catalyst with average Si/Al ratio 52 possesses similar activity as the HCl dealuminated catalyst with average Si/Al ratio 72. The maximum of cyclohexene conversion corresponds to the maximum of the adsorption capacity of reactants (Fig. 5).

Figure 6 presents the time dependence of cyclohexene conversion for ZSM-5 catalysts with various Si/Al ratio. In accordance to the experiments with the mordenites, the rate of cyclohexene hydration increases with increasing Si/Al ratio. This behaviour is also demonstrated by the temperature dependence of cyclohexene conversion in runs lasting 4 h (Fig. 7).

Results of the experiments at different ratios of water/cyclohexene are presented in Fig. 8 which show that this ratio does not play an important role in hydration of cyclohexene. This fact agrees with a behaviour of a multiphase system with a component slightly soluble in another one (water in cyclohexene)^{12}. So, an increase in the total amount of water does not significantly affect the concentration of water in cyclohexene, i.e. the overall rate is influenced mainly by other reaction conditions (e.g. L–S mass transport). This results in a small increase of the conversion with increasing water/cyclohexene ratio.

The comparison of zeolite catalysts with the Si/Al ratio above 30 has shown that under identical reaction conditions faujasite, HCl treated mordenite, the EDTA treated mordenite and ZSM-5 hydrate cyclohexene with 8, 12.5, 18 and 6% conversion, respectively (the selectivity about 99%). We suppose that the activity of the catalyst for hydration of cyclohexene results from the synergistic effect of the acid strength of zeolite primary and secondary pore structure which influences the efficiency, lipophilicity and accessibility of acid sites.

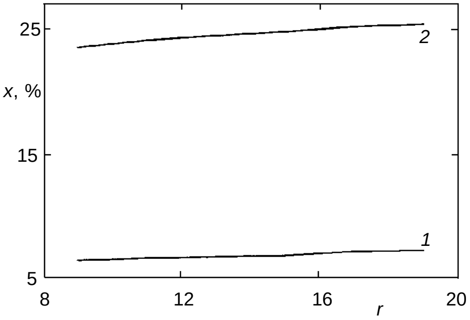

FIG. 8
Conversion of cyclohexene (*x*, %) vs initial molar ratio (*r*) of water to cyclohexene at 10 MPa, 200 °C for *1* ZSM-5 with the Si/Al = 40.1, *2* mordenite with Si/Al = 71

All the catalysts tested have been easily regenerated by calcination at 450 °C for 4 h. Threefold repetition of the catalytic tests showed practically the same catalytic activity after the catalyst regeneration.

REFERENCES

1. Cawse N. J., Henry P. J., Swartzlander W. M., Wadia H. P.: *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 9, p. 365. Wiley, New York 1980.
2. Nahagara H., Kohishi M. (Asahi Chem. Ind.): Japan 6 281 332 (1986); Chem. Abstr. *109*, 24506 (1988).
3. Mizukami F., Maeyama R. N. S., Tsuchiya T., Shinuzu K., Imamura J.: Sekiyu Gakkaischi *28*(2), 172 (1985); Chem. Abstr. *103*, 87527 (1985).
4. Waller F. J. (E.I. du Pont de Nemours and Co.): U.S. 4 595 786 (1986); Chem. Abstr. *105*, 78568 (1986).
5. Paneman H. J., Beenackers A. C. M.: Ind. Eng. Chem. Res. *31*, 1425 (1992).
6. Asahi Chem. Ind.: Japan 104 029 (1984); Chem. Abstr. *103*, 123 068 (1985).
7. Asahi Chem. Ind.: Japan 63 250 334 (1988); Chem. Abstr. *110*, 74 908 (1989).
8. Olsson R., Rollman L.: J. Inorg. Chem. *16*, 651 (1977).
9. Beaumont R., Barthomenf D.: J. Catal. *26*, 218 (1972).
10. Holzbecher Z., Churacek J.: *Analyticka chemie*. SNTL, Praha 1987.
11. Breck D. W.: *Zeolite Molecular Sieves*. Wiley, New York 1974.
12. Doraiswamy L. K., Sharma M. M.: *Heterogeneous Reactions*. Wiley, New York 1984.