

## Hydration of ethylene in the vapour phase over NAPO-5 and ZAPO-5

C KANNAN, S P ELANGO VAN<sup>+</sup>, M PALANICHAMY and  
V MURUGESAN\*

Department of Chemistry, Anna University, Madras 600 025, India

<sup>+</sup> Department of Chemistry, Sri Venkateswara College of Engineering,  
Sri Perumbudur 603 105, India

MS received 20 April 1998; revised 29 July 1998

**Abstract.** Hydration of ethylene in the vapour phase over NAPO-5 and ZAPO-5 molecular sieves has been carried out between 300 and 450°C. The products formed are isobutanol, ethanol and *n*-butanol. The effects of temperature, time on stream and partial pressure of water vapour on ethylene conversion and products selectivity have been studied. Increase of the partial pressure of water vapour increased the selectivity of ethanol and *n*-butanol, but decreased the selectivity of isobutanol. Formation of ethanol and *n*-butanol is observed to be dependent on Bronsted acidity whereas formation of isobutanol is proved to be dependent on both Bronsted and Lewis acidities.

**Keywords.** Molecular sieves; solid acid and ethylene hydration.

### 1. Introduction

Synthesis of alcohols from ethylene is an industrially important reaction, because the products namely ethanol, isobutanol and *n*-butanol have important industrial applications. For example, ethanol is used as an important beverage, a substitute for petrol under the name power alcohol and as a solvent, isobutanol in the manufacture of isobutylene, a monomer for the production of polyisobutylene and *n*-butanol as a solvent for fats, waxes and resins. Impregnated mineral acid catalysts such as H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> were reported<sup>1</sup> in the literature for the synthesis of alcohols. But the use of mineral acids exhibited low activity, corrosion problems and environmental concern. ZnO-TiO<sub>2</sub>, zirconium tungstate<sup>3</sup> and niobic acid<sup>4</sup> have also been proposed as suitable alternative catalysts for ethylene hydration, but they also have the problem of acid depletion, reproducibility and lower activity. Catalyst of the ferrierite type-zeolite<sup>5</sup> has overcome all the problems and was found to be active even at 200°C. In the present investigation, vapour phase hydration of ethylene has been carried out over NAPO-5 and ZAPO-5 molecular sieves which are ecofriendly catalysts possessing both Bronsted and Lewis acid sites. In contrast to the conventional catalysts, in ethylene hydration over NAPO-5 and ZAPO-5 molecular sieves, isobutanol was also formed in addition to ethanol. Eventhough the temperature used in this study was higher than those over the reported catalysts<sup>5</sup>, the unexpected formation of isobutanol attracted the investigators to optimise the experimental conditions and the partial pressure of water vapour to obtain high selectivity of isobutanol.

\*For correspondence

**Table 1.** Synthesis conditions, molar compositions and total acidity of aluminophosphate based molecular sieves

Catalysts	Gel composition M	pH		Temperature °C	Time h	Molar composition	Total acidity mmol/m <sup>2</sup>
		Before	After				
NAPO-5	0.1 NiO:TEA: Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> : 40 H <sub>2</sub> O	4.9	9.0	175	24	0.05 NiO: 0.95 Al <sub>2</sub> O <sub>3</sub> : P <sub>2</sub> O <sub>5</sub>	0.0013
ZAPO-5	0.1 ZnO:TEA: Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> 40 H <sub>2</sub> O	4.4	9.5	175	24	0.07 ZnO: 0.93 Al <sub>2</sub> O <sub>3</sub> P <sub>2</sub> O <sub>5</sub> H <sub>2</sub> O	0.0015

## 2. Experimental

### 2.1 Synthesis and characterisation

NAPO-5 and ZAPO-5 molecular sieves were synthesised by hydrothermal crystallisation using aluminium isopropoxide, orthophosphoric acid, zinc oxide and nickel acetate as the sources for aluminium, phosphorus, zinc and nickel respectively and dipropylamine as template by adopting the method described in our earlier paper<sup>6-8</sup>. The gel composition, pH, temperature and synthesis time are given in table 1. Characterisation of the samples synthesised has been described elsewhere<sup>6-8</sup>. The data corresponding to acidity for both catalysts obtained from pyridine desorption are given in table 1.

### 2.2 Catalytic studies

The reactor system was a fixed-bed, vertical flow type reactor made up of quartz tube of 40 cm length and 2 cm internal diameter. The quartz reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The bottom of the reactor was provided with a thermowell in which the chromel - alumel thermocouple was kept to measure the temperature at the middle of the catalyst bed. About 2 g of the catalyst was placed in the reactor and supported on either side with a thin layer of quartz wool and ceramic beds. The top portion of the reactor was connected to a mixing chamber. Water was fed into the mixing chamber through one inlet by a syringe infusion pump that can be operated at different flow rates and the other inlet was connected to pure ethylene gas generator. Ethylene was generated separately by dehydrating ethanol using phosphoric acid between 75 and 100°C. Its purity was checked by G.C. before metering into the reactor. The flow rate of ethylene was controlled by controlling the addition of ethanol to phosphoric acid. The bottom of the reactor was connected to a coiled condenser and a receiver in which the products were collected. The liquid products were analyzed using a Hewlett Packard gas chromatograph 5890 A with a flame ionization detector. The side tube of the receiver was connected to an Orsat apparatus for measuring the unreacted ethylene.

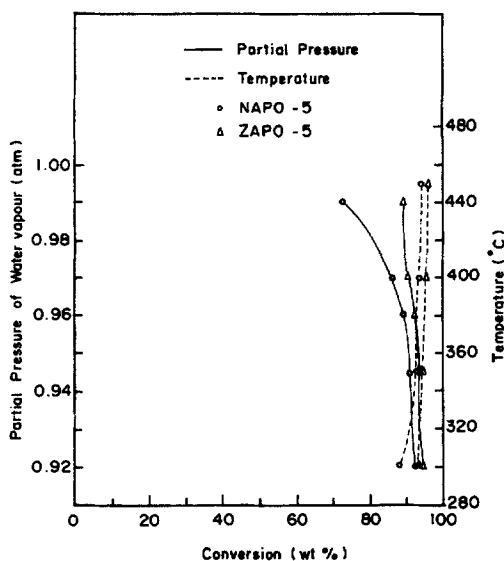
### 3. Results and discussion

NAPO-5 and ZAPO-5 molecular sieves were synthesized by placing 0.05 M of Ni and 0.07 M of Zn in the respective framework. Their molar composition and total acidity are given in table 1. As the substitution of trivalent aluminium by Ni in NAPO-5 is less than that of Zn in ZAPO-5, the associated Bronsted acidity of NAPO-5 (0.00055 mmol/m<sup>2</sup>) is also less than ZAPO-5 (0.00088 mmol/m<sup>2</sup>). In this investigation, NAPO-5 and ZAPO-5 were used as catalysts to study the hydration of ethylene. Time on stream was performed to compare their catalytic activity. The products obtained for both catalysts were ethanol, isobutanol and *n*-butanol, and their selectivity was in the order isobutanol > ethanol > *n*-butanol at low temperature but at high temperature the order became ethanol > isobutanol > *n*-butanol. The effects of partial pressure of water vapour and temperature on the selectivity of alcohols are discussed in the following sections.

#### 3.1 Effect of partial pressure of water vapour

Since water was one of the components of the reaction, its influence on the selectivity of alcohols was studied by varying its partial pressure viz., 0.92, 0.96, 0.97 and 0.99 atm at 350°C. At lower values of partial pressure, the conversion (figure 1), and the selectivity for isobutanol were high (figure 2), but at higher values the conversion decreased (figure 1), and the selectivity of both ethanol and *n*-butanol increased with consequent decrease in the selectivity of isobutanol as shown in the figure 2. Although hydration reaction involves addition of water to ethylene, activation of water by Bronsted acid sites of the catalyst was expected to be necessary for this reaction as shown in the reaction scheme 1.

Adsorption of water on the Bronsted acid sites makes its protons labile, and this facilitates interaction of these protons with ethylene adsorbed in its immediate vicinity.



**Figure 1.** Effect of partial pressure of water vapour and temperature on ethylene conversion over NAPO-5 and ZAPO-5

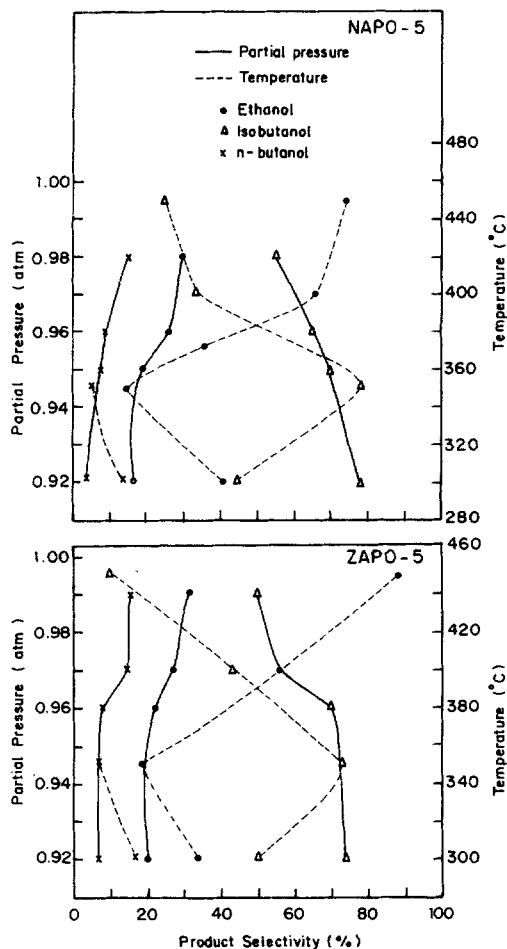
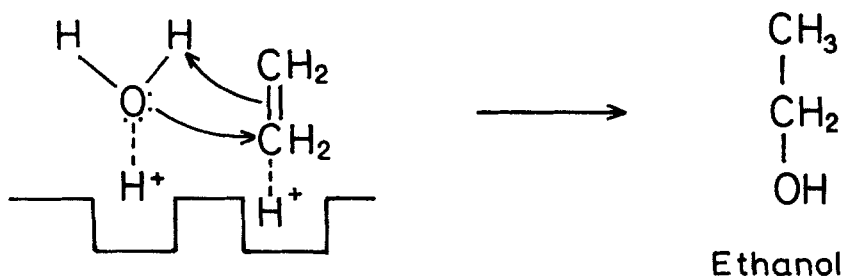
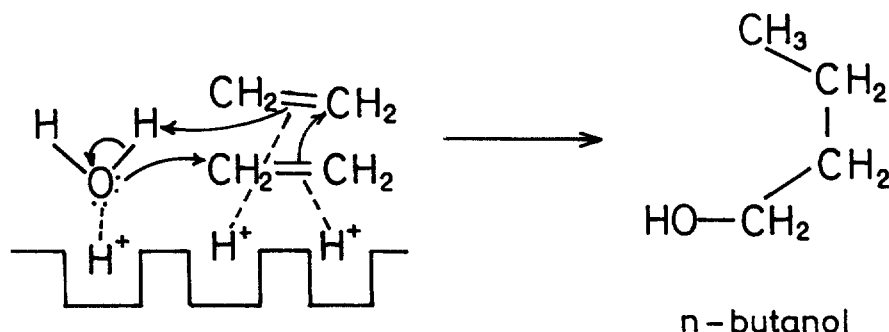
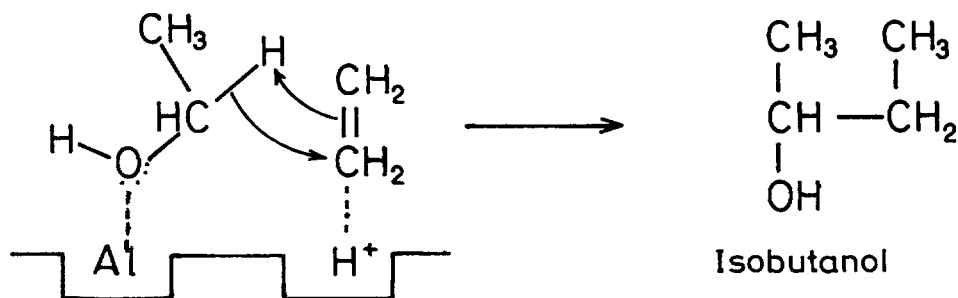


Figure 2. Effect of partial pressure of water vapour and temperature on product selectivity over NAPO-5 and ZAPO-5



Scheme 1.

It subsequently favours nucleophilic attack of ethylene with water to give ethanol. In the formation of isobutanol, co-ordination of alcoholic OH with Lewis acid sites was necessitated in order to make one of its methylene protons with its bonding pair interacting with the nearby adsorbed ethylene on Bronsted acid sites as shown in the



reaction scheme 2. In order to enlighten this fact, ethanol as such was used as the feed in the reactor at 450°C. In addition to the formation of a large amount of ethylene, a small amount of isobutanol was also formed.

Selectivity of isobutanol decreased with increase of partial pressure of water vapour and this would be possible only if the Lewis acid sites previously available for ethanol co-ordination remained masked with excess water by adsorption. But selectivity of ethanol and *n*-butanol increased with increase of partial pressure of water vapour. Formation of *n*-butanol required adsorption of a water molecule and two ethylene molecules on Bronsted acid sites planted at closer distances as shown in the reaction scheme 3. As an increase of water vapour pressure decreased the formation of isobutanol, the ethylene molecules which have been used for the formation of isobutanol were used up largely in the formation of ethanol and *n*-butanol. As one would expect leaching of aluminium from the catalyst by water vapour used in the reaction, the catalysts were characterised with XRD for the change of crystallinity after the reaction. There was negligible change in the crystallinity of the catalysts.

### 3.2 Effect of temperature

The influence of temperature on the reaction was investigated to reach favourable conditions for high selectivity of isobutanol in this reaction. The influence of temperature on the ethylene conversion and selectivity to the products was studied at 300, 350, 400 and 450°C and the results obtained are given in figure 2. The increase of temperature did not show much variation on ethylene conversion (figure 1), but

increased the selectivity of ethanol. Ethanol selectivity showed an increase up to a temperature of 350°C, followed by an unexpected significant decrease at 350°C. In contrast to selectivity of ethanol, isobutanol showed a significant increase of selectivity at 350°C but above this temperature, the selectivity decreased. This inverse behaviour of ethanol selectivity over isobutanol looked very interesting and hence demanded further investigation. At 300°C, ethylene and water vapour adsorbed over Bronsted acid sites react to produce ethanol. This ethanol migrates to Lewis acid site and then reacts with ethylene adsorbed on Bronsted acid site, to produce isobutanol. But ethanol and isobutanol showed almost similar selectivity at 300°C. At 350°C, ethanol would have reached much activation to react with ethylene to give isobutanol with more selectivity than that at 300°C. But at 400 and 450°C, ethanol desorption becomes more important than its migration to a Lewis acid site, adsorption and reaction with ethylene to produce isobutanol. Hence ethanol selectivity increased with a consequent decrease in isobutanol selectivity. Although *n*-butanol formation was observed at 300 and 350°C, its complete disappearance at 400 and 450°C would be due to some coke formation, which would prevent close existence of three protonic sites necessary for *n*-butanol formation.

### 3.3 Effect of time on stream

The activity of catalysts on hydration of ethylene was investigated by time on stream at 350°C with partial pressure of water vapour at 0.92 atm. The results obtained are presented in table 2. Ethylene conversion decreased with time on stream but ethanol selectivity increased. Conversion of ethylene depends on hydration of ethylene to ethanol, reaction of ethylene with ethanol to produce isobutanol and simultaneous hydration of two ethylene molecules to give *n*-butanol. In all these three reactions, ethylene is adsorbed on Bronsted acid sites but the third reaction requires more Bronsted acid sites than the first and the second reactions as are shown in the reaction scheme 1, 2 and 3. As coke formation is observed over the catalysts in the later stages of time on stream, many of the Bronsted acid sites would have been blocked and hence the first and last reactions which depend on more Bronsted acid sites could not be very favourable. The third reaction is much less unfavourable than the first reaction, as it requires three Bronsted acid sites located at closer distances, and hence formation of *n*-butanol disappears ultimately. Although conversion of ethylene is less, the selectivity

**Table 2.** Effect of time on stream on ethylene hydration.  
Partial pressure of water vapour 0.92 atm Temperature - 350°C

Catalysts	Time h	Conversion wt%	Product selectivity %		
			Ethanol	Isobutanol	<i>n</i> -butanol
NAPO-5	1	92	15	78	6
	2	88	41	41	16
	3	82	51	17	30
	4	35	60	8	32
NAPO-5	1	94	20	73	6
	2	87	65	25	10
	3	79	72	11	15
	4	40	80	3	17

of ethanol is high. The increase in selectivity of ethanol is attributed to its failure in participating in the reaction of isobutanol formation by getting adsorbed on Lewis acid sites, as a result of its prevention to adsorption over these sites by water molecules. In the latter stages of time on stream the number of free water molecules that compete with ethanol for adsorption is more and hence ethanol is largely prevented from adsorption and isobutanol formation.

#### 4. Conclusion

It is concluded that ethylene hydration over NAPO-5 and ZAPO-5 gave isobutanol, ethanol and *n*-butanol. It has been observed that increase in partial pressure of water vapour blocks the Lewis acid sites and reduces isobutanol selectivity. Bronsted acid sites favour the formation of ethanol. But in the presence of Lewis acid sites, the ethanol formed reacts further with ethylene to produce isobutanol.

#### References

1. Devon R and Schwartz M 1972 *Chem. Eng. New York* **4** 50
2. Tanabe K, Ishiya C, Matsuzaki I, Ichikawa I and Hideshi H 1972 *Bull. Chem. Soc. Jpn.* **45** 47
3. Momose H, Kusumoto K, Izumi Y and Mizutani Y 1982 *J. Catal.* **77** 554
4. Ogasawara K, Iizuka T and Tanabe K 1984 *Chem. Lett.* 645
5. Iwamoto M, Tajima M and Kagawa S 1985 *J. Chem. Soc., Chem. Comm.* 228
6. Elangovan S P, Krishnasamy V, Murugesan V and Arabindoo B 1995 *J. Chem. Soc. Faraday Trans.* **91** 4471
7. Elangovan S P, Krishnasamy V and Murugesan V 1995 *Bull. Chem. Soc. Jpn.* **68** 3659
8. Elangovan S P, Krishnasamy V and Murugesan V 1996 *Catal. Lett.* **36** 271