Alkylation of benzene with propene on Beta zeolites under supercritical conditions

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Alkylation of benzene with propene on a series of Beta zeolites under gaseous, liquid, vapor–liquid coexistence and supercritical conditions has been investigated. The highest yield of cumene and stability of the catalysts were observed when the reaction was carried out on Ga-modified H-Beta under supercritical conditions near the critical point, which may be ascribed to the effective dissolution and diffusion of the coke precursors deposited on the zeolites.

KEY WORDS: alkylation; benzene; propene; Beta zeolite; supercritical conditions.

1. Introduction

Cumene is an important intermediate product due to its elegant conversion into phenol and acetone. It is manufactured exclusively by alkylation of benzene with propene either in liquid or gas phase; Friedel–Crafts systems or proton donors are used as catalysts. In the liquid-phase process, H_2SO_4 or $AlCl_3$ is used at 35–40 °C, or alternatively HF at 50–70 °C, with a low propene pressure of up to 0.7 MPa. The majority of the current operating processes use the UOP route in the gas phase, in which the alkylation is carried out on H_3PO_4/SiO_2 catalysts promoted with BF_3 at 200–250 °C and 2–4 MPa. An excess of benzene is normally used to minimize the facile further alkylation of cumene [1].

Recent process developments concern the use of zeolite catalysts, which could be an alternative for a more environmentally friendly and noncorrosive process without the release of acidic catalyst components. Several zeolites, including ZSM-5, Y, and mordenite, were reported to be good catalysts for this reaction [2–5]. Zeolite Beta was found to be more active and more selective than Y zeolite in liquid phase, but leads to fast oligomerization even at low temperature [6,7].

Two commercial processes producing cumene have been developed by Mobil and CDTECH, respectively. The first one operates in a fixed-bed reactor with ZSM-5 as a catalyst [8,9] and the second in a catalytic distillation column reactor using Y zeolites [10]. However, the rapid deactivation of zeolite catalysts due to the accumulation and enlargement of the coke precursors in the channels and at the external surface of zeolites is still a substantial problem to resolve.

Supercritical fluid (SCF) technology is one of the new technologies that have been developing quickly since the 1980s in the chemical industry. Performing heterogeneously catalyzed reactions under supercritical conditions, rather than in gas or liquid phase, could be an interesting option for increasing throughput and prolonging catalyst lifetime [11].

Alkylation under supercritical conditions is chosen to enhance the reaction rate, improve the selectivity, slow down the deactivation of the catalyst, and make the process more environmentally benign. Fan *et al.* [12] have reported the supercritical-phase alkylation of isobutene with isopentane on solid acid catalysts. The results showed that the liquid-like densities and enhanced transport properties of supercritical fluids are exploited to extract coke precursors *in situ*, thereby to extend the catalyst activity. Moreover, the operation in the regions near the critical point was most desirable for the effective removal of the coke precursors.

In this work, alkylation of benzene with propene on a series of Beta zeolites under gaseous, liquid, vapor–liquid coexistence and supercritical conditions has been investigated. The highest cumene yield and catalyst stability were observed when the reaction was carried out under supercritical conditions near the critical point, and the possible reasons for this have been discussed. To improve the catalyst behavior, modification of Beta zeolites by Zn and Ga was also investigated.

2. Experimental

2.1. Catalyst preparation

H-Beta zeolite ($SiO_2/Al_2O_3 = 30$) was first calcined at 550 °C in air for 3 h and then crushed into 40–60 mesh.

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Ga- and Zn-H-Beta zeolites were prepared by impregnation of H-Beta zeolite with aqueous solutions of $Zn(NO_3)_2$ and $GaCl_3$, respectively, for 16 h at room temperature, and then the samples were dried at 120 °C for 3 h and further calcined at 550 °C for 5 h.

2.2. Catalytic activity tests

The catalytic reaction was performed in a micro fixed-bed flow reactor with 6.0 mm i.d.; about 130 mg catalyst (40–60 mesh) was used per run. Before the reaction, the catalyst was first treated under a nitrogen flow from room temperature to reaction temperature, and then the nitrogen flow was switched to benzene and the pressure in the reactor was adjusted by pumping benzene. After the pressure of the reaction system reached the desired value, propene was pressurized into the system and the ratio of benzene to propene flow rate was set as 5:1 (mole ratio).

The liquid products were collected in a trap with an ice-water bath and analyzed with an FID gas chromatograph (Shimadzu GC-7A), equipped with an OV-101 column and argon as a carrier gas. The cumene yield was then obtained by benzene conversion and cumene selectivity.

2.3. Catalyst characterization

Surface area and textural properties of the catalysts were measured by nitrogen adsorption with an ASAP2000 of Micromeritics. The catalysts were degassed for 4–5 h prior to the measurement under 6.7 Pa at 300 °C (for fresh catalysts) or 200 °C (for used catalysts), respectively.

3. Results and discussion

3.1. Selection of reaction conditions

Alkylation of benzene and propene over Beta zeolites has been carried out in industry with a benzene/propene mole ratio of 3–6 at 160–200 °C and 1.5–3.0 MPa. The high-pressure vapor–liquid equilibria of the binary system benzene and propene have been studied by Guo *et al.* [13]; the critical point of the system with the mole ratio of benzene/propylene being 5 was determined as 5.8 MPa and 270 °C. Based on the equilibria data, the phase diagram of benzene + propene at this composition was given in figure 1, which showed that the phase state of the reaction system can be classified as liquid, vapor–liquid, vapor, gas and supercritical phase. Therefore, the catalytic tests were carried out at pressures of 3.1, 4.5, 6.2 and 7.2 MPa, and temperatures of 223, 252, 272 and 290 °C as asterisked in the figure to include all these regions.

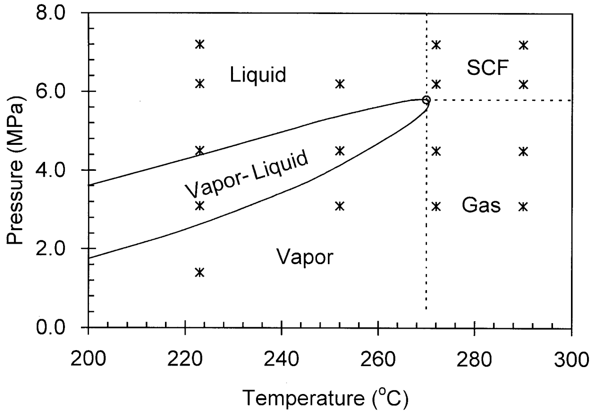

Figure 1. Phase diagram of benzene + propene at a mole ratio of benzene/propene of 5 and the operating conditions selected for the catalytic activity tests.

3.2. Alkylation of benzene with propene in different phases

Alkylation near critical temperature: The reaction of benzene with propene was first investigated under different pressures at 272 °C (near the critical temperature). At this temperature, the dependence of cumene yields upon the time on stream in supercritical (272 °C, 7.2 MPa), near-critical supercritical (272 °C, 6.2 MPa), near-critical gaseous (272 °C, 4.5 MPa) and gaseous phases (272 °C, 3.1 MPa) was compared in figure 2. When the reaction is operated in near-critical supercritical phase, the highest cumene yield (16.7%) was observed, and the deactivation of the catalyst was also not so obvious with a catalyst lifetime of 60 h. Contrarily, the cumene yields were lower and the catalysts deactivated much more sharply when the reactions were carried out in the gas phase.

Ideally, a reaction mixture with liquid-like density yet gas-like transport property would be required to enhance the reaction rate and to extract the coke-forming oligomers effectively from the catalyst. The effective dissolution and diffusion of the coke precursors deposited on the zeolites are capable of maintaining the activity of the acid sites and thereby prolonging the catalyst

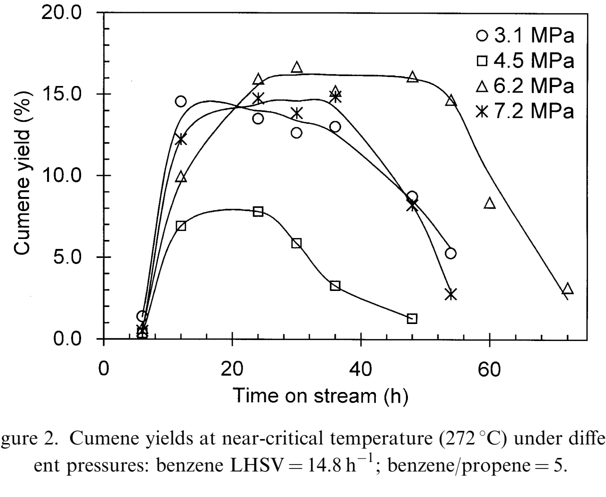

Figure 2. Cumene yields at near-critical temperature (272 °C) under different pressures: benzene LHSV = 14.8 h^{-1}; benzene/propene = 5.

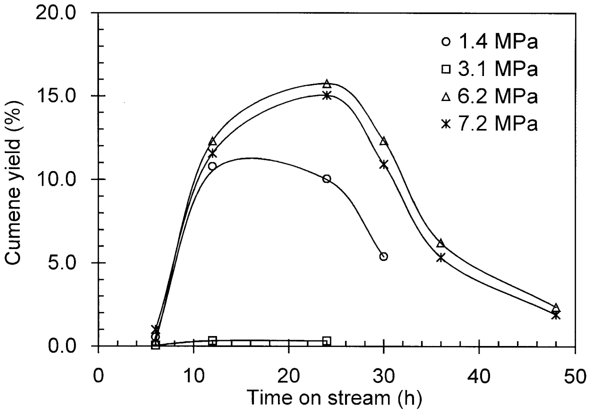

Figure 3. Cumene yields at 223 °C (below the critical temperature) in different phases: benzene LHSV = 14.8 h^{-1}; benzene/propene = 5.

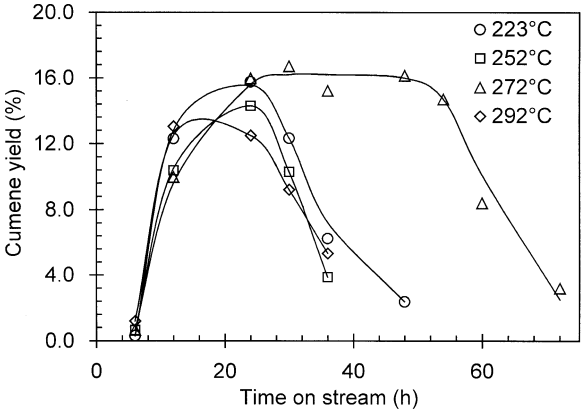

Figure 4. Cumene yields under 6.2 MPa (above the critical pressure) at different temperatures: benzene LHSV = 14.8 h^{-1}; benzene/propene = 5.

life. This may be the reason for the high cumene yields and long catalyst life under near-critical supercritical conditions.

It is interesting that the lowest yield of cumene appeared in the near-critical gas phase, along with a sharp decrease of the catalyst lifetime. The reason may be that the state of reaction intermediates and product mixture was near the vapor–liquid coexistence region. The yields of cumene under supercritical condition (7.2 MPa) and in the gas phase (3.1 MPa) are also lower than that under near-critical supercritical condition, with a shorter lifetime (47–48 h) of the catalyst. All these may suggest that the phase behavior and reaction mechanism are very complicated and need further thorough research.

Alkylation below critical temperature: There exist three regions of phase state below the critical temperature, *i.e.*, liquid at high pressure, vapor at low pressure and liquid-vapor coexistence at medium pressure. In figure 3, the reaction behaviors in liquid phase (223 °C, 6.2 and 7.2 MPa), vapor–liquid phase (223 °C, 3.1 MPa) and vapor phase (223 °C, 1.4 MPa) are compared. The cumene yield in liquid phase was much higher than those in the vapor or vapor–liquid coexistence region; and the effect of pressure was limited in the liquid phase. This may prove that the liquid mixtures also exhibit some abilities to extract the coke precursors and then enhance the reaction rate and prolong the catalyst life. Surprisingly, almost no conversion was observed in the vapor–liquid coexistence region. This may be explained by two reasons: the composition of propene in the liquid film in contact with the catalyst was very low, and the coexistence of both liquid and vapor could cause the collapse of the catalyst structure, as discussed in the literature [14].

Alkylation above critical pressure: The reaction mixture may exist as liquid or supercritical fluid when the pressure is above critical pressure. The reaction behaviors at 6.2 MPa and different temperatures are given in figure 4. An obvious maximum in the cumene yield and the longest lifetime occur under near-critical supercritical condition at 272 °C. In liquid phase, the yield of cumene decreased slightly, with the temperature increasing from 223 to 252 °C. The near-critical supercritical fluid with optimal densities and transport properties was capable of removing the coke precursors from the strong acid sites and preventing them from turning to consolidated coke. Under supercritical condition at higher temperature (292 °C), the yield of cumene is also very low. This may be due to the severe oligomerization and coking at high temperature [15].

Comparison of reactions in different phases: The results of reaction under different conditions are listed in table 1.

Table 1
Reaction behavior in different phases.

Phase	P (MPa)	T (°C)	Conv. (%)	Selec. (%)	Yield (%)	Life (h)[a]
Critical point	5.8	270	–	–	–	–
Supercritical-fluid near-critical point	6.2	272	19.1	87.3	16.7	60
Supercritical fluid	7.2	272	16.7	89.2	14.9	47
Liquid near-critical point	6.2	252	15.8	90.6	14.3	32
Gas near-critical point	4.5	272	9.8	79.4	7.8	32
Vapor–liquid	3.1	223	0.3	79.8	0.2	–
Liquid	6.2	223	17.6	89.7	15.8	32
Vapor	1.4	223	13.7	78.9	10.8	30
Gas	3.1	292	15.1	84.0	12.7	48

[a] Reaction time when benzene conversion decreased to 60% of the maximum.

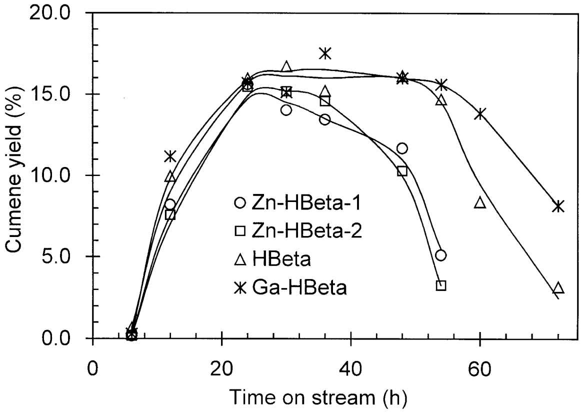

Figure 5. Cumene yields under 6.2 MPa and 272 °C (near-critical SCF) on the modified Beta zeolites: Zn-H-Beta-1 (2.1 wt Zn), Zn-H-Beta-2 (4.1 wt Zn), and Ga-H-Beta (0.6 wt% Ga); benzene LHSV = 14.8 h^{-1}; benzene/propene = 5.

By comparing the reactions in gas phase, liquid phase, vapor–liquid coexistence region, near-critical supercritical fluid and supercritical fluid, it can be concluded that the combination of liquid-like density and gas-like transport properties under near-critical supercritical condition is desirable for effective removal of the coke precursors. Thus, the highest yield of cumene and the longest lifetime of the catalyst can be obtained under supercritical conditions near the critical point.

3.3. Modification and characterization of the catalysts

The alkylation of benzene with propene on Zn- or Ga-modified Beta zeolites are compared under near-critical supercritical conditions, as shown in figure 5. Zn-H-Beta shows a lower activity than H-Beta. However, Ga-H-Beta shows a higher activity and a slower deactivation rate than H-Beta.

The BET surface and pore characters of catalysts are shown in table 2. The introduction of Zn^{2+} (Zn^{2+}, 4.12 wt%) results in the decrease of the BET surface area and pore volume of the catalysts, while the introduction of Ga^{3+} (Ga^{3+}, 0.62 wt%) shows almost no influence on the surface area and pore volume. The deactivated Ga-H-Beta after reaction under near-critical supercritical conditions for 72 h also shows higher surface area and pore volume than the deactivated Zn-H-Beta. These may also explain why the Ga-modified H-Beta is capable of enhancing the reaction rate and prolonging the catalyst life.

The BET surface areas and pore volumes of H-Beta catalyst after reaction in near-critical supercritical phase for 36 h are much lower than those of H-Beta catalyst after reaction in near-critical gaseous phase for 36 h. This also proves the ability of the supercritical fluid to extract coke precursors and then enhance the reaction rate and slow down the deactivation, since the decreases of surface area and pore volume are mainly caused by coke formation.

4. Conclusions

Alkylation of benzene with propene on H-Beta, Zn- and Ga-modified Beta zeolites in the gas, liquid, vapor–liquid coexistence region, near-critical supercritical phase and supercritical phase has been investigated. The highest cumene yield and stability of the catalysts were observed when the reaction was carried out on Ga-H-Beta under near-critical supercritical conditions, which may be ascribed to the effective dissolution and diffusion of the coke precursors deposited on the zeolites.

Acknowledgments

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Table 2
Surface area and pore volume of fresh and used catalysts.

	BET area (m^2/g)	Micropore area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)
H-Beta (fresh)	312.4	215.7	0.309	0.102
Ga-H-Beta (0.6 wt%, fresh)	315.4	212.6	0.312	0.100
Zn-H-Beta (4.1 wt%, fresh)	266.9	186.4	0.275	0.088
H-Beta (after reaction in near-critical gas for 36 h)	66.0	4.5	0.195	0.001
H-Beta (after reaction in near-critical SCF for 36 h)	185.5	105.2	0.249	0.050
Ga-H-Beta (0.6 wt%, deactivated)	134.7	59.8	0.229	0.028
Zn-H-Beta (4.1 wt%, deactivated)	105.2	37.4	0.194	0.017

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