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Enhancement of 1-Propanol Selectivity in Propene Hydration over Zeolites HNU-3 and HZSM-5

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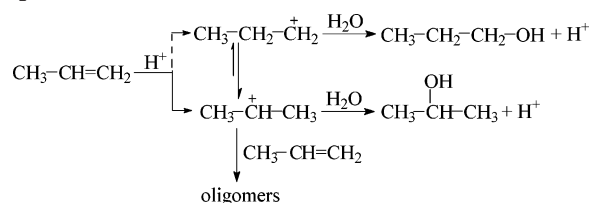
Catalytic attempts as well as thermodynamic considerations were employed to explore possible measures for enhancing the yield of 1-propanol in propene hydration. The cost of 1-propanol production may be largely reduced if it can be produced from the direct hydration of propene. The thermodynamic considerations suggest that equilibrium distribution of 1- and 2-propanol depends almost solely on reaction temperature; the selectivity of 1-propanol increases linearly with the temperature. Catalytic tests over zeolites HNU-3 and HZSM-5 prove that the reaction behavior is related to the pore structure and surface acidity of zeolites, which could be adjusted through modification with SiCl_4 or NH_4F . Modification of zeolites may suppress the formation of byproduct oligomers, but has only limited improvement on 1-propanol yield. Strong acidity of zeolites is favorable for the hydration to approach the reaction equilibrium, and therefore enhances the selectivity of 1-propanol.

1. Introduction

For the hydration of propene, the isomer 2-propanol predominates over 1-propanol in the products. Actually, 2-propanol is commercially produced from the direct hydration of propene with supported phosphoric acid, acidic cation-exchange resin, heteropolyacids, or zeolites as catalysts.¹ On the other hand, it is devious and tanglesome to get 1-propanol. Although 1-propanol can be obtained in small scale through sophisticated separation from the product mixture of propene hydration or higher alcohol synthesis with syngas as feedstock, it is mainly produced via two routes:² (1) propene is first epoxidized to propylene oxide, and propylene oxide is then hydrogenated on a noble metal catalyst to give 1-propanol; (2) propionaldehyde is first produced through carbonylation of ethene with CO and H_2 , and then 1-propanol is obtained from hydrogenation of propionaldehyde. As a result, 1-propanol is much more expensive than 2-propanol. It was generally accepted that the cost of 1-propanol production may be reduced largely if it can be produced from the direct hydration of propene.

The hydration of propene is generally believed to proceed via a mechanism of carbenium formation.³ As shown in Scheme 1, a propyl carbenium is formed from protonation of propene molecule over a surface acid site; it then undergoes the addition of a water molecule. The reaction terminates with desorption of an alcohol molecule and reconstruction of the surface acid site. The reaction follows the Markovnikov rule, because 2-propyl carbenium is much more stable than 1-propyl carbenium due to the large energy difference between them. As a side reaction, oligomers can also be formed through the addition of another propene molecule rather than water. Kinetically, the hydration of propene over HZSM-5 zeolites may follow a Langmuir–Hinshelwood mechanism.^{4,5}

Scheme 1. Possible Reaction Pathways in the Hydration of Propene



Since Tokunaga and Wakatsuki reported an example of anti-Markovnikov hydration of terminal alkynes to aldehydes by using a water-soluble ruthenium catalyst in 1998,⁶ direct hydration of unsaturated bond to form anti-Markovnikov products has attracted much attention; however, the catalytic hydration of olefins to primary alcohols remains a challenge. Zeolites own special pore channels in dimensions comparable to those of reacting molecules and therefore are effective for shape-selective reactions, in which the reaction pathway is strongly determined by the framework geometry and steric constraints. Toluene disproportionation, methanol ammoniation, and cyclopentene hydration are good examples of shape-selective applications.^{7–9} Moreover, the acid properties of zeolites may also play an important role in acid-catalyzed hydrocarbon transformation. It is then presumed that the yield of anti-Markovnikov product 1-propanol in propene hydration may be enhanced by making use of the characteristics of zeolites with proper pore structure and acidity.

The objective of this work is to explore possible measures for enhancing the yield of 1-propanol in propene hydration. Thermodynamic considerations were employed to investigate the effects of reaction temperature, pressure, and initial mole ratio of water/propene (R_{WP}) on the equilibrium conversion of propene and distribution of propanol isomers. Catalytic tests over modified zeolites HNU-3 and HZSM-5 were used to examine the effects of pore opening and acid intensity of zeolites on the propene conversion and 1-propanol selectivity in propene hydration.

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2. Thermodynamic Considerations

To obtain the equilibrium conversion of propene and product distribution of propanol isomers, the following stoichiometric reactions for propene hydration were assumed:



The equilibrium constants of two reactions are defined as follows:

$$K_1^0 = K_{P,1} K_{\phi,1} P^0 = \left(\frac{x_{2-\text{C}_3\text{H}_7\text{OH}}}{x_{\text{C}_3\text{H}_6} x_{\text{H}_2\text{O}}} \right)_{\text{eq}} \left(\frac{\phi_{2-\text{C}_3\text{H}_7\text{OH}}}{\phi_{\text{C}_3\text{H}_6} \phi_{\text{H}_2\text{O}}} \right)_{\text{eq}} \frac{P^0}{P} \quad (3)$$

$$K_2^0 = K_{P,2} K_{\phi,2} P^0 = \left(\frac{x_{1-\text{C}_3\text{H}_7\text{OH}}}{x_{\text{C}_3\text{H}_6} x_{\text{H}_2\text{O}}} \right)_{\text{eq}} \left(\frac{\phi_{1-\text{C}_3\text{H}_7\text{OH}}}{\phi_{\text{C}_3\text{H}_6} \phi_{\text{H}_2\text{O}}} \right)_{\text{eq}} \frac{P^0}{P} \quad (4)$$

Here ϕ_i and x_i are the fugacity coefficient and mole fraction of component i , respectively. As described elsewhere,^{10,11} the equilibrium constants K_1^0 and K_2^0 can be calculated from the heats of formation, entropies, and heat capacities of each component¹² and the fugacity coefficients ϕ_i can be calculated from the Soave–Redlich–Kwong (SRK) equation of state.¹³ The equilibrium conversion of propene and distribution of two propanol isomers can then be gained by solving eqs 3 and 4 simultaneously with the Newton–Raphson method.

To examine the effects of operating conditions (T , P , and $R_{W/P}$) on the equilibrium conversion of propene and distribution of propanol isomers, the hydration of propene was examined at temperatures of 100–420 °C, pressures of 0.1–10 MPa, and $R_{W/P}$ of 1–10.

3. Experimental Section

3.1. Catalyst Preparation. Zeolites HNU-3 and HZSM-5 were used as catalysts for propene hydration. NaNU-3 was hydrothermally synthesized in a Teflon-lined stainless steel autoclave at 150 °C with Mepiquat chloride (1,1-dimethylpiperidinium chloride) as template.¹⁴ As-synthesized NaNU-3 has a pore size of 3.6×4.8 Å and a silica/alumina mole ratio of 20. It was further converted to HNU-3 through ion exchange with 1 mol/L hydrochloric acid 6 times, followed by calcination in air at 550 °C for 4 h. HZSM-5 (silica/alumina mole ratio of 25) was obtained from the Catalyst Plant of Nankai University, China. It was calcined in air at 550 °C for 3 h before use.

For the modification of HNU-3 by chemical liquid deposition (CLD), 2.5 g of vapor-saturated HNU-3 sample was mixed with 20 mL of *n*-hexane and 5 mL of SiCl_4 . This mixture was stirred at ambient temperature for 5 h, dried at 60 °C for 12 h to evaporate the solvent, and then calcined at 500 °C for 5 h. This procedure may be performed once, twice, and four times; the final catalyst samples are then referred to as SiNU-3(1), SiNU-3(2), and SiNU-3(4), respectively.

NH_4F -modified HZSM-5 was obtained by impregnating 2.5 g of HZSM-5 with ca. 4 mL of aqueous solution of NH_4F of different concentrations (incipient wetness). After drying at 120 °C overnight, the samples were activated stepwise in air at 250 °C for 5 h and then at 500 °C for another 4 h. The samples prepared with the initial NH_4F loadings of 1.0, 4.0, 7.0, 10.0, and 15.0 wt % were denoted as FZSM-5(1), FZSM-5(4), FZSM-5(7), FZSM-5(10), and FZSM-5(15), respectively.

$\text{Ga}(\text{NO}_3)_3$ -modified HZSM-5 (GaZSM-5 with a Ga loading of 0.81 wt %) was prepared through ion exchange. To achieve

that, 2.5 g of HZSM-5 was exchanged twice with 75 mL of 0.03 mol/L $\text{Ga}(\text{NO}_3)_3$ aqueous solution at 80 °C for 2 h. After filtrating and washing with deionized water, the sample was then dried at 120 °C for 12 h and calcined at 550 °C for 3 h.

3.2. Catalyst Characterization. X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance X-ray diffraction spectrometer with Cu K α radiation (154.06 pm, 40 kV, and 40 mA) in the range of 2θ between 5° and 50°. The relative crystallinity of HZSM-5 samples was determined based on the area of characteristic peaks in the 2θ range of 22.5°–25.0° in accordance with the method of Kulkarni et al.¹⁵ by assuming that the crystallinity of the original HZSM-5 sample was 100%.

The BET surface area of the catalysts was measured by nitrogen adsorption at 77.4 K with a TriStar 3000 gas absorption analyzer (Micromeritics Instrument Co., USA). The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement.

To determine the acidic properties of zeolites, NH_3 -TPD was performed in a TP-5000 quartz microreactor (Tianjin-Xianquan, China) connected with a thermal conductivity detector (TCD) and a mass spectrometer (Omni Star 200). About 50 mg of sample was used in each measurement. The catalyst sample was first pretreated in situ in air at 500 °C for 1 h, followed by purging with nitrogen (50 mL/min) at the same temperature for 1 h and then cooling to 120 °C. Then it was saturated with dry ammonia through pulse injection. The sample was further flushed with nitrogen flowing at 120 °C for 30 min to remove any physically adsorbed ammonia. After that, the sample was heated to 550 °C at a ramp of 10 °C/min in the nitrogen flow. The exhaust gases were detected and monitored by the TCD and mass spectrometry.

3.3. Reaction and Analytical Procedures. The hydration of propene was performed in a stainless steel tube reactor of 8.0 mm i.d. equipped with a backpressure regulator. For each test, about 1.0 g of catalyst (crushed and sieved to 40–60 mesh) was loaded in the reactor. Prior to the reaction, the catalyst was pretreated in situ under a nitrogen flow at 500 °C for 3 h and then cooled to the reaction temperature. After that, distilled water and propene (99.9 wt %) were pressurized into the system with two metering pumps (DB-80, Beijing Weixing Manufactory). In this work, the reaction pressure was set as 7.0 MPa and the temperature from 220 to 330 °C. The mole ratio of water to propene was fixed at 4.63, and the propene weight hourly space velocity (WHSV) was controlled at 0.84 h^{-1} . The effluents including products propanol isomers and side products oligomers were decompressed through the backpressure regulator and condensed in a trap with an ice–water bath, collected at regular intervals, and then analyzed by off-line gas chromatographs. A TCD gas chromatograph (Shimadzu GC-8A) equipped with a $3 \text{ m} \times 3 \text{ mm}$ Porapak-Q/S column was used for analyzing water content. Another flame ionization detector gas chromatograph (Shimadzu GC-14B) equipped with a $60 \text{ m} \times 0.25 \text{ mm}$ OV-101 capillary column was used for analyzing unconverted propene, propanol isomers, and oligomers.

A good overall mass balance was obtained for all catalytic tests; the overall mass of products collected during the reaction covered about 95–100% of the mass of fed reactants. Because all the catalytic tests in this work were performed in a microreactor and only a small quantity of catalyst was used (packed in the isothermal area), the limitation of external/internal mass transfer and temperature nonuniformity in the catalyst bed may be eliminated. These were affirmed by the preliminary tests under different space velocities and with various catalyst pellet sizes at 280 °C using HNU-3 as catalyst. Therefore, the results

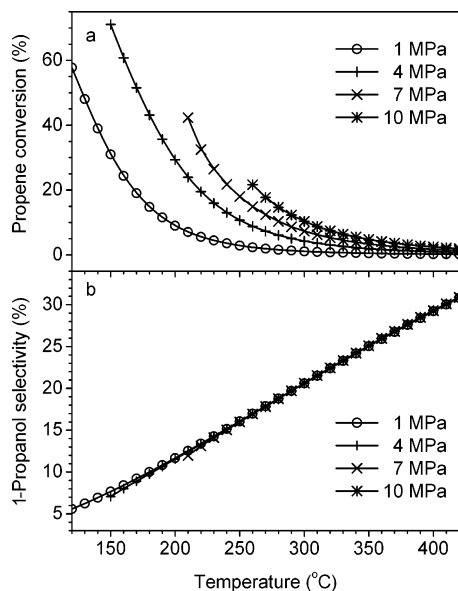


Figure 1. Effects of temperature and pressure on the equilibrium conversion of propene (a) and selectivity of 1-propanol (b) in propene hydration with an initial mole ratio of water/propene ($R_{W/P}$) being 4.63.

should be in the kinetic regime and represent the intrinsic performance of each catalyst.

4. Results and Discussion

4.1. Equilibrium Propene Conversion and Product Distribution. The equilibrium conversion of propene and selectivity of 1-propanol in propene hydration with an initial mole ratio of water/propene ($R_{W/P}$) being 4.63 at different temperatures and pressures are shown in Figure 1. Because the hydration is an exothermic reaction, the equilibrium conversion of propene decreases significantly with increasing temperature. At 7.0 MPa, the equilibrium conversion of propene decreases from 32.5% to 1.4% with an increase in temperature from 220 to 420 °C. On the other hand, it is also a volume contracting reaction; an increase in pressure is then favorable for a higher propene conversion. It should be noted that only gas-phase hydration is considered in this work; therefore there is a lack of data in the region of low temperature and high pressure where a phase transformation may occur.

The initial mole ratio of water/propene also has certain influences on the propene equilibrium conversion; as shown in Figure 2, the conversion increases slightly with $R_{W/P}$.

On the other side, the equilibrium distribution of propanol isomers is rather insensitive to the pressure and water/propene ratio; it depends actually alone on the reaction temperature (Figures 1 and 2). The equilibrium selectivity of 1-propanol increases almost linearly with the temperature; for example, 1-propanol selectivity at 7.0 MPa increases from 13.1% to 30.9% with an increase in temperature from 220 to 420 °C. These suggest that temperature will be a key processing parameter for enhancing the yield of 1-propanol in propene hydration.

4.2. Effects of Modification on Properties of Zeolites. As shown by the XRD pattern in Figure 3, the as-synthesized HNU-3 zeolite has the structure of LEV with high crystallinity and there are no visible peaks from any impurities. XRD patterns of original and NH_4F -modified HZSM-5 samples show that all these samples take the typical MFI pattern (Figure 4). Relative crystallinities of these samples as well as BET surface areas are given in Table 1.

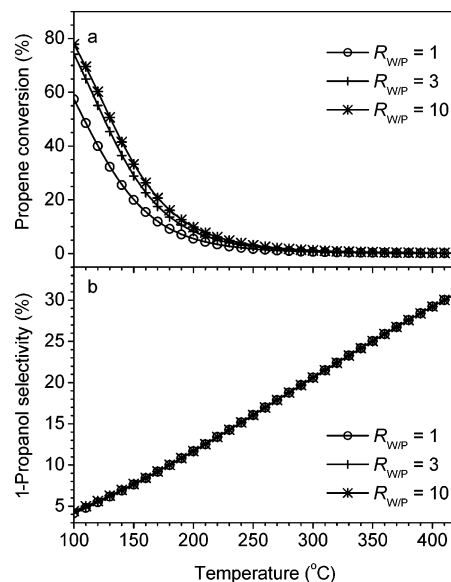


Figure 2. Effects of initial mole ratio of water/propene ($R_{W/P}$) on the equilibrium conversion of propene (a) and selectivity of 1-propanol (b) in propene hydration under 1.0 MPa.

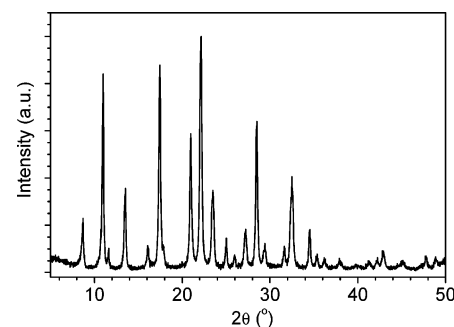


Figure 3. XRD pattern of as-synthesized HNU-3 zeolite.

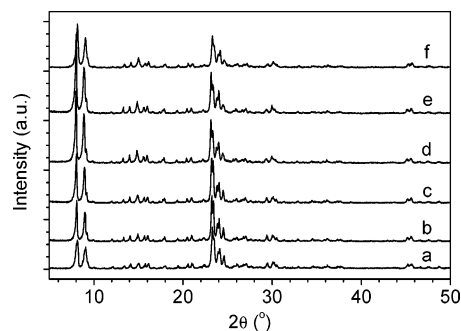


Figure 4. XRD patterns of NH_4F -modified HZSM-5 zeolites: (a) HZSM-5; (b) FZSM-5(1); (c) FZSM-5(4); (d) FZSM-5(7); (e) FZSM-5(10); (f) FZSM-5(15).

As listed in Table 1, the micropore surface area of HNU-3 sample is 379 m^2/g ; it decreases only slightly for once and twice SiCl_4 -CLD treatments, but decreases markedly after CLD treatment for 4 times. This means a partial blockage of zeolite pores by SiO_2 deposited on it through the SiCl_4 -CLD treatment. With moderate NH_4F modification, the micropore surface area of HZSM-5 may increase to some extent, but high NH_4F loading can cause a partial collapse of HZSM-5 zeolite structure, which results in a significant decrease in the relative crystallinity and surface area.

The acidity of HZSM-5 can be adjusted by modifications with $\text{Ga}(\text{NO}_3)_3$ and NH_4F , which was characterized by NH_3 -TPD, as shown in Figure 5. The acidity was further evaluated by integration of the profiles, as listed in Table 2. Becker and

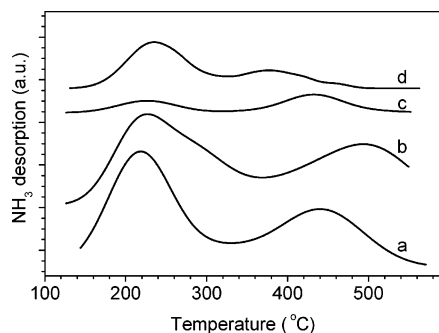


Figure 5. NH_3 -TPD profiles of HZSM-5 zeolites with various modifications: (a) HZSM-5; (b) FZSM-5(7); (c) FZSM-5(15); (d) GaZSM-5.

Table 1. Properties of Various Modified Zeolites

sample	relative crystallinity (%)	BET surface area (m^2/g)	
		total	microporous
HNU-3		464	379
SiNU-3(1)		450	367
SiNU-3(2)		428	352
SiNU-3(4)		223	161
HZSM-5	100	347	253
GaZSM-5		338	241
FZSM-5(1)	99	356	269
FZSM-5(4)	100	357	266
FZSM-5(7)	100	352	247
FZSM-5(10)	96	334	228
FZSM-5(15)	81	327	190

Kowalak observed a considerable increase in catalytic activity in cumene cracking over mordenites and faujasites treated with NH_4F ; a calorimetric measurement of NH_3 adsorption heat indicated an increase in the acid strength.¹⁶ This may be due to the interaction of Al–F species formed intracrystalline with the existing protonic sites. It was further proved that the surface acidity of HZSM-5 can be enhanced by incorporation of NH_4F in a relatively low concentration.¹⁷ In this work, as shown in Figure 5, the acidity of HZSM-5 is weakened by $\text{Ga}(\text{NO}_3)_3$ modification, but can be strengthened by proper NH_4F modification (especially with the initial NH_4F loading on HZSM-5 being 4.0–10.0 wt %).

4.3. Effects of Temperature on Propene Hydration over HZSM-5. The effects of temperature on propene conversion and product distribution (1-propanol, 2-propanol, and oligomers) in propene hydration over HZSM-5 are shown in Figure 6. The propene conversion increases monotonically with the temperature, which seems to be contrary to the thermodynamic suggestions. The reason is that the possibility of propene oligomerization is not included in the thermodynamic consideration, but the oligomerization is serious here in the actual catalytic tests, especially at a high temperature.

At 220 °C, propene conversion is 14.2% with 2-propanol selectivity of 99.9%. Under the same reaction conditions, however, the equilibrium values for propene conversion and 2-propanol selectivity are 32.5% and 86.9%, respectively. Therefore the reaction is far from equilibrium and under the control of kinetic factors. With increasing reaction temperature, the yield of oligomers increases largely and the oligomers become the dominant products at a temperature above 270 °C; this contributes to the high propene conversion. The product 2-propanol from Markovnikov hydration is exclusive at low temperature, while 1-propanol can be detected at temperatures above 220 °C. The selectivity of 1-propanol increases slightly with the temperature at first, reaches a maximum at 250 °C, and then decreases with further increase in temperature. The 1-propanol/2-propanol ratio, however, increases always along

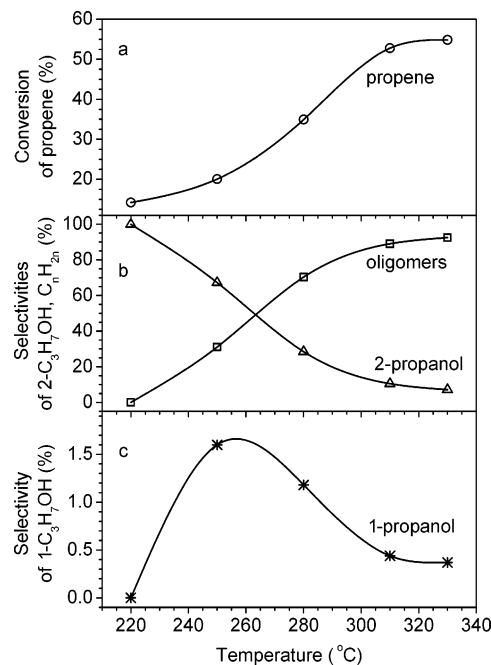


Figure 6. Effects of temperature on conversion of propene (a), selectivities of 2-propanol and oligomers (b), and selectivity of 1-propanol (c) in propene hydration over HZSM-5 under 7.0 MPa ($R_{W/P} = 4.63$, propene WHSV = 0.84 h^{-1} ; data were acquired after 1 h on stream).

Table 2. Integration of NH_3 -TPD Profiles of Various Modified Zeolites

zeolite	weak acid		strong acid	
	peak temp (°C)	area (au)	peak temp (°C)	area (au)
HZSM-5	218	139	440	92
FZSM-5(7)	227	148	493	101
FZSM-5(15)	226	18	432	28
GaZSM-5	235	58	377	30

with the reaction temperature. Current results may suggest that a high temperature is necessary to get a considerable amount of 1-propanol, but one must find a way to reduce the serious oligomerization at high temperature.

4.4. Effect of Pore Size of Zeolites on Propene Hydration.

The size of the 1-propanol molecule (ca. $3.1 \text{ \AA} \times 4.4 \text{ \AA}$) is somewhat smaller than that of 2-propanol (ca. $3.6 \text{ \AA} \times 4.3 \text{ \AA}$) with a branch chain; narrow pores in zeolites with a size equivalent to a propanol molecule will favor the diffusion and formation of 1-propanol. Proper reduction of the opening size of pore channels in zeolites could increase the shape selectivity of catalysts. Modification of zeolites by chemical liquid deposition (CLD) of silicon-containing agents (such as SiCl_4) can form a thin layer of SiO_2 on the pore channels, which is an efficient method to adjust the aperture of zeolites. When the molecule of modifying agents is larger than the pore opening of zeolites, only pore opening size is reduced; the internal surface remains unchanged but the external surface sites may be passivated.¹⁸ In this work, the pore opening of HNU-3 was adjusted through the different modification cycles of SiCl_4 -CLD and calcination.

Hydration of propene over HZSM-5 and HNU-3 with various modification cycles was carried out at 280 °C, 7.0 MPa, a propene WHSV of 0.84 h^{-1} , and $R_{W/P}$ of 4.63, as shown in Table 3. Both propene conversion and oligomer selectivity for the hydration over HNU-3 are much lower than those over HZSM-5, while 1-propanol selectivity over HNU-3 (3.7%) is higher than that over HZSM-5 (1.2%). This may be explained by the aperture difference between NU-3 ($3.6 \text{ \AA} \times 4.8 \text{ \AA}$) and ZSM-5 ($5.3 \text{ \AA} \times 5.6 \text{ \AA}$).

Table 3. Conversion of Propene and Selectivities of Propanol Isomers and Oligomers in Propene Hydration over HZSM-5 and HNU-3 Modified with SiCl₄-CLD^a

catalyst	propene conversion (%)	selectivity (%)			
		2-propanol	1-propanol	oligomers	$R_{1-2\text{-propanol}}$
HZSM-5	34.9	28.5	1.2	70.3	0.042
HNU-3	9.3	90.0	3.7	6.3	0.041
SiNU-3(1)	7.9	93.9	3.5	2.6	0.037
SiNU-3(2)	7.5	95.4	3.6	1.0	0.038
SiNU-3(4)	3.4	96.1	3.3	0.6	0.034

^a Reaction conditions: 280 °C, 7.0 MPa, $R_{W/P}$ = 4.63, propene WHSV = 0.84 h⁻¹. Data were acquired after 1 h on stream.

Table 4. Conversion of Propene and Selectivities of Propanol Isomers and Oligomers in Propene Hydration over HZSM-5 with Various Modifications^a

catalyst	propene conversion (%)	selectivity (%)			
		2-propanol	1-propanol	oligomers	$R_{1-2\text{-propanol}}$
HZSM-5	34.9	28.5	1.2	70.3	0.042
GaZSM-5	7.4	93.8	2.8	3.4	0.030
FZSM-5(1)	9.5	83.4	3.8	12.8	0.046
FZSM-5(4)	9.2	90.9	5.7	3.4	0.063
FZSM-5(7)	10.8	92.2	6.8	1.0	0.074
FZSM-5(10)	10.0	92.3	6.0	1.7	0.065
FZSM-5(15)	9.9	89.5	4.8	5.7	0.054

^a Reaction conditions: 280 °C, 7.0 MPa, $R_{W/P}$ = 4.63, propene WHSV = 0.84 h⁻¹. Data were acquired after 1 h on stream.

The modification of HNU-3 by SiCl₄-CLD will further depress the conversion of propene as well as the selectivity of oligomers, while the selectivity of 1-propanol remains at a stable level. Oligomer molecules have relatively larger kinetic diameters than propanol and propene molecules; their formation can be suppressed significantly over HNU-3 with narrow pores due to the steric hindrance. Modification of HNU-3 by SiCl₄-CLD leads to reduced pore openings and makes external surface active sites passivated to a great extent; this results in a further decrease in the selectivity of oligomers and conversion of propene.

With HNU-3 as catalyst at 280 °C and 7.0 MPa, the conversion of propene is close to the equilibrium value (10.3%), while the formation of oligomers is suppressed effectively. Although 1-propanol selectivity is higher than that with HZSM-5, it is still much lower than the selectivity at an equilibrium distribution (18.8%, Figure 1). Further modification has little effect on enhancing the yield of 1-propanol; the reason may be that (1) the size of the -OH group is so small that the discrimination between two propanol isomers is not enough to bring up a distinct shape selectivity or (2) the large energy barrier to the formation of 1-propyl carbenium prevents 1-propanol from massive formation to approach the equilibrium distribution.

4.5. Effect of Acidity of Zeolites on Propene Hydration.

As indicated in Scheme 1, propene hydration over HZSM-5 zeolite follows the Langmuir–Hinshelwood mechanism and the addition of water is the rate-determining step;^{4,5} 2-propyl carbenium is much more stable than 1-propyl carbenium due to the large energy difference between them.³ Proper acidity of zeolites should be helpful to enhance the stability of propyl carbenium and then change the distribution of two propanol isomers. Therefore, the acidity of HZSM-5 was adjusted by modifications with Ga(NO₃)₃ and NH₄F.

The catalytic results of HZSM-5 with various modifications are listed in Table 4. Propene conversion in hydration over Ga(NO₃)₃-modified GaZSM-5 is much lower than that over the

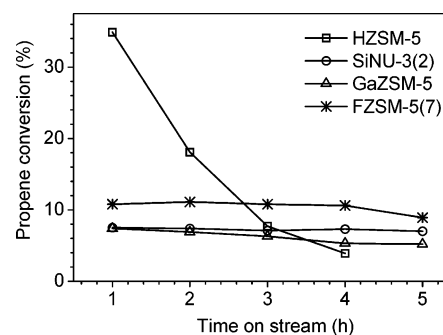


Figure 7. Hydration of propene over various modified zeolites: propene conversion with time on stream. Reaction conditions: 280 °C, 7.0 MPa, $R_{W/P}$ = 4.63, propene WHSV = 0.84 h⁻¹.

original HZSM-5. However, the modification with NH₄F can significantly enhance the selectivity of 1-propanol and suppress the formation of oligomers. For NH₄F-modified HZSM-5, propene conversion and 1-propanol selectivity increase first with the NH₄F loading, reach a maximum with the initial NH₄F loading of 7.0 wt %, and then decrease with further increase in NH₄F loading due to a partial collapse of zeolite framework under high concentration of NH₄F (Table 1).

Further investigation indicates that the sites of strong acidity may be responsible for the propene hydration, which can be enhanced through NH₄F modification with proper NH₄F loading. For example, the highest yield of 1-propanol was obtained over the catalyst FZSM-5(7). On the other hand, oligomerization will more likely take place on the sites of relatively weak acidity. The acidity of HZSM-5 is weakened by Ga(NO₃)₃ modification, and the acidity density of GaZSM-5 is much lower than that of HZSM-5. Then, over GaZSM-5, propene conversion is decreased and the formation of oligomers is suppressed. The increase in the density of strong acidic sites, enhancement of acidic strength, and suppression of weak acidic sites may promote the formation of propanol over oligomerization. Moreover, strong acidity of zeolites is also helpful to enhance the rate of propanol formation, which makes the distribution of propanol isomers closer to the equilibrium value; this may be favorable to enhance the yield of 1-propanol.

4.6. Catalyst Deactivation. The changes of propene conversion with time on stream over various catalysts are shown in Figure 7. A rapid deactivation is observed with HZSM-5 as catalyst in propene hydration; propene conversion decreased from 34.9% to 3.9% within 4 h. However, SiNU-3(2) zeolite with small pore size is relatively more stable. Modification of HZSM-5 can improve its catalytic stability significantly, though this also markedly reduces its initial activity; the activities of GaZSM-5 and FZSM-5(7) remain stable with 4 h on stream. Moreover, the oligomerization of propene is reduced over the modified zeolites (Table 4). These suggest that the catalyst deactivation in propene hydration may mainly result from the oligomerization of propene; carbonaceous deposition is formed from the oligomers produced that are adsorbed on the active sites, which may block the zeolite pores and cause the catalyst deactivation. Reducing the oligomerization is an effective way to improve the catalyst stability for propene hydration.

5. Conclusions

Catalytic attempts as well as thermodynamic considerations were employed to explore possible measures for enhancing the yield of 1-propanol in propene hydration.

Thermodynamic considerations suggest that the equilibrium distribution of propanol isomers is rather insensitive to the

pressure and water/propene ratio; it depends alone on the reaction temperature. The equilibrium selectivity of 1-propanol increases almost linearly with the temperature; temperature is a key processing parameter for enhancing the selectivity of 1-propanol in propene hydration.

Catalytic tests of zeolites HZSM-5 and HNU-3 in hydration of propene indicate that the actual selectivity of 1-propanol is far from the equilibrium value due to kinetic restraints. The reaction behavior is related to the pore structure and surface acidity of zeolites, which could be adjusted through modification with SiCl_4 or NH_4F . Narrowing the pore openings through SiCl_4 -CLD modification has a limited effect on enhancing the yield of 1-propanol, but it is effective to suppress the oligomerization of propene. The increase in the density of strong acidic sites, enhancement of acidic strength, and suppression of weak acidic sites through proper NH_4F modification are helpful to enhance the selectivity of 1-propanol and suppress the formation of oligomers. Strong acidity of zeolites is favorable for the hydration to approach equilibrium and therefore enhances the selectivity of 1-propanol.

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