Hydration of Cyclohexene in a Fixed-Bed Reactor with Micromixer

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Abstract Cyclohexene hydration was investigated in a fixed-bed reactor with a micromixer. The results showed that the use of the micromixer increased the solubility of cyclohexene in the aqueous phase and thus promoted the reaction. The conversion of cyclohexene and selectivity for cyclohexanol reached 9% and 99% respectively. The reaction time was shortened to 0.3 h.
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Cyclohexanol is an important industrial intermediate used to produce adipic acid and caprolactam for making nylon. Traditionally cyclohexanol is produced by the oxidation of cyclohexane. This process suffers from several drawbacks such as poor selectivity   extremely large recycles and explosion hazards. In the 1990s Asahi developed a commercial process for the hydration of cyclohexene using HZSM-5 as the catalyst [1]. Compared with the oxidation of cyclohexane the hydration process is promising as it is a low pressure reaction with very high selectivity towards cyclohexanol and has minimal disposal problems due to the use of a solid acid catalyst [2,3]. In this process the reaction is carried out in a stirred tank in a batch mode. Up to now reports on the process of cyclohexene hydration in a fixed-bed reactor are rare.

The main problem in the hydration process is the extremely poor miscibility of the two reactants namely water and cyclohexene. The solubility of cyclohexene in water is about 0.02% at 298 K [4]. Due to this the reaction rates are very low. Improving the solubility of cyclohexene in water is the key to a faster hydration process. Panneman *et al* [5] recommended the use of a co-solvent sulfolane to overcome the solubility constraints. However apart from safety considerations the use of sulfolane will result in an additional cost associated with its separation from the reaction mixture.

In the past decade microreactor chemical technology has attracted much attention for its excellent mass and heat transfer properties [6~8]. Micromixers have large surface area-to-volume ratios and short mass transfer distances on account of their small characteristic dimension. These properties offer advantages for the intensification of the process and low hold-ups. For example Dummann *et al* [9] intensified the mixing of inorganic acid and benzene in a capillary microreactor. Thus a micromixer could be used to intensify the mixing of water and cyclohexene to promote the hydration process.

In this study we developed a fixed-bed reaction system to investigate the hydration of cyclohexene with deionized water. In order to promote the mixing of the two immiscible fluids the reaction system was equipped with a micromixer.

The micromixer consisted of two cover sheets and a microchannel wafer that were etched on stainless steel using chemical etching [10]. As shown in Fig 1 the wafer was composed of a convective micromixer and a circular micromixer. The overall dimensions of the micromixer wafer were 73 mm long
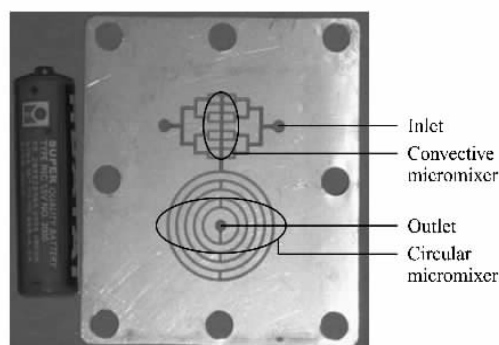

Fig 1   Structure of the microchannel wafer

63 mm wide and 0.4 mm thick. The width and depth of the convective channel were 800 and 200 μm respectively while the width and depth of the circular channel were 600 and 200 μm respectively.

Superfine HZSM-5 with Si Al = 33 was synthesized from sodium silicate silica gel aluminosulfate and amine by crystallization at different temperatures [11] and characterized by transmission electron microscopy TEM and temperature-programmed desorption TPD of NH_3. In general a stainless steel tube of 2 mm inner diameter was used as the reactor and the catalysts were packed in it. The micromixer was set before the reactor. Typically the system was pressured up to 0.7 MPa and then reactants were pumped into the micromixer and sent through the packed catalyst. The products were collected in a liquid collector. The samples were withdrawn at different time intervals and analyzed. The reactants and products from both the aqueous and organic phases were determined using a gas chromatograph GC 9790 equipped with a flame ionization detector. A 30 m capillary column SE-54 was used to separate the different components in the product. The composition of the organic and aqueous phases was determined by the internal standard method. Chlorobenzene and acetone were chosen as the internal standards for the organic and aqueous phases respectively.

The conversion of cyclohexene and selectivity for cyclohexanol were defined as follows

$$X = \frac{\text{moles of cyclohexene consumed}}{\text{moles of cyclohexene fed}}$$

$$S = \frac{\text{moles of cyclohexanol formed}}{\text{moles of cyclohexene consumed}}$$

The TEM image and NH_3-TPD profile of superfine HZSM-5 are shown in Figs 2 and 3 respectively. From Fig 2 the crystal size of the HZSM-5
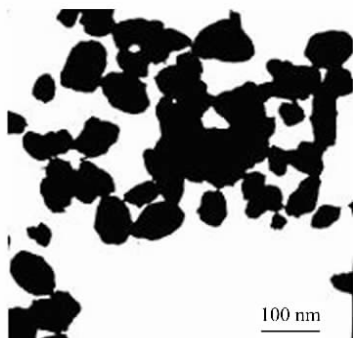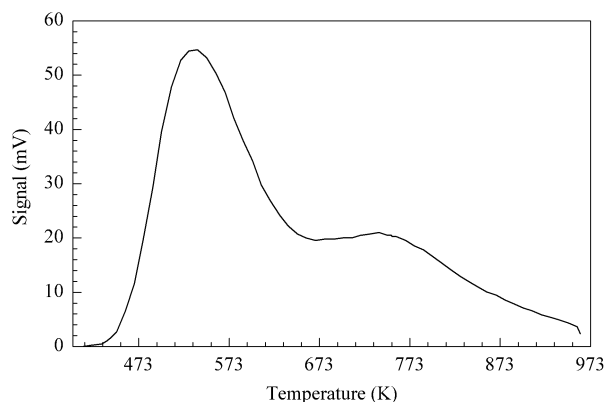

Fig 3 NH$_3$-TPD profile of superfine HZSM-5

was smaller than 100 nm and agglomerated. Fig 3 shows that there were two types of acid sites in the zeolite most of which were weakly acidic.

The results of mixing and hydration in the micromixer and a three-way valve with an inner diameter of 3 mm are shown in Table 1. The hydration of cyclohexene in the reaction system with the micromixer was better than that with the three-way valve. From the literature [5] we know that the two phases are immiscible and the reaction is greatly influenced by the mixing of the two liquids. Owing to the larger specific area of the micromixer the interface between the aqueous and oil phases increased greatly compared with the three-way valve and this enhanced the mixing of the two liquids. Thus the aqueous cyclohexene content in the micromixer is higher than that in the three-way valve and the hydration benefits from this improvement.

Table 1 Hydration of cyclohexene with or without a micromixer

Condition	Specific area m^2 m^3	c^a %	X %	S %
Micromixer	17000	0.017	9.46	99.37
Three-way valve	1300	0.008	5.27	99.10

Reaction conditions 403 K 0.7 MPa WHSV = 3.3 h^{-1} aqueous organic reactant molar ratio = 9.9 reaction time = 4 h.
[a] Mass fraction of cyclohexene in the aqueous phase.

The activity of the fresh and regenerated catalysts with time on stream is shown with the micromixer in Fig 4. The conversion and selectivity over the fresh and regenerated catalysts were nearly unchanged indicating that the catalyst can be well regenerated.

Table 2 gives the comparison of our results with some other hydration processes. It is seen that compared with the homogeneous hydration catalyzed by
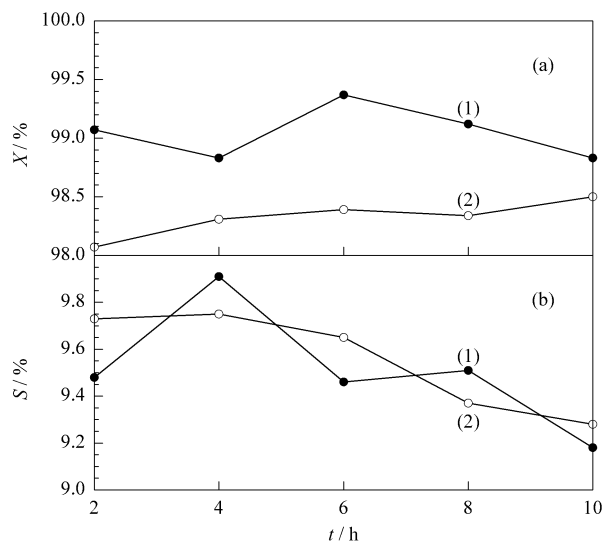

Fig 2 TEM image of superfine HZSM-5

Fig 4   **Activity of superfine HZSM-5 catalysts with time on stream   with the micromixer**
1   Fresh catalyst   2   Regenerated catalyst
Reaction conditions   403 K   0.7 MPa   WHSV = 3.3 h^{-1}
aqueous organic reactant molar ratio = 9.9

p-toluene sulphonic acid   the heterogeneous reaction showed a lower activity and higher selectivity due to the shape selectivity of the zeolite. Compared with the Asahi hydration process   the hydration in a fixed bed reached the level in a stirred tank   but the reaction time was shortened from 2 to 0.3 h   and there was no need for a separation process of the catalyst from the product mixture.

In this article   we demonstrate the structure of a micromixer and a fixed-bed reaction system to carry out the reaction between two immiscible liquids   in this case   the hydration of cyclohexene. Compared with a three-way valve   the fixed-bed reactor integrated with a micromixer can greatly improve the conversion of cyclohexene. Also   the selectivity for cyclohexanol is increased due to the improvement in liquid mixing. Compared with the traditional stirred tank hydration process   our reaction system has the advantages of shortened reaction time and lower investment and operation cost.

Table 2   **Comparison of cyclohexene hydration in the fixed-bed reactor with some existing processes**

Process	Catalyst	Reactor	T K	t h	X %	S %
Asahi [12]	p-toluene sulphonic acid	stirred tank	353~423	0.5~3.0	38~85	>97
Asahi [1]	HZSM-5	stirred tank	403	2.0	9~12	>99
This work	HZSM-5	fixed bed with micromixer	403	0.3	>9	>99

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9%   99%   0.3 h.

ZSM-5