

Liquid Phase Hydration of FCC C₄ Mixtures Catalyzed by Zeolite Catalysts

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Methyl *tert*-butyl ether (MTBE) as an octane promoter in automobile fuels has been phased out in some countries due to environmental problems. This motivates substantial interest in finding new ways for upgrading gasoline^[1-2]. The use of a replacement for MTBE , such as ethanol , is a feasible method to enhance the oxygenates and increase the octane number of gasoline^[3]. However , ethanol does not mix well with gasoline because of its tendency to separate from the fuel in the presence of water , and a solvent to improve the solubility of ethanol in the fuel must be added. Butyl alcohols (including *tert*-butyl alcohol , 2-butanol and 1-butanol) are good additives for improving the solubility of ethanol and also for upgrading the octane number and increasing the oxygenates in the gasoline.

The hydration of butylenes to butyl alcohols is a commercially important reaction as the products , 2-butanol and *tert*-butyl alcohol , have several industrial applications. The industrial production of aliphatic alcohols by the hydration of olefins in the presence of

cationic exchange resins is a widely used process. However , these catalysts have the fatal disadvantage of deactivation due to the elimination of the sulphonyl group during operation , and the activity cannot be recovered by a sulphonation treatment. It has been claimed that zeolite catalysts can be used for the direct hydration of butylenes under moderate pressure in liquid phase^[4-7]. However , the olefin used in these processes is pure 1-butylene , and the cost of the hydration products is much higher than that of gasoline , thus , adding butyl alcohols produced from the above processes to gasoline is limited for economic reasons. The aim of this work is to investigate the hydration of mixed C₄ hydrocarbons over zeolite catalysts to provide a way to increase the value of FCC (fluidized catalytic cracking) C₄ hydrocarbons by the production of an inexpensive butyl alcohol component.

The C₄ hydrocarbon mixtures were obtained from Dalian Petrochemical Co. , and the composition of two samples (before and after the MTBE process) is listed in Table 1.

Table 1 Composition of mixed C₄ hydrocarbons

Sample	Composition (%)						
	Isobutane	<i>n</i> -Butane	Isobutylene	1-Butylene	<i>Cis</i> -2-butylene	<i>Trans</i> -2-butylene	Others
MC ₄ -1	36.29	9.08	16.71	12.61	9.42	14.61	1.28
MC ₄ -2	36.60	11.98	0.13	16.02	13.00	21.00	1.27

MC₄-1 , mixed C₄ hydrocarbons before the MTBE process ; MC₄-2 , mixed C₄ hydrocarbons after the MTBE process.

ZSM-5 (Si/Al = 60) and β (Si/Al = 46.2) zeolites were obtained from Fushun Petrochemical Co. , PetroChina. All the zeolites were first ion-exchanged to the ammonium form by treatment with 0.1 mol/L NH₄NO₃ solution and then calcined at 550 °C for 3 h to obtain the acidic H-form. The catalytic hydration of the C₄ hydrocarbon mixtures was performed in a

high pressure reaction system at 80 ~ 180 °C under 5.0 MPa. The effluent was collected in a chilled flask , and the liquid products were analyzed on a Varian CP-3800 gas chromatograph equipped with an FFAP capillary column (25 m) and an FID detector. 1,4-Dioxane was used as an internal standard. Typical reaction results of the hydration of the C₄ hydro-

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carbon mixtures over different zeolite catalysts are shown in Table 2.

Table 2 Reaction results of hydration of mixed C₄ hydrocarbons over different zeolite catalysts^a

Catalyst	Reactant	t/°C	Solvent ^b	Yield(%)	
				Tert-butyl alcohol	2-Butanol
HZSM-5	MC ₄ -1	100	no	18.3	— ^d
HZSM-5	MC ₄ -1	120	no	25.1	—
HZSM-5	MC ₄ -1	140	no	20.0	0.1
HZSM-5	MC ₄ -1	120	THF ^c	51.0	0.2
HZSM-5	MC ₄ -1	120	1,4-dioxane	1.6	—
HZSM-5	MC ₄ -1	120	ethanol	23.2	—
HZSM-5	MC ₄ -2	140	no	0	4.1
Hβ	MC ₄ -1	140	no	15.8	0.7
Hβ	MC ₄ -2	120	no	—	7.1
Hβ	MC ₄ -2	140	no	—	11.5
Hβ	MC ₄ -2	160	no	—	7.5

^aReaction conditions : $\alpha(\text{H}_2\text{O})/\alpha(\text{C}_4) = 4$, $\text{WHSV}(\text{C}_4) = 1 \text{ h}^{-1}$, $p = 5.0 \text{ MPa}$.

^b $n(\text{solvent})/n(\text{H}_2\text{O}) = 1/20$.

^cTHF, tetrahydrofuran.

^dTrace amount or below detectable limits.

As is evident from Table 2, HZSM-5 and Hβ are effective catalysts for the hydration of C₄ hydrocarbon mixtures under moderate reaction conditions. Tert-butyl alcohol is the main hydration product on both HZSM-5 and Hβ catalysts when MC₄-1 is the reactant. This suggests that isobutylene is more active than n-butylene in the hydration process, which is in accord with most works. In all cases, no polymerization products were observed except in the hydration of MC₄-1 over the Hβ catalyst, where traces of dimers of isobutylene were detected by GC-MS. This may be mainly attributed to the channel systems of the different zeolites. ZSM-5 zeolite possesses a two-dimensional channel system with 10-rings of 0.53 nm × 0.56 nm and 0.51 nm × 0.55 nm, while beta zeolite possesses a relatively bigger pore mouth (0.66 nm × 0.67 nm and 0.56 nm × 0.56 nm), which may contribute to the formation of isomers.

The reaction temperature is an important parameter in the hydration process. It influences the reaction rate and is also a major factor in the distribution of alcohols in the organic and aqueous phases, which will further affect the equilibrium of the forward reac-

tion (hydration of olefins) and the backward reaction (dehydration of alcohol). The temperatures at which there are maximum yields of butyl alcohols are 120 and 140 °C for the hydration of MC₄-1 and MC₄-2, respectively.

The addition of an appropriate solvent, such as THF, to the system can improve the yield of butyl alcohols. This may be accounted for by increased butylenes in the water phase as the added THF is miscible in both water and C₄ hydrocarbons. Moreover, the THF can extract butyl alcohols from water, which favors the forward reaction. It is interesting that adding 1,4-dioxane and ethanol, they are also miscible in both water and C₄ hydrocarbons, hardly enhanced the hydration reaction, but decreased the yields of butanols. The modification of alcohols solubility in the organic and aqueous phases by adding different solvents affects the relative rates of the hydration and dehydration reactions, which results in a change in the yields of butyl alcohols. Moreover, the adsorption and diffusion of solvents in the molecular sieve catalysts can further affect the conversion of the reactants, which also influence the reaction rate of hydration. This aspect needs further experiments. In the hydration of MC₄-2, in which n-butylenes are the main olefins and there is only a small quantity of isobutylene, Hβ is more effective than HZSM-5 for the formation of 2-butanol and the concentration of oligomers in the bulk liquid reaction medium is below their detection limits.

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