THE EFFECT OF EXTRA-FRAMEWORK ALUMINUM IN DEALUMINATED ZSM-5 ZEOLITES ON THE TRANSFORMATION OF AROMATIC HYDROCARBONS*

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H-ZSM-5 zeolite was dealuminated by steaming under “mild” and “severe” conditions at 675 and 975 K for 71.5 and 0.5 h, respectively. It resulted in a comparable number of Al atoms released from the zeolite framework, although of their different nature. The “mild” zeolite steaming yielded Al species easily removable from the zeolite by an acid leaching, in contrast to the zeolite steamed at “severe” conditions. The extra-framework Al species contributed to both a substantially higher *para*-selectivity in toluene disproportionation and its alkylation with ethylene and to an increased rate of side reactions leading to the zeolite deactivation by coke formation in toluene alkylation with ethylene.

Dealumination of ZSM-5 zeolites by steaming is a way how to modify their activity and to improve especially their selectivity with respect to particular hydrocarbon synthesis or its further transformation[1,2]. The steaming process releasing evidently the tetracoordinated framework aluminum into the extra-framework sites decreases the number of bridging OH groups. It is evident that the degree of dealumination strongly depends on the steaming conditions. With variation of temperature and time of steaming, a broad range of Si/Al ratio is achieved. The structure of extra-framework Al species strongly depends on the conditions of the steaming and a zeolite type. These Al

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species, consisting of tetra-, penta- and octahedrally coordinated Al cations, range from a single charged Al complexes up to polymeric oxo-Al species[3,4].

It has been shown that simultaneous presence of bridging OH groups and Lewis sites (positively charged Al species) enhances zeolite oligomerization and cracking activity[2,3,5]. However, till now, the effect of extra-framework Al species formed by the ZSM-5 zeolite steaming on its activity and *para*-selectivity in transformations of aromatics has not been investigated. It has been recently reported that the presence of single metal cations (Al, Fe, Mn) located in the cationic sites slightly enhances zeolite *para*-selectivity and, simultaneously, increases the rate of the zeolite deactivation by coking[6]. On the other hand, the presence of Fe cations attached to the “external” surface of silylated ZSM-5 zeolite strongly increases the rate of subsequent isomerization reactions, decreasing thus profoundly the resulting *para*-selectivity[7].

The aim of this investigation was to demonstrate the effect of the extra-framework aluminum species on the acidic and catalytic properties of ZSM-5 zeolites in toluene disproportionation and in its alkylation with ethylene. Moreover, the effect of the presence of extra-framework species on the rate of the deactivation during catalytic run is also discussed. The H-ZSM-5 zeolites dealuminated by steaming and those subjected to acid leaching by nitric acid after dealumination are compared. The feasibility of the extraction of extra-framework Al depends strongly on the temperature of the steaming process. At lower temperatures, more extra-framework Al species are easily removed from the zeolite, in contrast to the zeolites dealuminated at higher temperatures[1].

EXPERIMENTAL

The H-ZSM-5 zeolite dealumination by steaming and its subsequent extraction with an aqueous HNO_3 have been already described in detail elsewhere[1]. The Na-ZSM-5 zeolite (original Si/Al 15.5) was converted into its H-form by fourfold treatment with 0.2 M HNO_3 in a batch procedure. The H-ZSM-5 zeolite was heated in a stream of air and steam (water pressure of 90 kPa) at 675 K for 71.5 h (indicated as “mild” dealumination, D1) and at 975 K for 0.5 h (“severe” dealumination, D2) to obtain zeolites of a comparable degree of dealumination. Each sample was subsequently treated with 2 M HNO_3 at 375 K resulting in a partial extraction of the extra-framework aluminum species formed during the steaming process (D1ex, D2ex). The amount of the extracted aluminum was determined by chemical analysis in the acid solution. The amount of the remaining framework aluminum was calculated from the ammonium ion-exchange capacity of dealuminated zeolites. The zeolites mixed with a binder (35.0 wt.% of Aerosil-200 and 65 wt.% of the zeolite) were used for catalytic testing.

X-Ray diffraction patterns were obtained with a HZG 4 diffractometer employing Ni-filtered CuKα radiation. Zeolite characterization with respect to the bridging OH groups and the ammonia adsorption by IR spectra (Specord M 85, Zeiss Jena) as well as temperature programmed desorption of ammonia (TPDA) are described in detail elsewhere[8,9].

The zeolite void volume was estimated from the sorption capacity for argon measured in a static apparatus at 13.30 kPa of argon at a temperature of 80 K on the samples pretreated at 720 K in vacuum of 10^{-4} kPa for 16 h.

The toluene reactions were performed in vapour phase, in a continuous glass down-flow micro-reactor at atmospheric pressure (toluene concentration 18.5 vol.% in the feed, toluene to ethylene molar ratio 3.8). Toluene disproportionation was carried out at a temperature of 770 K and WHSV 2.7 h^{-1}, and toluene alkylation with ethylene at 620 K and WHSV 10.0 h^{-1}. The reaction products were analyzed by means of an "on-line" high-resolution capillary gas chromatograph HP 5890 Series II (for details see refs[10,11]).

RESULTS AND DISCUSSION

Physico-Chemical Characterization

Although the dealuminated zeolites do not differ significantly with respect to their framework silicon to aluminum (Si/Al_f) molar ratio, and, therefore, to their number of the extra-framework aluminum, the number of extractable extra-framework aluminum atoms differ substantially (Table I). A long-time steaming at a lower temperature clearly favours formation of the extra-framework aluminum species exhibiting higher solubility in acidic solution. X-Ray diffraction patterns of all the investigated zeolites, dealuminated and those after the subsequent extraction, show no significant changes compared to original ZSM-5 (Fig. 1), indicating that no collapse of the zeolite structure has proceeded either during dealumination procedures or during subsequent extractions. A slight decrease in the unit cell parameters of dealuminated zeolites is in agreement with the removal of aluminum from the framework and/or with an extraction of extra-framework aluminum species from the channel system.

The IR band at 3 740 cm^{-1} reflects terminal SiOH groups of the Aerosil binder and the H-ZSM-5 zeolite (Fig. 2). As expected, the dominant band at 3 610 cm^{-1} (bridging

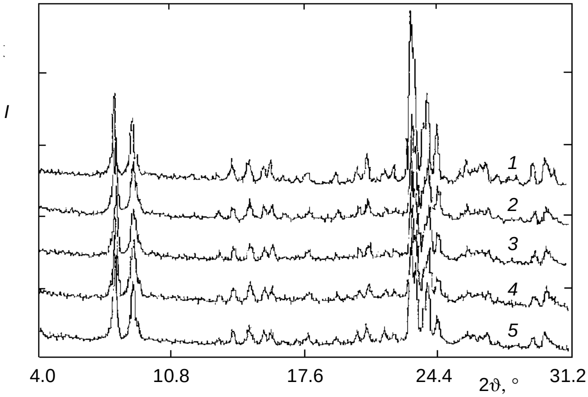

FIG. 1
X-Ray diffraction pattern of parent and modified zeolites: *1* original H-ZSM-5, *2* D2, *3* D2ex, *4* D1, *5* D1ex

SiOHAl groups) of the parent H-ZSM-5 is substantially decreased by dealumination, in accord with the release of Al atoms from the framework. On the other hand, after dealumination, both zeolites exhibit a band at 3 660 cm^{-1} (Fig. 2), characteristic for the OH groups bonded to the extra-framework aluminum cations. Because of its relatively

TABLE I
Characteristics of zeolites

Catalyst	Si/Al_f[a]	Si/Al_e[b]	Degree of extraction %	TPDA[c]	Sorption capacity[e]	1 616 cm^{-1}[d]	1 460 cm^{-1}[d]
D1	108.2	18.1	–	0.23	3.98	0.05	0.28
D1ex	108.2	23.6	23.2	0.25	4.04	0.00	0.31
D2	85.9	18.9	–	0.23	4.05	0.06	0.32
D2ex	118.7	19.9	5.2	0.20	3.95	0.03	0.22

[a] Si/Al_f framework molar ratio; [b] Si/Al_e extra-framework molar ratio; [c] mmol OH/g, corresponding to the high temperature peak of TPDA; [d] normalized intensity of the IR bands: 1 616 cm^{-1} – NH_3 coordinated to Lewis sites, 1 460 cm^{-1} – NH_4^+; [e] sorption capacity for argon (mmol/g).

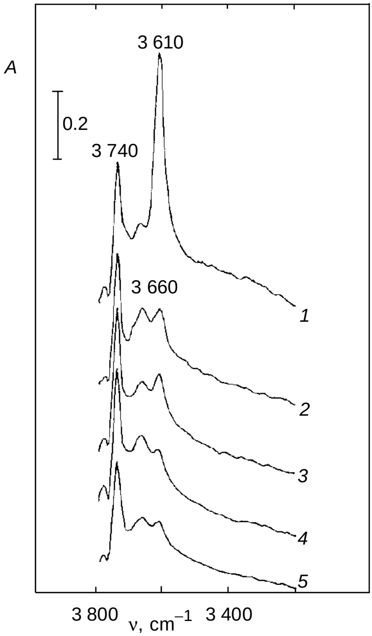

FIG. 2
IR spectra (OH vibration region) for the parent, dealuminated and acid extracted zeolites: *1* original H-ZSM-5, *2* D1, *3* D1ex, *4* D2, *5* D2ex

low intensity, the aluminum species generated by the dealumination process are supposed to be rather highly aggregated, non-hydroxylated species. Moreover, with the H-ZSM-5 zeolite dealuminated under “mild” conditions, its acidic extraction causes removal of a substantial amount of the extra-framework aluminum species, while the degree of the extra-framework aluminum species removal from the zeolite steamed at higher temperatures is much lower (Table I). It should be stressed that no visible collapse of the structure after dealumination and extraction was observed, as indicated by X-ray diffraction.

IR spectra of adsorbed ammonia on zeolites (after ammonia adsorption the zeolites were subjected to evacuation at room temperature for 18 h to remove weakly held ammonia) confirm the above results. A comparison of the normalized absorption intensity at the band maximum (Table I) shows that the acidic extraction of dealuminated zeolites substantially decreases the amount of adsorbed ammonia on the Lewis sites (1 616 cm^{-1}), in accordance with the amount of Al extracted into the acidic solution. The degree of extraction of extra-framework Al species is more pronounced with the “mildly” dealuminated zeolite. A slight increase in the NH_4^+ band (1 460 cm^{-1}) of the D1 zeolite after acidic extraction indicates that cationic extra-framework aluminum species are replaced by H^+ Brønsted acid sites. On the other hand, for the “severely” dealuminated zeolites, the number of Brønsted sites is lower after the acid extraction of the zeolite. It again indicates that different extra-framework aluminum species are formed during the dealumination via “mild” and “severe” conditions. In the case of “mild” dealumination, extra-framework species are charge balanced cations in the ZSM-5 structure, and via acid treatment a part of them is substituted by protons. As for “severely” dealuminated zeolite, the number of Si–OH–Al groups is lower after extraction in acidic media (as demonstrated by both IR of OH groups and TPDA), which can be explained only by a leaching of framework Al atoms from the D2 dealuminated zeolite. However, it should be emphasized that both X-ray diffraction data as well as sorption capacities for argon do not indicate some collapse of the structure during both dealumination and extraction processes (Fig. 1, Table I).

Catalytic Tests

The toluene conversions and product compositions observed in toluene alkylation with ethylene and toluene disproportionation for the dealuminated zeolites are given in Tables II and III. The overall selectivity to ethyltoluenes in toluene alkylation with ethylene exceeds 96 wt.%, while toluene disproportionation to benzene and xylenes is accompanied by a significant dealkylation leading to formation of about 20% of C_1 – C_4 aliphatics. A substantially higher *para*-selectivity in both reactions has been found for both xylenes and ethyltoluenes, compared to thermodynamic equilibrium concentration (39.7 – 43.8 vs 24.3 at 770 K for *p*-xylene[12] and 48.5 – 82.7 vs 33.4 at 620 K for *p*-ethyltoluene[13]). The toluene conversion in individual reactions has been practically of

TABLE II
Toluene alkylation with ethylene (WHSV 10.0 h^{-1}, temperature 620 K, toluene to ethylene molar ratio 3.8, time-on-stream 15 min)

Parameter	Catalyst			
	D1	D1ex	D2	D2ex
Toluene conversion, *c*, %	16.3	19.9	16.8	17.7
Selectivity, vol.% to				
p-ethyltoluene	81.7	47.0	79.8	69.8
m-ethyltoluene	13.9	46.9	15.5	25.3
o-ethyltoluene	–	0.5	–	0.1
benzene	0.6	1.0	0.5	0.6
p-xylene	1.3	1.1	1.4	0.1
m-xylene	0.2	0.4	0.2	0.2
o-xylene	–	0.1	–	<0.1
ethylbenzene	1.1	1.6	1.2	1.2
higher aromatics	1.2	1.4	1.4	1.7
Coking[a], % = $(C_{15} - C_{135})/C_{15}$	3.7	1.6	6.5	2.5

[a] Coking expresses a decrease in toluene conversion from time-on-stream of 15 min to 135 min relative to toluene conversion at 15 min of time-on-stream.

TABLE III
Toluene disproportionation (WHSV 2.7 h^{-1}, temperature 770 K, time-on-stream 15 min)

Parameter	Catalyst			
	D1	D1ex	D2	D2ex
Toluene conversion, *c*, %	5.4	9.2	5.4	6.4
Selectivity, vol.% to				
benzene	40.4	44.5	40.6	43.8
p-xylene	18.0	11.4	16.9	13.6
m-xylene	14.0	19.5	13.6	15.6
o-xylene	4.1	8.1	4.8	6.3
ethyltoluenes	–	0.6	–	0.7
higher aromatics	–	0.3	–	–
$C_1 - C_4$ aliphatics	23.5	15.6	24.1	20.0
Coking[a], % = $(C_{15} - C_{135})/C_{15}$	7.6	12.2	4.6	5.5

[a] See footnote in Table II.

the same value for both dealuminated zeolites D1 and D2 and no substantial differences in the zeolite *para*-selectivity have been observed. This corresponds also to the same number of framework Al atoms and extra-framework Al species for these zeolites. As expected, the lower *para*-selectivity in xylenes compared to ethyltoluenes has been found for toluene disproportionation which proceeds at a higher temperature. Moreover, smaller differences in transport rates among smaller xylene isomers can be expected in contrast to more bulky ethyltoluenes.

It is evident that the presence of the extra-framework aluminum species formed by the steaming of the zeolite affects substantially its catalytic behaviour. After the extraction of a part of the extra-framework species, particularly that exhibiting a positive charge, the toluene conversions in both reactions are higher compared to those of the steamed zeolites (D1ex and D2ex vs D1 and D2, respectively). It means that the simultaneous presence of Brønsted and Lewis sites has no positive effect on the rate of transformations of aromatic hydrocarbons, as the Dex zeolites clearly contained the lower amount of extra-framework Al species. Surprisingly, for both Dex zeolites, the higher toluene conversion (in both reactions) was observed, even though for D2ex compared to D2, the lower number of bridging OH groups was found in TPDA and IR. Therefore, for both dealuminated zeolites treated in acid media, the increase in the conversion can be explained only by an increase in the diffusion rate of reactants and products resulting from the removal of some extra-framework aluminum species from the zeolite channels, and for "mildly" dealuminated zeolite also by a partial replacing of the extra-framework aluminum charged species by the bridging OH groups (cf. Table I), as well. Although a part of extra-framework aluminum species has been removed from the zeolites via treatment in acid media, no substantial differences has been found in the sorption capacities of these two samples, compared to dealuminated ones. The expected changes in the transport rate of reactants and products are reflected

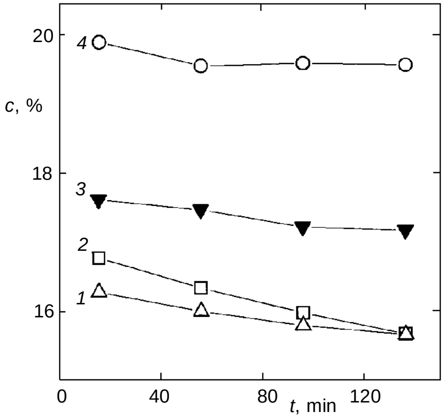

FIG. 3

Time-on-stream (t) dependence of toluene conversion c (%), in toluene alkylation with ethylene (WHSV 10.0 h^{-1}, temperature 620 K, toluene to ethylene molar ratio 3.8), for: *1* D1, *2* D1ex, *3* D2, *4* D2ex also in the higher *para*-selectivity in xylenes and ethyltoluenes for the steamed zeolites which contain in their channels the higher amount of the extra-framework Al species compared to the acid extracted dealuminated zeolites.

The catalytic effect of the extra-framework aluminum species (Lewis sites) is clearly demonstrated for toluene disproportionation in Table III. The enhancement of the rate of toluene dealkylation leading to $C_1 – C_4$ aliphatics for dealuminated zeolites is evident compared to the extracted zeolites.

Deactivation

The presence of the extra-framework Al species, especially those exhibiting electron-acceptor properties, affects also the rate of zeolite deactivation. Even though no significant effect of simultaneous presence of Brønsted and Lewis sites has been observed during the transformation of aromatics, the catalytic effect of the extra-framework Al is clearly demonstrated in the enhancement of dealkylation reaction of toluene during its disproportionation. The conversion of toluene to $C_1 – C_4$ products is substantially decreased, especially when comparing D1 and D1ex (from ca 24 to ca 16%, Table III) after leaching particularly of charged extra-framework Al species. For both couples of dealuminated and extracted zeolites (D1–D1ex and D2–D2ex) a decrease in conversion is lower (for Dex compared to D), although the level of conversion is higher. Two effects likely contribute to this finding: ethylene oligomerization, leading expectably to coke formation, is supported by the simultaneous presence of Brønsted and Lewis sites. Moreover, the presence of the extra-framework species contributes to the retainment of the formed products in the zeolite channels, increasing their contact time and, thus, enhancing their further transformation leading to high molecular weight products. This finding is in agreement with the higher *para*-selectivity and faster deactivation found for H-ZSM-5 zeolites, where a part of protons was substituted for Fe, Al and Mn cations[6]. On the other hand, with toluene disproportionation over steamed zeolites (Table III) the deactivation is lower due to the increase in the rate of dealkylation. The smaller molecules can then easily diffuse out of the pores of these zeolites. This effect probably plays a major role in comparison with the lowering of transport hindrances after partial aluminum extraction.

CONCLUSIONS

It has been found that the presence of the extra-framework aluminum species in the zeolite channels formed via zeolite dealumination by steaming plays an important role in the catalytic transformation of aromatics. All the extra-framework Al species cause a decrease in the zeolite inner volume and, thus, contribute to the increased *para*-selectivity. This is accompanied also by the retainment of the reaction products inside the zeolite channels and, therefore, in a longer reaction contact time, causing further transformation of reaction products That leads to the formation of high-molecular weight products – coke, and zeolite deactivation. Besides the effect of the extra-framework Al on the geometry of the zeolite inner volume, the extra-framework Al species, bearing a positive charge, Lewis sites, contribute to the catalytic activity of the zeolite. They enhance ethylene oligomerization in toluene alkylation with ethylene, leading to high-molecular weight products and to zeolite deactivation by coking. Therefore, the positive effect of the presence of the extra-framework Al species on the enhancement of *para*-selectivity is, on the other side, compensated by the faster zeolite coking and by tendency to dealkylation. Some contribution of Lewis sites to the transformation rate of aromatics was not evidenced.

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