

Acidity of the external surface of modified pentasil catalysts and its resistance to mechanical treatment

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Abstract

The influence of mechanical treatment on acidic and catalytical properties of the external surface ZSM type zeolites by paramagnetic probe method was investigated. The zeolite external surface was modified by covering with silica, orthophosphoric acid treatment and exchange of zeolite acidic protons to lithium ions. It was shown, that due to mechanical treatment the achieved changes in surface properties were destructed and the external surface was renovated.

The most significant property of pentasil zeolites is the small pore size of channels, the diffusion being the limiting stage of catalytical processes. So the contribution of external surface to the total activity of zeolite becomes noticeable and the selectivity of the process decreases.

A number of methods of modifying the external zeolite surface is known (ref. 1-4). Still there is no information on the stability and mechanical resistance of pentasil modifying cover.

MODIFICATION OF ZEOLITE SAMPLES

Series of pentasil zeolites in decationated form manufactured at GrosNII and Angarsknefteorgsintez were used. The external surface of zeolites was modified as follows:

- 1) treatment with orthophosphoric acid (1,25 wt.%),
- 2) ion exchange of protons to Li^+ ions via lithium complex with crown-ether, dicyclo-18-crown-6,
- 3) deposition of silica by adsorption of silicoorganic compounds - polymethylsiloxane (PMS) from heptane solution or tetraethoxysilane (TEOS) from the gas phase with following calcination at 723 K.

DETERMINATION OF ACIDITY AND SURFACE AREA

Determination of acidity. The data on acidic properties (coordinationally unsaturated-CU- Al^{3+} ions) and external surface area of zeolites by means of ESR spectrum analysis of adsorbed nitroxide - 2,2,6,6-tetramethylpiperidine-N-oxyl - were obtained. The ESR spectra were registered on X-band radiospectrometer.

The hfs of nitroxide ESR spectra consists of 3 lines, corresponding to the nonbonded electron with N nucleus ($I=1$) interaction. Information on nitroxide surrounding can be obtained from its ESR spectra. The value of anisotropic hfs constant is in accordance with electron spin density on nitrogen atom. The nitroxide interacts with acid site, the electron spin density increases, as well as A_{H}^{N} . When the nitroxide interacts with a CU cation,

nucleous of which has a magnetic moment, each of the nitrogen hfs splits again, as in the case of dehydroxylated surface of silica alumina (^{27}Al , $I=5/2$).

The concentration of Lewis acid sites can be determined as a maximum of complexbonded radicals (Fig. 1,2). The kinetic diameter of nitroxide ($\sim 11 \text{ \AA}$) markedly exceeds the maximum size of pentasil channels, so nitroxide may be assumed to interact only with external surface of zeolite.

TABLE 1. The influence of modification and mechanical treatment on concentration of $[\text{Cu Al}^{3+}]$ and external surface area of zeolite. ($T = 923 \text{ K}$)

N°	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$N \cdot 10^{-17}$ site/g	S_{external} $\frac{\text{m}^2}{\text{g}}$	$N \cdot 10^{-16}$ $\frac{\text{S}}{\text{m}^2}$	The way of modification	$N \cdot 10^{-17}$ S/g	$S_{\text{ext.}}$ $\frac{\text{m}^2}{\text{g}}$	$N \cdot 10^{-16}$ $\frac{\text{S}}{\text{m}^2}$	Mechanical treatment condition	$N \cdot 10^{-17}$ S/g	$S_{\text{ext.}}$ $\frac{\text{m}^2}{\text{g}}$	$N \cdot 10^{-16}$ $\frac{\text{S}}{\text{m}^2}$
1.					During synthesis	16.0	16.0	0	1	8.5	22.5	0.38
									5 hours	5.5	13.5	0.41
									9 hours	5.5	16.5	0.33
2.	43	2.5	10	0.25	TEOS	0	5.0	0	I	5.5	22.0	0.25
3.	55	20	14	1.4	FMS	0	-	0	I	2.0	12	0.17
4.	55	20	14	1.4	Li^+	7.0	13.5	0.5	I	4.0	16	0.25
5.	90	10	18	0.55	H_3PO_4	4.5	18.0	0.25	I	5.5	16	0.34

I - pounding in Mortar.
II - grinding in a ball mill.



Fig. 1. ESR spectra of TEMPO, adsorbed on HZSM

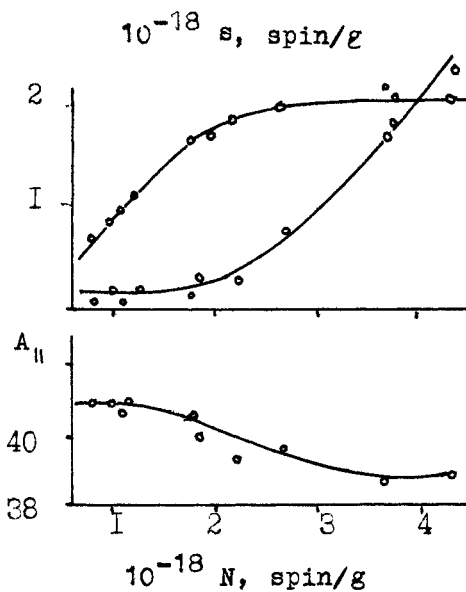


Fig. 2. The ratio between two forms of adsorbed TEMPO

- (a) - complexbonded with Al^{3+}
- noncomplexbonded TEMPO
- (b) $A_{||}^N$ dependence of adsorbed TEMPO concentration

Determination of external surface area. The value of zeolite surface area was determined from $S=N \cdot r^2$, where N-number of adsorbed radicals, r-average distance, with the help of "paramagnetic probe" method (ref. 3) based on measuring the average distances between random distributed nitroxides, by analysis of dipole-dipole broadening of ESR spectra. The samples of zeolites were calcinated in air for 2 hours and then in vacuum at 10^{-3} Pa (2 hours) at 923 K. Nitroxyl radicals were adsorbed from the vapour at room temperature.

The crystallinity of samples was determined by IR-spectroscopy with respect to the 450 cm^{-1} and 550 cm^{-1} bands. The mechanical treatment in ball mill or manually in a mortar during 30 min. was carried out.

The catalytic properties were estimated at sample activity in mesitylene conversion (flow reactor, $T=723$ K, $V_0=4,5$ h^{-1}) and ethylbenzene disproportionation (flow reactor, $T=723$ K, $V_0=2,0$ h^{-1}).

STABILITY OF MODIFYING COVER TO MECHANICAL TREATMENT

HS zeolites (pentasils) is the conglomerate of small crystals the external surface being 15-20 m^2/g . The acidity of its external surface is estimated as concentration of Al^{3+} CU ions, which depends on synthesis conditions and later processing. It's known that the external surface can be enriched with the aluminium ions or vice versa (ref. 8). There are a number of methods decreasing the acidity of external surface: desactivation of acid sites by covering with neutral substances (silica) and by treatment with "chemical reagents" (ref. 1-3). In our work both ways of modification were employed.

The value of surface acidity of SiO_2 modified samples was negligible (Table 1, sample 2,3) as well as mesitylene conversion, characterizing external surface catalytical activity, after modification of zeolite was undetectable (Table 2).

TABLE 2. Catalytic and acid properties of modified zeolite external surface. ($T=450^\circ$, $V_0=4,5$ h^{-1})

Catalyst	S_{external} m^2/g	$[\text{CU Al}^{3+}]$ $N \cdot 10^{-17}$, site/g	Mesitylene conversion %
HZSM	14,0	20	28
Li-ZSM	13,5	7	10
HZSM-PMS (SiO_2 -14%)	14,0	0	0

As for the ethylbenzene disproportionation sample 3 had high p-selectivity (Table 3).

It was found that silica cover is not resistant to mechanical treatment, after which the considerable acidity of the external surface was noticed (Table 1).

The acid site concentration per 1 m^2/g of external surface is equal to the value for initial zeolite, but per 1 g of sample the $[\text{Al}^{3+}]$ concentration is two times higher than for initial one at the account of surface area increase. Modifying cover obtained with the help of polymethylsiloxane is more stable (Table 1, sample 2). It's interesting that grinding of zeolite sample in ball mill gave the same result as pounding in mortar (Table 1). The crystallinity for all samples decreases by 10-15%, but even after 9 hours of processing it was not less than 50%.

TABLE 3. The influence of mechanical treatment on catalytic activity of modified pentasil in ethylbenzene disproportionation. ($T = 723 \text{ K}$, $V_0 = 2,0 \text{ h}^{-1}$)

Time	Conversion	Bensene+ diethylbensenes	Total selectivity	p-selectivity
sample 1 - zeolite, modified during synthesis				
15'	37,47	34,42	91,86	17,48
30'	32,18	30,35	94,31	26,93
45'	29,44	28,12	95,51	31,72
60'	28,46	27,22	95,65	34,87
after 5 hours in ball mill				
15'	43,33	39,58	91,35	10,92
30'	42,65	39,49	92,58	12,79
45'	42,97	39,48	91,88	12,32
60'	42,53	38,92	91,50	12,26
after 9 hours in ball mill				
15'	46,65	42,86	91,89	9,98
30'	45,44	41,82	92,04	11,09
45'	45,11	41,72	92,48	10,97
60'	44,51	41,17	92,50	11,31

While the chemical treatment is employed, the reactant interacts with acid sites of external surface, decreasing the acidity. So the treatment of dehydrated pentasils with phosphoric acid leads to lowering of acidity for two times and for three times in the case of acid proton exchange to Li^+ ion.

The large size of ligand - crown-ether - guarantees the reaction to proceed only with proton donor sites of external surface. Both of these methods decrease the acidity. Catalytical activity for these cases in mesitylene conversion decreases proportionally to acid properties (Table 2).

The mechanical treatment didn't practically affect the acid properties of phosphorated pentasils. As for ion exchanged sample, the acidity of the external surface even decreased. This effect can be explained with renovation of the external surface while pounding and formation of new conglomerates. The possibility of such explanation was confirmed by ESCA data. Thus the concentration of coordination-unsaturated Al^{3+} ions on the external surface exceeds 5 times this value in volume for that sample of zeolite.

The possibility of modifying cover destruction, renovation of the external surface must be taken into account while preparing the zeolite content catalysts.

REFERENCES

1. J.P. Gilson, E.G. Derouane, *J. Catalysis*, **88**, 538-541, (1984).
2. Li Dgon Kva, Ponomareva O.A., Sinitzina O.A. et al, *Kinetika i katalis*, **30**, 1461-1465, (1989).
3. Parenago O.O., Phionov A.V., Latysheva L.E. et al., *Kinetika i katalis*, **32**, 502-508 (1991).
4. Kaeding W., Chu C., Young L.B. et al, *J. Catalysis*, **67**, 159-164, (1981).
5. Lunina E.V., Lebedeva O.E., Motina A.D. et al, *Kinetika i katalis*, **28**, 1002-1006, (1987).
6. Lunina E.V., Lebedeva O.E., Aleksandrova H.L. et al, *Zurnal fizicheskoi khimii*, **60**, 183-190, (1986).
7. Courdier G., Naccashe C., Vedrine J.C. et al, *J. Chem. Soc., Chem. Comm.*, **24**, 1413-1414, (1982).
8. Derouane E.G., Detremmerie S., Gabelica Z., et al, *Appl. Catal.*, **1**, 201-227, (1981).