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Catalytic properties of aluminated sepiolite in ethanol conversion

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The aluminated sepiolite, obtained by alkaline treatment with $KAlO_2$, as well as the silver-exchanged aluminated sepiolite were tested in ethanol conversion. The reactions were performed at 280°C and with 50 Torr of ethanol in He. After the alumination through $KAlO_2$, ethanol dehydrogenation and ethanol dehydration resulted from the Lewis acidity. The dispersion of silver led to a bifunctional catalytic system and the overall catalytic activity and the selectivity towards the acetaldehyde production increased. As a result of the Prins reaction, a significant yield in butadiene was observed.

Keywords: ethanol transformation; butadiene; silver-exchanged aluminated sepiolite

1. Introduction

Fibrous mineral sepiolite, a magnesium silicate, exhibits two types of porosity; infinite regular zeolitic channels along the fiber axis with cross section $\sim (10 \times 4)$ Å^2, and a second set of irregularly shaped pores with a diameter around 100 Å [1,2]. The lattice is neutral and the measured cation exchanged capacity (CEC) is about 0.07 meq/g. The thermostability of the lattice is poor. The surface area starts to decrease after outgassing at about 150°C due the folding of the microporous structure [1,3,4]. Therefore, the use of sepiolite as a catalyst or a catalyst support is limited.

It was shown that the thermal stability can be improved by alumination, that is by the partial Si-by-Al substitution in the tetrahedral layer and the Mg-by-Al substitution in the octahedral layer. In addition, the latter leads to the generation of Lewis acidity and the former to an increase of CEC [5–8]. The efficiency of the alumination is higher when produced by an alkaline treatment with $KAlO_2$. The solid calcined at 300°C after ammonium exchange develops a surface area near 300 m^2 and a micropore volume of about 0.06 ml/g. The CEC increases up to 0.55 meq/g.

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Thus, it is possible to introduce silver by cation exchange in the aluminated sepiolite without significantly decreasing the crystallinity, thereby, generating a well-characterized bifunctional catalyst [9]. After activation at 350°C it contains relatively strong Lewis sites. Thus, alumination opens new opportunities for the use of sepiolites as catalysts or catalyst supports. Since papers devoted to the structural aspect of these aluminated sepiolites have been or are going to be published [7–9], these data will not be repeated here.

The aluminated sepiolite, obtained by an alkaline treatment with $KAlO_2$, as well as the silver-exchanged aluminated sepiolite were tested in ethanol conversion. The ethanol conversion on sepiolites was studied earlier [8,10,11,13]. With its cross section of 0.23 nm^2 ethanol is able to enter the structural micropore and probe all the surface area, thereby, showing up the catalytic properties of the modified sepiolite. Alcohol conversion proceeds via dehydration and dehydrogenation, therefore, probing both acid base and redox functions.

2. Experimental

The preparation of the ammonium-exchanged aluminated sepiolite and its characterization were described in detail in ref. [8]. This sample is called A Al(K)SP. Ag-sepiolite was made by stirring A Al(K)SP in 0.1 M $AgNO_3$ overnight and rinsing twice with water. This sample is labeled Ag Al(K)SP. The silver concentration in the catalyst was that corresponding to CEC (about 6.0 wt%). At room temperature, Ag Al(K)SP has the same X-ray diffractogram as A Al(K)SP. After calcination at 400°C new reflections characteristic of metallic silver and Ag_2O are observed. At this temperature the surface area of Ag Al(K)SP is about 200 m^2/g and the micropore volume is 0.036 ml/g. These values are close to that reported for Al(K)SP, not exchanged by ammonium [9].

The reactions were performed at 280°C and with 50 Torr of ethanol in He. The reaction system is a conventional, home-built and greaseless flow system, working at atmospheric pressure. The reaction products were analyzed in situ by GS with a column 23% SP-1700 on 80/100 Chromosorb Paw, 30′ × 1/18″ OD.

3. Results and discussion

The contact time-dependence of the total conversion is shown for A Al(K)SP and Ag Al(K)SP in fig. 1. Numerical values for the specific activity a are obtained from

$$a = (p/s)\,\mathrm{d}x/\mathrm{d}t,$$

where p is the partial pressure, x is the % conversion, and s is the specific area of the catalyst (m^2/g). Thus, the unit for the activity a is Torr/m^2 min and the values

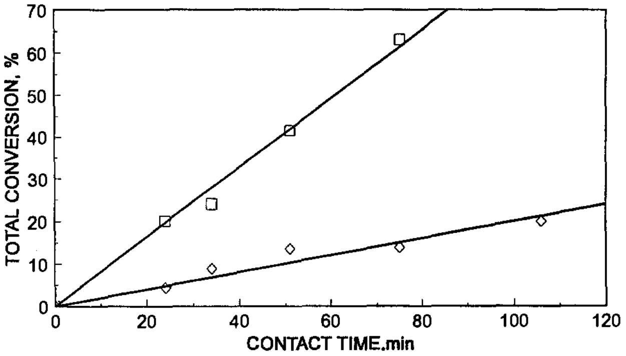

Fig. 1. Total conversion of ethanol on aluminated sepiolite as a function of contact time at 280°C and with 50 Torr of ethanol in He. (□) Ag Al(K)SP; (◇) A Al(K)SP.

of the initial rates are shown in table 1. The total activity is six times larger in Ag Al(K)SP than in A Al(K)SP (fig. 1, table 1).

The kinetic results for the four main products are displayed in fig. 2. The yield in acetaldehyde is about 10 times larger on Ag Al(K)SP than on A Al(K)SP. On the latter catalyst, the yield levels out after 20 min (fig. 2A). Diethyl ether production follows different trends on Ag Al(K)SP or A Al(K)SP. The ether yield is linear with contact time on the ammonium-exchanged catalyst while on Ag Al(K)SP the yield of ether increases rapidly at low contact time and levels out with increasing contact time (fig. 2B). If diethyl ether is an intermediate, the kinetic function which represents the formation of ethylene on Ag Al(K)SP should exhibit an induction period (fig. 2C). This would explain why the initial rate of ethylene production is equal to 0 in this case (table 1). Also, induction periods are observed for the butadiene production on both catalysts, but the induction time is much longer on A Al(K)SP than on Ag Al(K)SP (fig. 2D).

The selectivity towards each of the four reaction products is represented with respect to the total conversion in figs. 3 and 4 for A Al(K)SP and Ag Al(K)SP, respectively. The major difference between the two catalysts is in the production of acetaldehyde which results from ethanol dehydrogenation. As expected the activity of the redox center is much more pronounced on Ag Al(K)SP.

Table 1
Activity of two different samples of aluminated sepiolite

	Initial rate (Torr/min m^2)	
	A Al(K)SP	Ag Al(K)SP
total conversion	0.034	0.205
ethylene production	0.008	0
diethyl ether production	0.020	0.08
acetaldehyde production	0.005	0.11
butadiene production	0	0

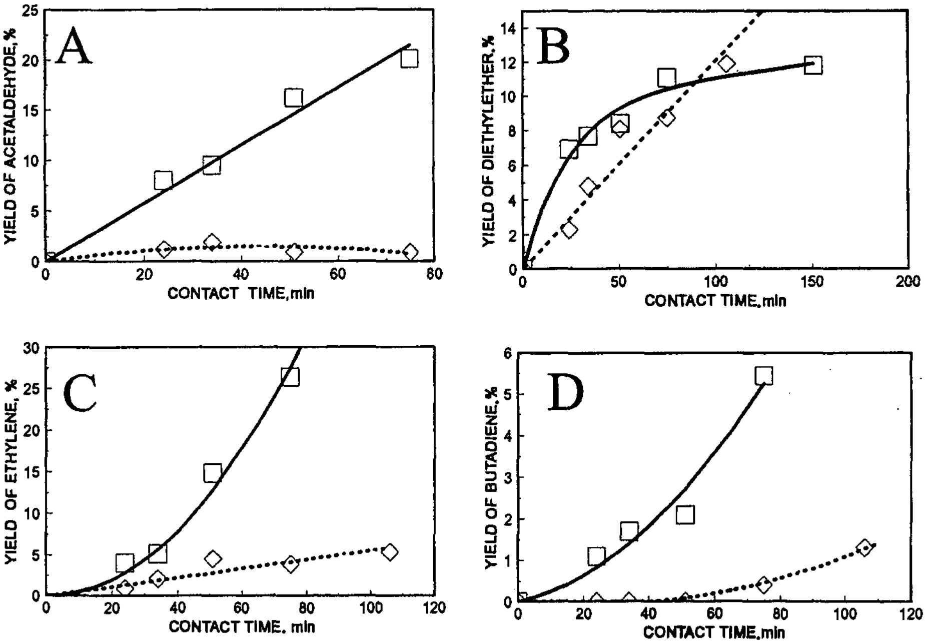

Fig. 2. Yield of products of ethanol conversion on Ag Al(K)SP and A Al(K)SP as a function of contact time at 280°C and with 50 Torr of ethanol in He. (□) Ag Al(K)SP; (◇) A Al(K)SP.

The selectivity towards $(C_2H_5)_2O$ should rank as the catalyst acidity. Thus, A Al(K)SP exhibits a higher selectivity than Ag Al(K)SP.

On A Al(K)SP the ether or ethylene selectivity hardly increases with total conversion. On Ag Al(K)SP selectivities towards ether and C_2H_4 change significantly and follow opposite trends, namely, the selectivity towards ethylene increases and that towards diethyl ether decreases as the total conversion increases. It can be sug-

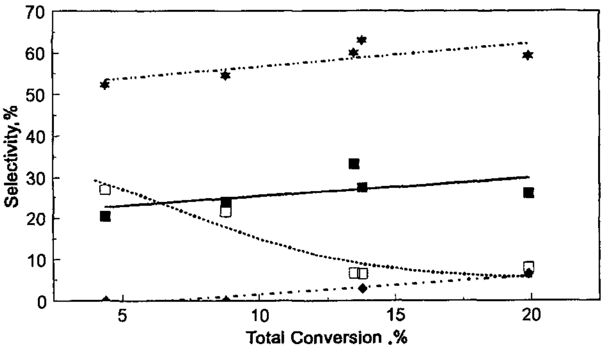

Fig. 3. Selectivity for ethanol conversion products on A Al(K)SP. (★) Diethyl ether; (■) ethylene; (□) acetaldehyde; (◆) butadiene.

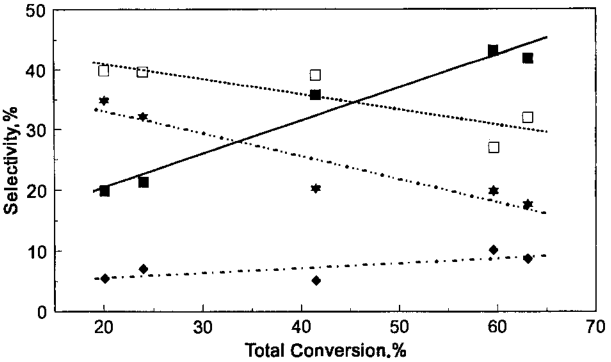

Fig. 4. Selectivity for ethanol conversion products on Ag Al(K)SP. (★) Diethyl ether; (■) ethylene; (□) acetaldehyde; (◆) butadiene.

gested that ethylene can be partly produced as a result of consecutive dehydration of diethyl ether on Ag Al(K)SP.

On A Al(K)SP the yield in butadiene is low. Diethyl ether and ethylene are the most abundant reaction products, indicating that this catalyst is primarily an acid catalyst. Nevertheless, the selectivity towards acetaldehyde is significant. Thus, it must be accepted that dehydrogenation of alcohol may occur on the Lewis sites, which were revealed on the surface of sepiolite by pyridine FTIR [8,9]. The dehydrogenation and dehydration can occur on the same type of sites. On untreated sepiolite, which does not have Lewis acidity, the only products of ethanol conversion are ether and ethylene; only dehydration of ethanol is observed [8].

Early on it was shown that acetaldehyde is the butadiene precursor [8,12]. The results of the present study support this conclusion, since the selectivity towards acetaldehyde and that towards butadiene follow opposite trends with conversion on both catalysts (figs. 3 and 4). On A Al(K)SP the acetaldehyde yield levels out or goes through maximum at increasing contact time (fig. 2A). The formation of butadiene may result from aldol condensation [12,14] schematically represented as

$$2CH_3CHO + H_2 \rightarrow C_4H_6 + 2H_2O$$

This mechanism requires simultaneous dehydration and hydrogen transfer.

Another possibility is the reaction between acetaldehyde and ethylene, which is known as the Prins reaction [8,15,16]. In this reaction, the hydrogen transfer is mediated by ethylene:

$$CH_3CHO + C_2H_4 \rightarrow C_4H_6 + H_2O$$

On Ag Al(K)SP both the butadiene selectivity and the ethylene selectivity increase linearly with total conversion (fig. 4). It is evident that there is linear regression between the butadiene yield and ethylene yield. This observation supports the Prins mechanism.

4. Conclusion

The results of the catalytic test illustrate that the modifications brought to the sepiolite lattice generate a new catalytic behavior. After the alumination through $KAlO_2$, ethanol dehydrogenation and ethanol dehydration result from the Lewis acidity. The dispersion of silver led to a bifunctional catalytic system and the overall catalytic activity and the selectivity towards the acetaldehyde production increase. As a result of the Prins reaction, a significant yield in butadiene is observed.

Acknowledgement

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