SYNTHESIS OF SEC-BUTANOL FROM n-BUTENES AND WATER WITH MOLECULAR SIEVE CATALYSTS

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Using n-butenes and water as feedstocks and molecular sieves as catalysts, effects of the reaction temperature, the reaction pressure, the weight hour space velocity (WHSV), and the ratio of water to n-butenes on the conversion of n-butenes were studied. The experimental results showed that the optimal reaction temperature, the pressure, the WHSV, and the ratio of water to n-butenes were 180 °C, 8.0 MPa, 0.2 h^{-1}, and 8, respectively; the single conversion of n-butenes and the selectivity of 2-butanol formation were found to be 35.52% and 99%, respectively.

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Introduction

n-Butenes are basic petrochemical and organic chemical products and due to their high combustion heat they are frequently burnt as fuel. The use of n-butenes as feedstocks improves the efficiency of raw material utilization and increases the economic income of a chemical plant.[1]

The preparation of 2-butanol from n-butenes and water is a well known process, which is catalysed by sulphuric acid,[2] strongly acidic ion-exchanger resins,[3] or heteropolyacids.[4]

Indirect hydration with sulphuric acid as catalyst can be described as follows. The reactor is a kind of tower, and the process consists of four steps, such as esterification, hydrolysis, fractionation, and dilution of sulphuric acid. Sec-butyl ether by-product formation occurred. When an industrial C_4 fraction containing n-butenes were pre-treated with 80% sulphuric acid[5], the butyl sulphate produced was transformed into 2-butanol via hydrolysis and fractionation. The advantages of the method were that the content of n-butenes was not limited, and the reaction conditions were mild and could be easily controlled. The main disadvantages were that the equipment was seriously corroded, thus requiring more investment, and large amount of sulphuric acid and alkaline material for its neutralization were required.

The ion-exchange resin catalyzed direct hydration reaction conditions were as follows: the reactor was a kind of cylinder which included the solid sulfonic acid resin catalysts. The life cycle of the catalyst was about one year. The process could be performed in a simple way, no corrosion of the equipment was observed. The main disadvantage of the method was that high content of n-butenes was required in the input stream and the single yield of 2-butanol was very low (less than 10%).

Heteropolyacid catalyzed direct hydration was peformed in the following way using the unit built in 1985: the reactor was a vertical stirred cylinder in which the catalyst was a mixture of molybdate and organic metal-containing additive. The optimal reaction temperature, pressure, single conversion of n-butenes, and selectivity for 2-butanol were found to be 200–230 °C, 19.0 MPa, 25–30%, and more than 97%, respectively. n-Butenes were proved to be not only simple reactants but also supercritical extracting agents. The efficiency of the reaction was very high, but the reaction required relatively high pressure.

In this paper, the reaction of n-butenes and water on molecular sieves as catalysts was studied. Effects of the reaction temperature, the pressure, and the WHSV, and the ratio of water to n-butenes on the conversion of n-butenes were determined. Experimental results indicated that the conversion of n-butenes and the selectivity for 2-butanol were higher and better than that of other methods.

Experimental section

Feedstock

n-Butenes were obtained from Fushun Ethylene Chemical Plant. The compositions of n-butenes used are shown in Table 1.

Table 1. Compositions of n-butenes

Components	C_2	$C_3^=$	C_3^0	iC_4^0	nC_4^0	$nC_4^=$
Composition, % m/m	0.14	0.17	0.04	0.06	0.15	99.44

Catalyst

Properties of the applied modified molecular sieve catalyst are presented in Table 2.

Table 2. Properties of molecular sieve catalyst

Particle size, mm	Length, mm	Stacking density, g*cm^{-3}	Intensity, kg*mm^{-1}
1.5~1.8	5~9	0.671	>10

Reaction principle

2-Butanol can be produced from n-butenes and water using molecular sieve as catalyst, according to Eqn. (1) and (2):

$$CH_2=CH\text{-}CH_2\text{-}CH_3 + H_2O \rightarrow CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3 \quad (1)$$

$$CH_3\text{-}CH=CH\text{-}CH_3 + H_2O \rightarrow CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3 \quad (2)$$

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Apparatus

n-Butenes and water were pumped into the reactor. When the reaction was completed, the product was separated in a separation tank. The final product and gases were discharged at bottom and top of the tank, respectively. The schematic drawing of the experimental apparatus is shown in Figure 1.

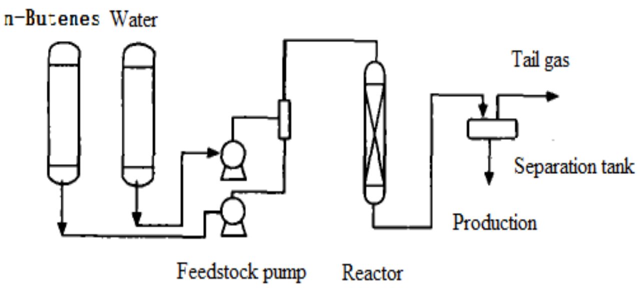

Figure 1. Schematic drawing of the experimental apparatus

Results and discussion

Effects of the reaction pressure and the WHSV on the conversion of n-butenes

Effects of the reaction pressure and the WHSV on the conversion of n-butenes were studied with keeping the reaction temperature and the ratio of water to n-butenes at values of 180 °C and 8, respectively.

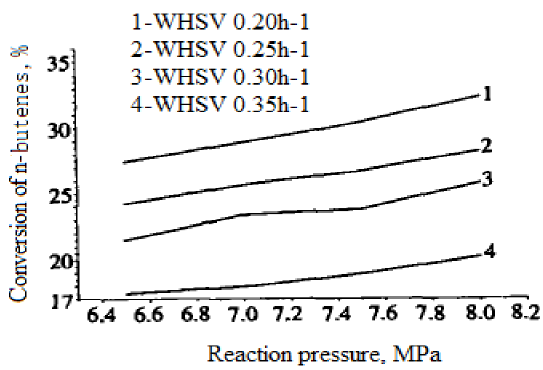

Figure 2. The relationship between the pressure, the WHSV, and the conversion of n-butenes

Figure 2 shows the relationship between the pressure, the WHSV, and the conversion of n-butenes. The conversion of n-butenes at the same WHSV increased with the increase of the reaction pressure, but the conversion of n-butenes at the same reaction pressure decreased with the increase of the same WHSV. The maximal conversion of n-butenes could be obtained at 8.0 MPa pressure and 0.2 h^{-1} weight hour space velocity.

Effects of the reaction temperature and the WHSV on the conversion of n-butenes

Effects of the reaction temperature and the WHSV on the conversion of n-butenes were studied at 8.0 MPa pressure and at the ratio of water to n-butenes of 8.

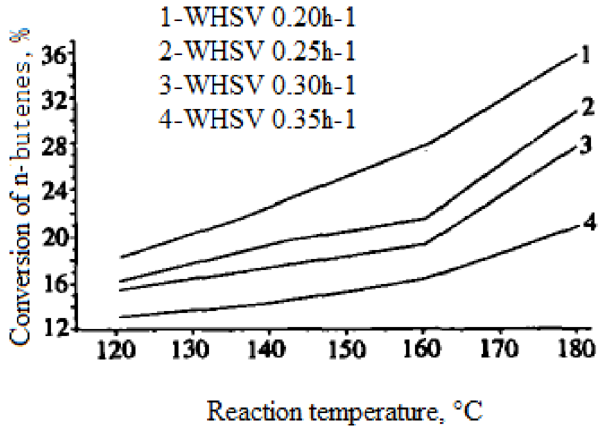

Figure 3. The relationship between the temperature, the WHSV, and the conversion of n-butenes

Figure 3 shows the relationship between the reaction temperature, the WHSV, and the conversion of n-butenes. The conversion of n-butenes at the same WHSV increased with the increase of the reaction temperature, but the conversion of n-butenes at the same reaction temperature decreased with the increase of the same WHSV. The conversion of n-butenes had a maximum value when the reaction temperature and the WHSV were 180 °C and 0.2 h^{-1}, respectively.

Effects of the ratio of water to n-butene and the WHSV on the conversion of n-butenes

The reaction pressure and the reaction temperature in these experiments were 8.0 MPa and 8, respectively. Effects of the ratio of water to n-butenes and the WHSV on the conversion of n-butenes were studied.

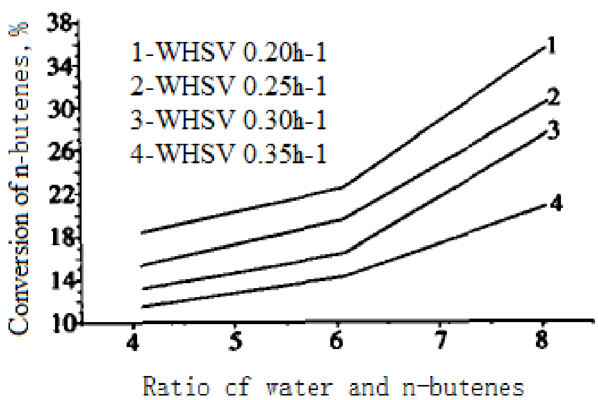

Figure 4. The relationship between the ratio of water to n-butene, WHSV, and the conversion of n-butenes

Figure 4 shows the relationships between the ratio of water to n-butenes, the WHSV, and the conversion of n-butenes. The conversion of n-butenes at the same WHSV increased with the increase of the ratio of water to n-butenes, but the conversion of n-butenes at the same ratio of water to n-butenes decreased with the increase of the same WHSV. The conversion of n-butenes had a maximum value when the ratio of water to n-butenes and the WHSV were 8 and 0.2 h^{-1}, respectively.

Based on experimental data, the regression resulted in a three-variable equation, which can be written as follows:

$$\varphi, \% = A + BX_1 + CX_3 + DX_1X_2 + EX_2^2 \quad (3)$$

where φ - the conversion of butanes, in %,

X_1 - the pressure, MPa,

X_2 - the ratio of water to n-butenes

X_3- the WHSV, h^{-1}.

A= –159.08

B= 33.88

C=0.64

D=332.89

E=15960.52

Conclusion

Using water and n-butenes as feedstocks and molecular sieves as catalysts, effects of the reaction temperature, the pressure, the WHSV, and the water/n-butenes ratio on the conversion of n-butenes were studied. The experimental results obtained are as follows:

(1) The conversion of n-butenes at the same WHSV increased with the increase of the reaction temperature, the pressure, and the water/n-butenes ratio.

(2) The conversion of n-butenes at the same reaction temperature, the same reaction pressure, and the same water/n-butenes ratio decreased with the increase of the WHSV**.**

(3) Molecular sieve catalysts exhibit high activity and conversion efficiency in the n-butene water reaction. Good economic and social benefits can be obtained using this type of molecular sieve catalysts in the reaction of n-butenes with water.

References

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