

Synthesis of Primary Alcohol from H₂ and CO over Exchanged Zeolites

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We have used NaX zeolites exchanged by transition metals such as copper and zinc for the synthesis of methanol, ethanol and butanol. The influence of the H₂/CO ratio, the temperature and the contact time are examined at a constant pressure of 50 bars. The experimental results show that the conversion of the carbon monoxide to isobutanol is maximum at a temperature of 523K. It also increases with the H₂/CO ratio and the contact time. With pressure, size of the particle and H₂/CO ratio constant, we found no variation in the activity of the catalyst over 500 hours for the same conversion to isobutanol.

INTRODUCTION

It is well known that the use of a copper and zinc oxide or zinc and chromium oxide mixture is the most important catalytic way to synthesize alcohol from the hydrogenation of the carbon monoxide¹⁻³. The products are mainly composed of C₁ to C₆ hydrocarbons with the presence of undesirable reactions such as coke deposition and CO₂ formation. The syntheses are made under very strong conditions such as high temperatures (573K-773K) and several MPa. Many attempts have been made to lower these conditions using as catalysts either mixtures of metal oxides⁴⁻⁵ or zeolites in their sodium and exchanged forms⁶. In this paper, the reaction of CO and H₂ on an NaX zeolite exchanged by transition metals (mainly Cu, Zn) have been tested in the pressure/temperature regime for which isobutanol formation is thermodynamically possible.

EXPERIMENTAL

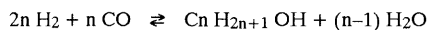
The starting material was an NaX molecular sieve powder. Before ion exchange of NaX, the zeolite was impregnated in a sodium solution (1M) for two weeks and dried at 393K for 2 days. The exchanged zeolites were prepared by treating the NaX

molecular sieve with solutions of the respective transition metal nitrates at room temperature. Highly exchanged samples were prepared by repeated ion exchange. The solid was then washed in water several times and dried at 393K in an oven. The extent of ion exchange was determined by analysing the resulting solution by atomic absorption spectrophotometry. All zeolites were calcined 15 hours at 673K.

After grinding and sieving, the samples were pelleted. As described previously⁷ the reaction was carried out in a fixed bed type reactor with a continuous flow system under 5 MPa. Thermal pretreatment was carried out in a mixed stream of hydrogen and nitrogen (5 % H₂) at a temperature which had been slowly increased to 773K for 3 days. The gas mixture was then allowed to flow over the catalyst. Reactant and products were analysed by means of gas chromatography.

RESULTS AND DISCUSSION

The primary alcohol that may be formed by hydrogenation of the CO by the reaction



is isobutanol, when $n = 4$. Since the isobutanol catalytic synthesis is characterized by an important heat release, it is necessary to study the thermodynamics of the reaction in order to establish the optimum conditions for isobutanol synthesis. The method is based on determination of the pressure and the temperature effects on the heat of the reaction and chemical equilibrium. The theoretical curve is plotted on the Fig. 1.

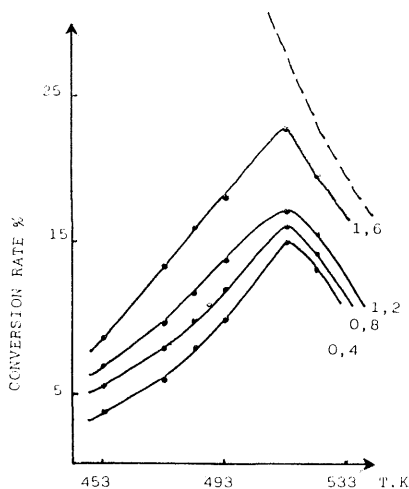


Fig.1. Effect of reaction temperature on isobutanol formation rate - experimental - theoretical.

Experimentally, we have studied the effect of three parameters: the temperature, the contact time and the H_2/CO ratio.

The temperature range chosen is from 453 to 623K. Under 453K the chromatograph detects only CO , H_2 and a weak peak of methane. Above 623K the important heat of the reaction increases the temperature to 773K. At this limit, coke formation take place on the zeolite and leads to poisoning of the catalyst. The contact time is varied from 0.4 to 1.6 s. Analysis of the condensed phase shows the formation of methanol, ethanol, isobutanol and small quantities of ketones and dimethylether.

TABLE 1

*Products distribution in %, $T = 513K$
Contact time 2 s, formation rate 21.2 %*

gas	$CO + H_2$	CO_2	CH_4	C_2H_6	H_2O	others
	80	5	3	2	3	7
liquid	methanol	ethanol	H_2O	butanol	dibutyl ether	others
	4.03	0.24	29.85	65.32	0.61	0.5

As shown in Table 1, the hydrocarbon product is essentially isobutanol, the others were less than 5 %. Table 2 shows the conversion ratio to butanol versus the temperature and contact time. The conversion of CO to alcohol begins at 453K and increases to a maximum at 513K before it decreases (Fig.1). The selectivity to iso-

TABLE 2

Effect of temperature and contact time on isobutanol formation rate

T.K	contact time	0,4 s	0,8 s	1,2 s	1,6 s
453		4. %	5.63 %	6.92 %	8.41 %
473		5.6	7.91	9.54	10.
483		8.1	10.02	11.93	15.7
493		10.	11.3	14.	17.81
513		13.02	16.13	17.5	23.
523		2.9	10.	18.2	20.

butanol formation is up to 87 %. The effect of contact time on the rate of alcohol formation is shown in Fig.2. The rate increases linearly with the contact time which has been varied from 0.2 to 1.6 s. It increases also with the temperature in the range studied 453K to 513K.

The same rate is observed for a fresh catalyst and a catalyst which has been used once at another reaction temperature. Over 523 K, the formation rate decreases with contact time and the activity of the catalyst, after being used, never shows the original value when the catalyst is used again at 523K. However removal of copper or zinc from the catalyst system is not detected at the higher reaction temperature. These

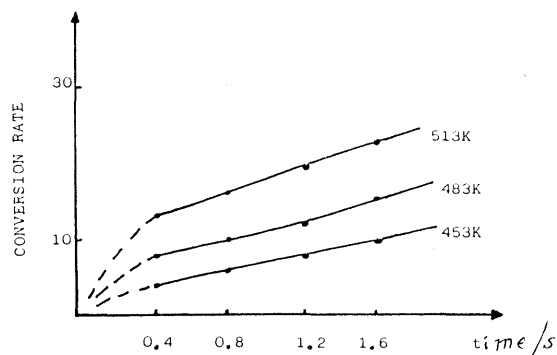


Fig.2. Effect of contact time on the formation rate at 453 K, 483 K and 513 K.

results suggest that an irreversible deactivation of the active site occurs at reaction temperatures higher than 523 K. The formation of isobutanol also increases with the ratio of H_2/CO (Fig.3). We have chosen for this work a H_2/CO ratio equal to 3.

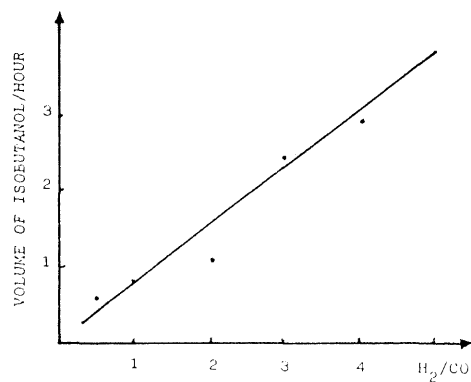


Fig.3. Effect of the H_2/CO ratio

Fig. 4 shows the dependence of catalytic activity of zeolite on the duration of catalyst operation. One may observe a period of time during which the yield of liquid hydrocarbons is constant for a long time, up to 22 days.

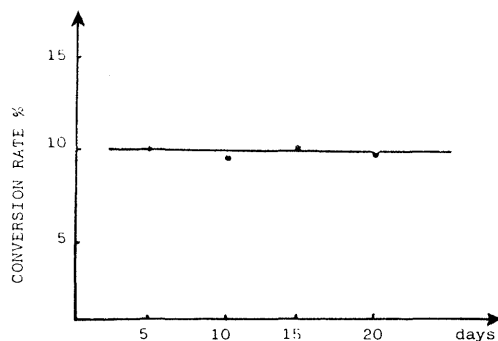


Fig. 4. Variation of CO transformation to isobutanol as a function of the period of catalyst operation. $T = 493\text{ K}$.

CONCLUSION

The Cu-Zn catalyst shows a high activity for the conversion of CO at 523 K under a pressure of 5 MPa. The main product in this reaction is isobutanol, although a small amount of methanol was also formed. This catalyst presents a good selectivity and is active for a long time at 523 K.

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SAŽETAK**Sinteza primarnog alkohola iz H_2 i CO uz modificirane zeolite***A. Bengueddach, Z. Derriche i J.-C. Goudeau*

U sintezi metanola, etanola i butanola primijenjeni su NaX-zeoliti u kojima je Na kation nadomješten bakrom i cinkom. Istražen je utjecaj omjera H_2/CO , temperature i vremena reakcije, uz konstantni tlak od 50 bara.

Eksperimentalno je pokazano, da su uz modificirani katalizator, tlak i temperatura konverzije CO u izobutanol znatno niži (523K, 50 bara) od dosada opisanih, te da iscrpak raste s omjerom H_2/CO i vremenom reakcije.

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