

# Catalysts for Hydration of Cyclohexene to Cyclohexanol

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**Abstract** The hydration of cyclohexene was determined in a stirred tank of 100 mL in a batch mode in the presence of modified or unmodified resin as catalyst. The ion-exchange sulfonate resin was modified with alkyl secondary amine. At an optimum amination rate of 15%, the conversion of cyclohexene reached to 22% and the selectivity of cyclohexanol was 95.6%. In a temperature range of 90—150 °C, the activity and selectivity of the modified resin catalyst were much higher than those of the unmodified resin catalyst, which was attributed to the inclusion formed between cyclohexene and alkyl chain and also the quasi-lipophilic phase formed around the outer surface of resin beads. The formed quasi-lipophilic phase formed enhanced the conversion of cyclohexene and depressed the formation of by-products.

**Keywords** Hydration; Cyclohexene; Ion-exchange resin; Modification; Amination rate

## 1 Introduction

Cyclohexanol is one of the important bulk chemicals, which has been used widely in the chemical industries as an intermediate for the production of polymers (Nylon 6,6 and Nylon 6). Conventionally, cyclohexanol is produced from the oxidation of cyclohexane, which features high energy consumption and explosion hazard. On the other hand, the production of cyclohexanol by direct hydration of cyclohexene is much more promising as it bases on low pressure reaction with high selectivity towards cyclohexanol and has minimal disposal problems due to the use of solid acid catalyst<sup>[1–4]</sup>. The catalysts frequently used in this process are zeolite<sup>[5–10]</sup> or ion exchange resins<sup>[11,12]</sup>. The critical issue in the hydration process is the extremely poor miscibility of the two reactants (water and cyclohexene). The solubility of cyclohexene in water is about 0.02% at 298 K<sup>[13]</sup>. This results in low reaction rate. Therefore, the solubility enhancing of cyclohexene in water is the key to a faster hydration process. Incorporation of sulfolane as co-solvent enhanced the reaction solubility<sup>[14]</sup>. However, besides the safety consideration, the use of sulfolane results in an additional processing cost for its separation from reaction mixture. In a previous work<sup>[15]</sup>, we studied the hydration of butene to 2-butanol with modified sulfonated polystyrene resin as catalyst. It was found that the activity of the reaction was improved greatly as compared with that of the reaction catalyzed by the unmodified sulfonated polystyrene resin. Since the system of butene hydration is similar to that of cyclohexene hydration, we also studied the hydration of cyclohexene with the modified sulfonated polystyrene resin as catalyst. The obtained results demonstrate that the conversion of cyclohexene was improved substantially. To the best of our knowledge, this is the first example of the cyclohexene hydration with a modified

sulfonated polystyrene resin as a catalyst.

## 2 Experimental

### 2.1 Materials

All the chemicals were purchased from Shanghai Medical Instrument Limited Company, which were analytical reagents that were utilized without further purification. The ion-exchange resin D008 was produced by Kairui Chemical Company of China.

### 2.2 Modification of Ion-exchange Resin

The modified ion-exchange resin was prepared from D008 as matrix by the following procedure. Pyridinium sulfonate resin was first generated by the reaction between ion-exchange resin and pyridine. Then, sulfonyl chloride resin was produced by the reaction between pyridinium sulfonate resin and thionyl chloride. At last, the modified ion-exchange resin was generated by the reaction between sulfonyl chloride resin and alkyl secondary amine<sup>[15]</sup>.

### 2.3 Characterization

Ion exchange capacity of the ion exchange resin was determined with the general NaOH titration method<sup>[16]</sup>.

The surface area and pore distribution of the resin was measured by means of mercury porosimeter method with a Quanta Chrome POREMASTER-60 Automatic Mercury Porosimeter.

The composition of dry modified ion exchange resin was determined with a VARIO EL CUBE Organic Element Analyzer.

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## 2.4 Catalytic Activity

The activity of the ion exchange resin catalysts for cyclohexene hydration was determined in a stirred tank of 100 mL in a batch mode. Briefly, 2 mL of catalyst, some amounts of water and cyclohexene were added to the reactor. The speed rate of stirring was fixed at 300 r/min. The reaction temperature was controlled by an oil bath. The reactants and products in aqueous and organic phases were determined using a gas chromatograph(GC902) equipped with a flame ionization detector. A 30 m capillary column(PEG-20M) was used to separate the individual components in the product.

## 3 Results and Discussion

### 3.1 Effect of Amination Rate

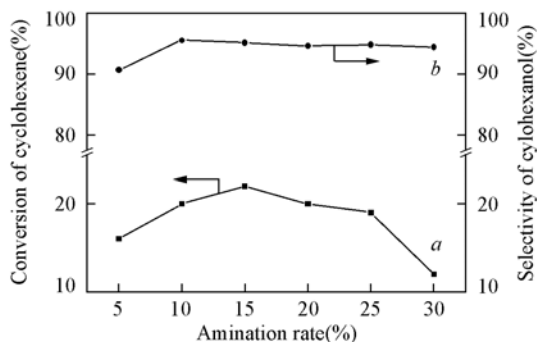
The sulfonyl chloride resin was aminated with  $\text{HN}(\text{C}_{18}\text{H}_{37})_2$ . The effect of amination rate on the cyclohexene conversion was tested. As shown in Table 1, the amination rate values obtained by two different methods are similar.

**Table 1** Effect of amination rate on the ion exchange capacity

Mass fraction of N(%)	Ion exchange capacity/(mmol·g <sup>-1</sup> )	Amination rate <sup>a</sup> (%)	Amination rate <sup>b</sup> (%)
0.287	3.34	5.02	5.05
0.511	3.16	9.95	10.1
0.708	2.99	14.8	15.0
0.878	2.81	19.4	20.2
1.02	2.64	24.2	25.1
1.13	2.46	29.6	30.1

*a.* Calculated from the N content; *b.* calculated from the ion exchange capacity.

The reaction conditions for cyclohexene hydration are shown as follows: reaction temperature was 140 °C, reaction time was 3 h and water/cyclohexene molar ratio was 2:1. As presented in Fig.1, the cyclohexene conversion increased with the amination rate when amination rate was lower than 15%. When amination rate further increased, the cyclohexene conversion decreased. It can be explained that as the amination rate increased, the global hydrophile-lipophile balance(HLB) number near the active center may be improved. This made it the easy for cyclohexene to overcome the barrier of hydroxonium ion/water complexes to reach to the active center forming carbenium ions and further to the product of cyclohexanol. On the other hand, as the amination rate increased, the ion exchange



**Fig.1** Effect of amination rate on the conversion(*a*) or selectivity(*b*)

capacity of the resin decreased and the quantity of hydroxonium ion also decreased, resulting in the reducing of the concentration of active centers and the number of carbenium ions. Its influence may overcome the favorable effect of global HLB number near the active center at some turning point. After that, the influence of ion exchange capacity may be a predominant factor. The selectivity of cyclohexanol had the tendency to be higher as the amination rate increased first and then remained unchanged.

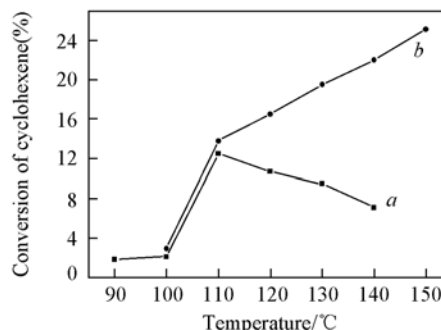
### 3.2 Influence of Reaction Temperature

The reaction conditions of cyclohexene hydration are as follows: reaction time was 3 h, water/cyclohexene molar ratio was 2:1 and amination rate of the modified resin was 15%. The physical properties of resin catalyst are listed in Table 2, where D008 represents the unmodified resin and D008G-15 represents the modified resin with an amination rate of 15%. It is clear that the physical properties of the resin were not obviously changed after modification.

**Table 2** Surface area and porosity data of resins

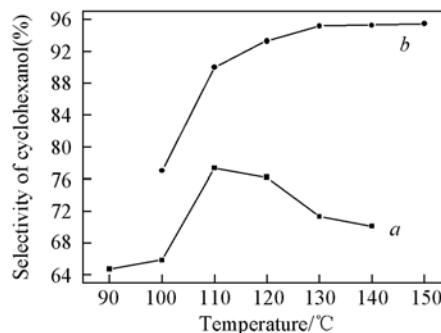
Resin	Surface area/(m <sup>2</sup> ·g <sup>-1</sup> )	Porosity/(mL·g <sup>-1</sup> )	Diameter/nm
D008	18.5	0.112	26.7
D008G-15	18.3	0.108	26.2

The influence of reaction temperature on the conversion of cyclohexene and selectivity of cyclohexanol are shown in Fig.2 and Fig.3 respectively.



**Fig.2** Conversion of cyclohexene vs. reaction temperature

*a.* Unmodified resin; *b.* modified resin.

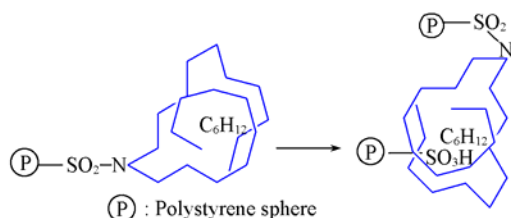


**Fig.3** Selectivity of cyclohexanol vs. reaction temperature

*a.* Unmodified resin; *b.* modified resin.

The tendency for the conversion of cyclohexene with reaction temperature in the presence of D008 is different from that of cyclohexene in the presence of D008-15. It can be seen

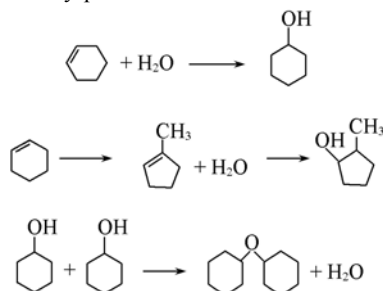
from Fig.2 that the conversion of cyclohexene first increased and then decreased with the increase of reaction temperature and was maximum at about 110 °C in the case of unmodified resin as catalyst. In the case of the modified resin as catalyst, the conversion of cyclohexene increased monotonously with the increase of reaction temperature in the reaction temperature range. The hydration of cyclohexene is a reversible exothermal process. Therefore, there exists an optimum temperature in the case of ordinary conditions. As the temperature increased, the dehydration rate increased faster than the hydration rate. At a certain temperature, the rates of the two reactions are equal. Then, the rate of dehydration was higher than the rate of hydration, resulting in the decrease of cyclohexene conversion. This result agrees with that of Wu *et al.*<sup>[17]</sup>. In the case of modified resin as catalyst, the reaction mechanism may be different from that at ordinary conditions. As shown in the following Scheme 1, an inclusive formed as in the case of the hydration of butene<sup>[15]</sup>, enhancing the conversion of cyclohexene.



**Scheme 1** Scheme of inclusive formation

On the other hand, the long chain of hydrocarbon attached to the resin altered the microenvironment of hydroxonium ions in vicinity to the long chain of hydrocarbon, forming a quasi-lipophilic phase around the hydroxonium ions. Since the solubility of cyclohexanol in water phase is much higher than that in organic phase, the concentration of cyclohexanol in vicinity to the hydroxonium ion was lower than that at normal conditions. Meanwhile, the dehydration of cyclohexanol also required the hydroxonium ion functionalizing as catalytic active center which was resisted by the quasi-lipophilic phase, breaking the restraint of thermodynamic equalization so as to be favorable to the hydration reaction.

The selectivity of cyclohexanol in the reaction is shown in Fig.3. The major by-products of the reaction were cyclohexyl ether and methyl cyclopentanol. The formation mechanism of cyclohexanol and by-products are illustrated in Scheme 2.



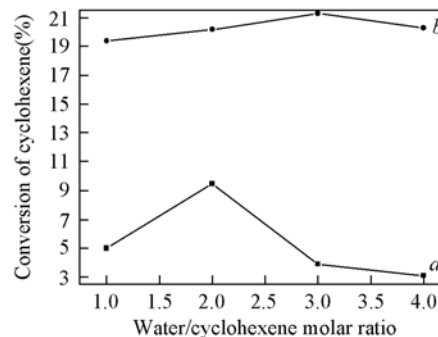
**Scheme 2** Formation mechanism of cyclohexanol and by-products

In the case of unmodified resin as catalyst, the tendency on the selectivity of cyclohexanol was similar to that on conversion of cyclohexene. Probably, the by-production required more active energy that was favored in higher temperature

region. In the case of modified resin as catalyst, the quasi-lipophilic phase around the hydroxonium ion restricted the by-production *via* changing the microenvironment of hydroxonium ions adjacent to the long chain of hydrocarbon. This is considered as cyclohexanol easily removed from the vicinity of hydroxonium ions in the microenvironment of quasi-lipophilic phase that has little chance to react further with the by-products such as cyclohexyl ether and methyl cyclopentanol, etc. The by-production also required the hydroxonium ion functionalizing as active center and needed more freedom space due to their larger volume or their more complicated reaction mechanism than cyclohexene hydration one. The formation of cyclohexyl ether needs two molecules of cyclohexanol, while the formation of methyl cyclopentanol should undergo the isomerization of skeleton. It can be imagined that the microenvironment was unsuitable to the side-reaction in the case of modified resin as catalyst as compared with the case of unmodified resin as catalyst.

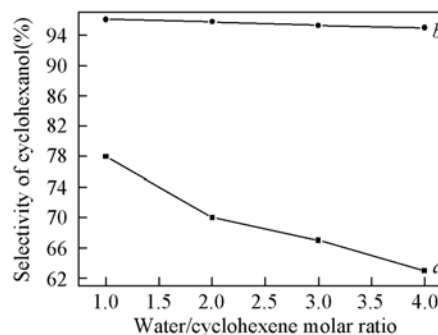
### 3.3 Influence of Water/Cyclohexene Molar Ratio

The reaction conditions for cyclohexene hydration are as follows: reaction time was 3 h, the reaction temperature was 130 °C and the amination rate of the modified resin was 15%. The influence of water/cyclohexene molar ratio on the conversion of cyclohexene and selectivity of cyclohexanol are shown in Fig.4 and Fig.5 respectively.



**Fig.4** Conversion of cyclohexene with increased water/cyclohexene molar ratio

a. Unmodified resin; b. modified resin.



**Fig.5** Selectivity of cyclohexanol with increased water/cyclohexene molar ratio

a. Unmodified resin; b. modified resin.

In the case of unmodified resin as catalyst, the conversion of cyclohexene first increased and then decreased sharply as the water/cyclohexene molar ratio increased and maximized at water/cyclohexene molar ratio of 2:1. In the case of modified

resin as catalyst, the conversion of cyclohexene was also changed in the similar way as the water/cyclohexene molar ratio increased, but the fluctuation was very small and the maximum conversion appeared at water/cyclohexene molar ratio of 3:1. According to Frilette results, the most active sites for the formation of carbenium ions are considered to be anhydrous, undissociated sulfonic acid groups, or their monohydrates<sup>[18]</sup>. In theory, the conversion of cyclohexene should increase with the increased amount of water. In the case of unmodified resin as catalyst, the amount of monohydroxonium ions decreased with the increase of water/cyclohexene molar ratio due to the hydrophilicity of resin, leading to the depression of reaction. At a certain point, the effects of water as reactant and monohydroxonium ions as active centers were comparable and the conversion of cyclohexene was maximum. When this certain point was surpassed, the effect of monohydroxonium ions was more than advantageous that of water as reactant and the conversion of cyclohexene decreased monotonously with increased water/cyclohexene molar ratio. In the case of modified resin as catalyst, since the quasi-lipophilic

phase around the hydroxonium ion depressed the formation of multihydroxonium ions, the effect of water on the reaction was not obvious as that in the case of unmodified resin as catalyst.

The influence of water/cyclohexene molar ratio on selectivity of cyclohexanol is presented in Fig.5. In the case of unmodified resin as catalyst, the selectivity of cyclohexanol decreased from 78% to 63% monotonously with increased water/cyclohexene molar ratio. As the water/cyclohexene molar ratio increased, the retention period of cyclohexanol in water phase increased, providing more chance for the side-reaction, while in the case of modified resin as catalyst, the selectivity of cyclohexanol maintained around 95% as the water/cyclohexene molar ratio increased. This is also attributed to the depression of by-production by quasi-lipophilic phase. Owing to the existence of the quasi-lipophilic phase layer, the cyclohexanol was easily removed from the vicinity of the monohydroxonium ions to the water phase, resulting in the depression of the further reaction to by-products. The so-called quasi-lipophilic phase layer around the outer surface of the ion-exchange sulfonate resin beads is illustrated in Fig.6.

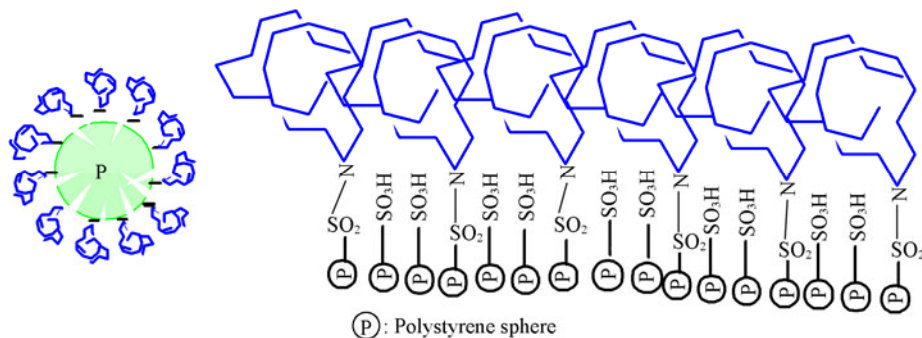


Fig.6 Quasi-lipophilic phase layer around the ion-exchange resin

## 4 Conclusions

The hydration of cyclohexene was studied with modified resin and unmodified resin as catalysts. The modification of ion-exchange sulfonate resin with alkyl secondary amine has a great effect on the activity and selectivity for the hydration of cyclohexene. At an optimum amination rate of 15%, the conversion of cyclohexene reached to 22% and the selectivity of cyclohexanol was 95.6%. In a temperature range of 90—150 °C, the activity and selectivity of modified resin catalyst are much higher than those of the unmodified resin catalyst. This is attributed to the inclusion formed between cyclohexene and alkyl chain and also the quasi-lipophilic phase layer formed around the outer surface of the ion-exchange sulfonate resin beads. Furthermore, the effect of water/cyclohexene molar ratio on the activity and selectivity for the modified resin catalyst was very small.

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