

CATALYTIC PROPERTIES OF STABILIZED ZEOLITES Y IN THE REACTIONS OF DIMETHYL ETHER AND OF THE TOLUENE DISPROPORTIONATION

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ABSTRACT

The catalytic properties of zeolites Y, stabilized under self-steaming conditions, were studied in the reactions of the dimethyl ether decomposition to hydrocarbons and of the toluene disproportionation. It has been found that Cu^{2+} cations introduced into the lattice of a stabilized, partially decationized zeolite enhance the zeolite activity in both the reactions. The favourable effect of the Cu^{2+} cations is mainly due to their easy reducibility leading to additional acidity. The Bronsted acidity form substantially increases the catalyst activity, while the Lewis form decreases the activity.

INTRODUCTION

Stabilized forms of decationized zeolites of the Y type exhibit some properties that differ from those of nonstabilized decationized zeolites /1-5/. The main advantages of stabilized samples involve the material stability in the processes of activation and regeneration at high temperatures. An interesting property, which is important for catalysis, is the localization of exchangeable cations in the large cavities in the crystal structure of these zeolites /4,5/. The possibilities in the use of these zeolites as catalysts in various processes have only rarely been described.

In the present paper, the catalytic conversion of dimethyl ether and the catalytic disproportionation of toluene were studied on H- and Cu-forms of stabilized zeolites Y. This study was stimulated by the fact that Cu^{n+} cations exert positive effects on the activity of zeolitic catalysts in many reactions involving carbonium ions /6,7/.

EXPERIMENTAL

A series of decationized zeolites $\text{NH}_4\text{Na-Y}$ with varying degree of the Na^+ exchange for NH_4^+ (15-80%) was studied. The materials were subjected to a stabilizing process in the form of powders, in a rotary quartz furnace. The ammonium zeolite form was decomposed in a closed system with a water vapour pressure of ca. 1.8 kPa (13 torr), by increasing the temperature up to 570°C at a rate of 4 degrees per minute. The H,Na-Y zeolite thus obtained and stabilized under hydrothermal conditions was further converted into the Cu^{2+} form in a CuSO_4 solution. The samples were washed, dried and their crystallinity was checked by argon adsorption, IR spectra and x-ray diffraction.

The state of the Cu cations in the zeolite was followed using the IR spectra of adsorbed CO and by photoelectron spectroscopy. The IR spectra were measured on a Nicolet MX-1 interferometer, using sample pellets 10-15 mg/cm^2 thick, in the transparent arrangement. The main characteristics of the samples are given in Table 1.

Tab. 1: Characteristics of zeolites Y

No	Symbol	Chemical composition of original zeolite mole					Sorption capacity, Ar	
		Na_2O	$\text{NH}_4\ 2\text{O}$	CuO	Al_2O_3	SiO_2	mmol/g Unstabilized in vac. 350°	Stabilized
1	NaY	0,94	-	-	1	5,4	10,4	-
2	$\text{NH}_4\text{Y-15}$	0,78	0,14	-	1	5,9	10,6	9,9
3	$\text{NH}_4\text{Y-37}$	0,61	0,35	-	1	5,8	11,1	10,1
4	$\text{NH}_4\text{Y-53}$	0,42	0,55	-	1	4,6	11,6	9,5
5	$\text{NH}_4\text{Y-62}$	0,31	0,61	-	1	4,3	11,3	10,7
6	$\text{NH}_4\text{Y-77}$	0,18	0,75	-	1	4,3	11,1	10,5
7	$\text{Cu, HY-St}^{1/}$	0,19	- ^{2/}	0,11	1	4,5	-	9,1
8	$\text{Cu, HY-St}^{1/}$	0,16	- ^{3/}	0,17	1	4,6	-	9,1

1/ Sample prepared from the stabilized sample No 5

2/ 0,35 H_2O structural OH groups

3/ 0,49 H_2O dtto

The catalytic tests were carried out in flow-through apparatus at atmospheric pressure. Dimethyl ether was injected in a mixture with nitrogen. The products of its conversion were analyzed chromatographically on a column packed with Carboxpack-C (Supelco) with 0.02%

picric acid /8/. Chromosorb P with 10% polydiethyleneglycol succinate 78^o, helium was used in the analysis of the products of toluene disproportionation. The composition of the isomers of aromatic hydrocarbons was determined on a chromatographic column packed with Benton 245 with a paraffin oil /9/.

The catalysts were activated for 8 hours in a stream of dry nitrogen at 350^oC prior to the reaction of dimethyl ether (DME). Before the disproportionation reaction of toluene, the samples were activated for 5 hours at 500^oC in the air stream. The toluene disproportionation was studied without the use of a carrier gas.

RESULTS AND DISCUSSION

1. Conversion of Dimethyl Ether into Hydrocarbons

The dimethyl ether conversion was studied at 300^oC and $WHSV = 1.2 \text{ h}^{-1}$ on a number of $\text{NH}_4, \text{Na-Y}$ zeolites with various NH_4^+ contents, in nonstabilized form (the ammonium form was decomposed at 350^oC in a stream of dry nitrogen) and in stabilized form (decomposition under hydrothermal conditions, 570^oC). The DME conversion yielded ca. 45-55% of the $\text{C}_1 - \text{C}_5$ aliphatic hydrocarbons; the main reaction products included ethylene and propylene, and saturated hydrocarbons, isobutane, isopentane and n-butane. The time course of the reaction and the composition of the products were analogous to those corresponding to the methanol decomposition on HY zeolites /10/. The catalyst activity is strongly affected by the presence of Bronsted acidic sites. These sites are more acidic in nonstabilized H,Na-Y zeolites than in stabilized zeolites /2,3,11/. In agreement with these facts, a lower DME conversion was found on stabilized zeolites see Fig. 1. For example, a H,Na-Y St catalyst with a 15% decationization is inactive at 300^oC, whereas its nonstabilized form with the same degree of decationization exhibits a 50% conversion of DME into hydrocarbons. The positive effect of Cu^{2+} cations introduced by ion exchange into the stabilized form, H,Na-Y St, with a 70% decationization, is manifested by a substantial increase in the catalyst activity: the conversion reaches 90% and the selectivity remains unchanged /12/.

It should be pointed out that H,Na-Y St zeolites lose their activity much faster than nonstabilized zeolites or stabilized zeolites containing copper cations, apparently because of rapid coking. As all stabilized zeolites contain extra-lattice, nontetrahedrally bonded aluminium that was released from the lattice T-positions during the stabilizing process /13,14/, it can be assumed that this form of aluminium is responsible for the intense formation of polyaromatics and

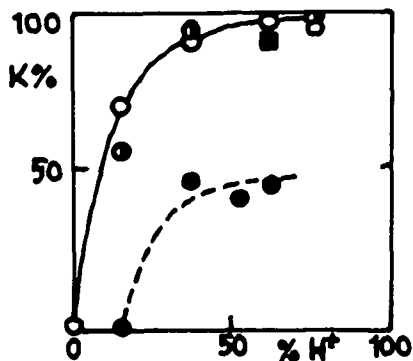


Fig. 1: Dependence of the conversion K of DME 30 min on the decationization degree at 300°C
 ○... nonstabilized Y zeolites activated at 350°C
 ●... nonstabilized Y zeolites dehydroxylated at 500°C
 ●... stabilized Y
 ■... Cu, H-Y St, (sample 7)

coke and that it hastens the loss of activity of these catalysts /15/. The presence of these Al species is probably not the only cause of zeolite deactivation, but it is known that these forms of aluminium, which have the character of a Lewis acid, strongly catalyze the oligomerization of ethylene, propylene and other unsaturated compounds /2, 3/. It cannot be excluded that the favourable effect of copper cations is related not only to the formation of additional Bronsted acidity after the reduction of Cu^{2+} to Cu^+ , but also to the displacement of a certain small fraction of readily exchangeable cationic forms of aluminium Al^{3+} , AlO^+ that also exhibit the highest Lewis acidity /16/. These readily exchangeable Al species may affect the reaction in the large cavities of a faujasite, while a substantial part of nontetrahedrally bonded aluminium remains in the lattice apparently in the sodalite units or in the form of associates with a low Lewis electron-acceptor strength /16.17/.

2. Toluene disproportionation

A decationized, stabilized H,Na-Y St zeolite and a Cu,H-Y St zeolite prepared from the former were studied in this reaction at various temperatures see Table 2 and with various methods of activation Table 3. A certain period, during which the activity increased, was observed with both the catalysts. The time after which a maximum toluene conversion and the maximum degree of disproportionation were attained the pertinent values are given in Tables 2 and 3 depended on the zeolite composition and the reaction temperature. This time was usually 2 to 4 hours and decreased at higher reaction temperatures. This phenomenon is apparently connected with the kinetic properties of the process, adsorption-desorption factors and with the effect of the reaction mixture on the formation of catalytically active sites. Toluene demethylation also occurred to a very small extent under the reaction conditions and was observable at higher reaction temperatures.

Tab. 2: Results of toluene disproportionation on stabilized Y zeolites

$$\text{LHSV} = 1,2 \text{ h}^{-1}$$

T, °C	Conversion of toluene %	Disproportionation degree %	Products w.% from the injected toluene				Composition of the C ₈ H ₁₀ fraction %				Composition of ethyltoluenes %		
			Benzene	xylenes	ethyltoluenes	trime-thylbenzene	o-xy-lene	m-xy-lene	p-xy-lene	ethylbenzene	o-	m-	p-
Zeolite H,Na-Y 62 St													
350	1,15	0,5	0,28	0,17	0,02	0,05	15	34	40	11	-	-	-
400	7,1	5,85	2,6	3,06	0,17	0,07	16	48	35	1	11	62	27
450	24,4	20,6	10,4	10,6	0,22	0,74	21	51	26,8	1,2	14	59	27
Zeolite Cu,H-Y 62 St (sample 8)													
350	15,0	13,2	5,76	6,81	0,16	0,44	19,0	52	29	traces	24	41	35
400	25,0	21,0	11,8	10,6	0,15	0,96	20	52,5	27	0,5	15	60	25
450	20,0	12,4	9,4	6,5	0,1	0,4	19	52	29	-	5	55	40

Tab. 3: Influence et the treatment on the catalytic properties of Cu,H-Y St /8/ zeolite
in the reaction of toluene disproportionation

Temperature of reaction $t = 350^{\circ}\text{C}$

LHSV = $1,2 \text{ h}^{-1}$

Sample No.	Conditions of the sample treatment	Toluene conversion %	Disproportionation degree %	Product in w. % from the injected toluene				Composition et the C_8H_{10} fraction %			Composition of ethyltoluenes			
				benzene	xylene	ethyltoluenes	trimethylbenzenes	o-xylene	m-xylene	p-xylene	ethylbenzene	o-benzenes	m-benzenes	p-benzenes
1	Air, 500°C , 5h	15,0	13,2	6,73	6,81	0,16	0,44	19	52	29	traces	24	41	35
2	Air, 500°C , 5h and CO , 400°C 5h	11,1	10,1	5,01	5,35	0,12	0,22	17	49	34	-	15	50	35
3	Treatment of sample No 2 after experiment													
	Air, 500°C , 5h	10,8	10,2	4,9	5,45	0,14	0,18	17	52	31	-	13	55	35
4	Air, 500°C , 5h and H_2 , 400°C , 5h	25,0	23,5	10,0	10,9	0,83	1,18	18	50,6	27	4,4	14	58	28
5	Treatment of the sample No 4													
	Air, 500°C , 5h	16,6	14,2	7,0	7,25	0,2	0,5	18	53	28,5	0,5	20	56	24

The fact that ethyltoluenes were formed with both catalysts in addition to sylenes, trimethylbenzenes and benzene is worth attention. This indicates the formation of carbene-type intermediates in the system, whose interaction with the CH_3 groups from xylenes produces ethyltoluenes. The possibility of the formation of ethylene by recombination of carbenes followed by alkylation of toluene cannot be excluded, although it seems that this recombination is less probable than the direct interaction /18/. These considerations are in agreement with the fact that the $\text{C}_1 - \text{C}_4$ hydrocarbons were found dissolved in the liquid reaction product.

After treatment of the Cu,H-Y St zeolite with carbon monoxide 400°C , 5 h the zeolite activity decreased by 25%, but the original value was not attained on reoxidation. On the other hand, the catalyst reduction by hydrogen 400°C , 5 h increased the conversion by 70%. The conversion attained the original value on reoxidation. It seems that copper cations have a direct effect on the formation of the zeolite active sites in this reaction.

As can be seen from the above results, the Cu,H-Y St zeolite is more active in the two reactions than the corresponding decationized stabilized zeolite. The increase in the activity is apparently caused by the formation of additional protonic acidity due to the reduction of Cu^{2+} cations to Cu^+ by hydrogen that is often present in trace amounts in the reaction products. In this way OH groups are formed in the zeolite structure, whose protonic acidity is higher than that of the OH groups in the stabilized H,Na-Y St zeolite from which the Cu,H-Y St zeolite was prepared. The relatively small amount of protons formed in the Cu,N-Y St zeolite can considerably increase the catalyst activity, if the steep dependence of the $(\text{CH}_3)_2\text{O}$ conversion on the degree of decationization Fig. 1. is taken into consideration.

The infrared spectra of a reduced zeolite given in Fig. 2 confirm certain changes in the spectrum of OH groups after treatment with hydrogen at 400°C . It can be seen that a higher reduction temperature leads to partial dehydroxylation of the sample, which is apparently also the reason of a mild decrease in the toluene conversion at a temperature of 450°C see Table 2, Cu,H-Y St zeolite. It can also be seen from the spectra of adsorbed carbon monoxide given in Fig. 3 that an intense band appears at 2140 cm^{-1} after the reduction with hydrogen; the band is characteristic of the $\text{Cu}^+ \dots \text{CO}$ complex. On the other hand, a zeolite treated with oxygen exhibits an intense band at 2160 cm^{-1} . Easy reducibility self-reducibility of copper ions is well known and has also been confirmed in our zeolites by photoelectronic spectra.

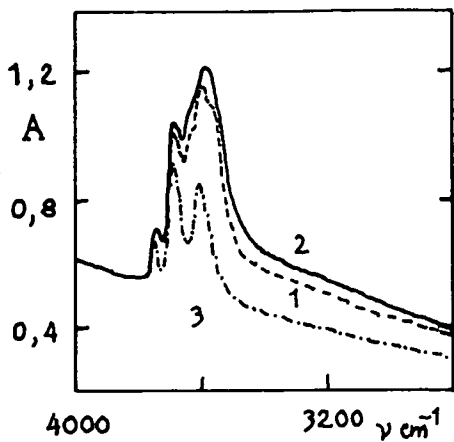


Fig. 2. Infrared spectra of Cu,H-YSt sample 8 in OH stretching region:
 1.. Activated in vacuo 350° , 8h
 2.. Reduced with H_2 , 350° 8h, vac. 1h
 3.. Reduced with H_2 , 600° 8h, vac. 350° , 1h

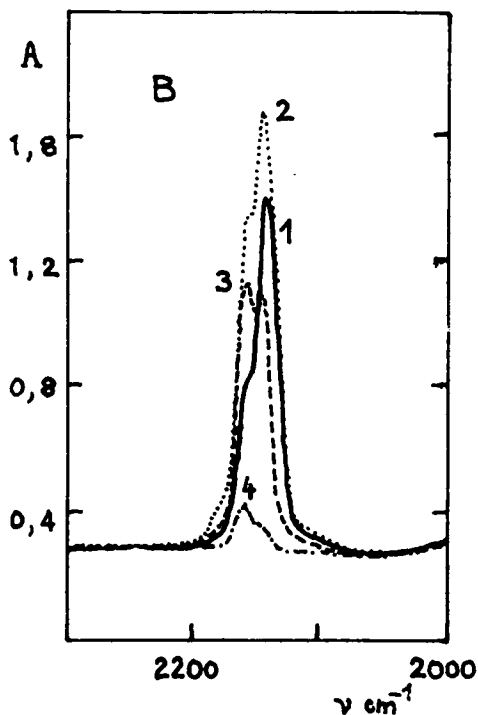
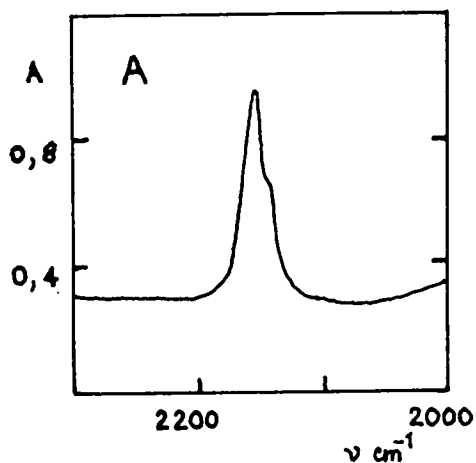


Fig. 3. Infrared spectra of adsorbed carbon monoxide on Cu,H-YSt (sample 8).

- A. Sample treated with oxygen, $p_{O_2} = 2$ Torr, $450^{\circ}C$, 8h in vacuo at 350° , 1h - adsorption of CO, $p_{CO} = 1$ Torr.
- B. Sample treated with hydrogen at $450^{\circ}C$, 4h, $p_{H_2} = 250$ Torr
 CO adsorption: 1.. $p_{CO} = 0,1$ Torr, 2.. $p_{CO} = 1$ Torr
 CO desorption: 3.. $p_{CO} = 4 \cdot 10^{-2}$ Torr, 4.. $p_{CO} = 10^{-4}$ Torr.

It should be pointed out that Cu^{2+} was reduced to Cu^+ very readily in the stabilized forms; at higher temperatures e.g. during the activation in vacuo at 350°C or at higher temperatures the presence of Cu^{2+} could not be detected using shake-up satellite lines /20/. During the reduction with hydrogen, only the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction was observed, but not the reduction to metallic copper. This reduction process was monitored by photoelectron spectroscopy and by the IR spectra of adsorbed carbon monoxide at 25°C ; absorption bands at 2140, 2160 and, at a 0 pressure above 25 Torr (3 kPa), also a band at 2180 cm^{-1} were only found. These bands correspond to valence vibrations of CO in the coordination sphere of copper cations. No absorption band characteristic of CO adsorbed on copper metal Cu^0 /21/ or of Cu carbonyls /22/ and located at lower wavenumbers was found with the studied zeolites.

The positive effect of Cu^{n+} cations need not be caused only by the formation of additional protonic acidity during the reduction, but may also be connected with coordination unsaturation of these cations. These coordination-unsaturated sites can ensure, together with the existence of protons in the lattice, the optimal configuration of the active sites on which active complexes can be formed that take part in the alkylation of the aromatic ring, isomerization and disproportionation /23/.

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