STRUCTURE AND SHAPE-SELECTIVE PROPERTIES OF MFI TYPE FERRISILICATES. A COMPARISON WITH ALUMINOSILICATE ANALOGUES*

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A comparison of H-forms of Fe- and Al-substituted silicates of MFI structure and of a comparable crystal size is given from the point of view of the acidity of SiOHMe groups, activity as well as *para*-selectivity in toluene disproportionation and toluene alkylation with ethylene. It has been found that SiOHFe groups exhibit weaker acidity than SiOHAl groups which is reflected in ammonia desorption at lower temperatures and lower toluene conversion for ferrisilicates. The ferrisilicates exhibit lower *para*-selectivity compared to aluminosilicates; moreover, higher coking is observed. While the aluminosilicates contain mostly aluminum in the framework sites forming SiOHAl groups, the ferrisilicates contain, besides Fe linked in SiOHFe groups, also tricoordinated Fe^{3+} cations or even extraframework Fe species. The latter two species can be responsible for a considerably higher coking of ferrisilicates compared to aluminosilicates. Simultaneously, such Fe species can contribute to observed lower *para*-selectivity of ferrisilicates in comparison with aluminosilicates, when they are located on the outer surface of zeolite crystals.

Iron substituted zeolites with MFI structure have been extensively studied during past decade. The Fe atoms in the zeolite silicate framework were supposed to tailor the acidity of the bridging SiOHFe groups in such a way that selective catalysts for some milder hydrocarbon transformations were obtained. These catalysts were applied even in industrial scale processes[1,2]. In the meantime detailed structural studies have revealed that the Fe-silicate is a more complicated material. It was demonstrated[2] by ESR[3-5], IR[3,6,7], XPS[6], X-ray diffraction[8,9], magnetic susceptibility, Moessbauer spectroscopy[10], adsorption desorption measurements[6,11,12], temperature programmed desorption of ammonia[6,9,10] and reduction by hydrogen[3,8] that besides the framework SiOHFe groups the tricoordinated Fe complexes located in the framework as well as extraframework Fe-oxide species of various composition

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are present in this material. It follows that the framework of Fe-silicates is less stable that of Al analogue which is understandable because of a larger diameter of the Fe cation compared to Al cation and the possible redox behaviour of the skeletal Fe atom. The catalytic function of the Fe-silicate material is affected by the coordination and location of Fe in its structure. It has been found that extraframework Fe-oxide species are active in dehydrogenation of *p*-ethyltoluene and *o*-ethyltoluene depending on their location in the zeolite channels and/or only on the crystal surface, respectively[13]. In acid-base catalyzed reactions, the reaction performance can be controlled not only by the acidity of SiOHFe groups but also by the tricoordinated Fe cations located in the framework as well as by extraframework oxide species especially in reactions which selectivity is controlled by the free diameter of the zeolite channels[14–18].

While the selectivity of Fe silicates with respect to e.g. methanol to olefins conversion and xylene isomerization (suppressed formation of aromatics and disproportionation of xylenes, respectively) is well documented and ascribed to the low acidity of SiOHFe groups[1,2], the function of ferrisilicates in *para*-shape selective reactions is far from being understood[19].

In the present paper toluene disproportionation and toluene alkylation with ethylene catalyzed by Fe silicates are investigated and compared to these reactions occurring on Al analogues. The iron-exchanged ZSM-5 zeolites with the Fe^{3+} located at the cationic sites as well as silylated zeolite with Fe ion supported on the external surface are used for explanation of the function of Fe silicates in *para*-selective transformations of aromatic hydrocarbons.

EXPERIMENTAL

Synthesis of ZSM-5 zeolites (aluminosilicates) with different Si/Al ratios, performed according to patent literature[20] was followed by the zeolite heat treatment in an oxygen stream at 820 K. The H forms of ZSM-5 zeolites were prepared by treating with 0·5M HNO_3. The aluminum free ferrisilicates with MFI structure were synthesized by mixing an acid solution of iron sulphate with sodium silicate solution at room temperature and aqueous solution of tetrapropylammonium bromide; the rest of the diluted sodium silicate solution was added to the resulting gel. The stirred mixture was placed in a teflon-coated stainless steel autoclave and kept under the autogenous pressure at 443 K for 48 h. The template was removed by calcination at 770 K for 7 h in air followed by three-fold exchange using NH_4NO_3 solution at 353 K for 2 h. The details of the synthesis of ferrisilicates are summarized elsewhere[19]. The resulting composition and characteristics of molecular sieves are given in Table I. For comparison, the FeH-ZSM-5 zeolite containing Fe^{3+} at cationic sites in the zeolite channel system, the SiH-ZSM-5 zeolite prepared by silylation of H-ZSM-5(45) and FeSiH-ZSM-5 containing Fe^{3+} mainly on the external surface of silylated H-ZSM-5 (prepared by Fe^{3+} impregnation of surface silylated zeolite SiH-ZSM-5) were used; for details see ref.[15].

The crystallinity of Fe- and Al-substituted silicates of MFI structure was checked by scanning electron microscope (SEM, Tesla B 300), IR spectra (Specord M 85) in the region of skeletal vibrations and by X-ray diffraction (WAG 4 diffractometer using CuK_α, Ni filter).

ESR spectra (ERS 220, ZWG Berlin) were monitored in the X-band region at 100 kHz frequency to establish the coordination of Fe^{3+} ion in ferrisilicates. The g values were referred to Mn^{2+} standard. The number of SiOHAl or SiOHFe groups in molecular sieves was estimated from the high temperature peak of the temperature programmed desorption curve of ammonia (TPDA) performed in a helium stream at the temperature increase of 20 K/min. Prior to TPDA the molecular sieves were dehydrated in an air stream at 770 K for 1 h and than equilibrated in a nitrogen with ammonia stream at 373 K for 0·5 h (see ref.[21]). From these data, the number of Al and Fe atoms forming framework bridging SiOHMe groups was calculated and compared with those obtained from the overall chemical analysis.

The acid base catalytic activity and *para*-selectivity of zeolites were tested in toluene disproportionation and toluene alkylation with ethylene. The reactions were performed in a glass down-flow microreactor at atmospheric pressure with an on-line gas chromatographic analysis (GC-FID-MSD Hewlett Packard 5890 II) using capillary column Supelcowax 10. The reaction run was carried out for time-on-stream (TOS) 200 min enabling to follow the catalyst deactivation. For comparison of the activity and *para*-selectivity of different molecular sieves the initial conversion and *para*-selectivity were used (TOS = 0). The disproportionation of toluene (18·5 vol. % of toluene in nitrogen) was carried out at 770 K and WHSV 2·7 h^{-1}. The alkylation of toluene with ethylene was performed in 18·5 vol. % of toluene and 4·9 vol. % cf ethylene in nitrogen at 620 K and WHSV 10 h^{-1}. Under these experimental conditions the selectivity to xylenes and ethyltoluenes exceeded 90 wt. % for aluminosilicates and 96 wt. % for ferrisilicates. In the following section only toluene conversion and *para*-selectivity expressed as a concentration of *p*-xylene in xylenes and *p*-ethyltoluene in ethyltoluenes are presented. In the case of toluene alkylation with ethylene, the toluene conversion was normalized to 100% of the theoretical conversion corresponding to a toluene to ethylene molar ratio 3·8.

RESULTS AND DISCUSSION

The synthesis of ferrisilicates in base media yielded samples of polycrystalline character (see Figs 1*a* – *c*). With decreasing content of Fe the crystals were better

TABLE I

Characteristics of molecular sieves (A analytical value, F framework value (in SiOHMe arrangement))

Molecular sieve	SiO_2/Me_2O_3 A	Me^a A	SiO_2/Me_2O_3 F	Me^a F	Me^b F
HFeSil(55)	55	3·37	75	2·48	74
HFeSil(65)	65	2·86	67	2·77	97
HFeSil(70)	70	2·67	85	2·20	82
HFeSil(134)	134	1·42	136	1·39	98
H-ZSM-5(45)	45	4·08	46	4·02	99
H-ZSM-5(90)	90	2·09	99	1·90	91
H-ZSM-5(1 200)	1 200	0·16	1 112	0·17	94

[a] Number of metal (Fe or Al) atoms per unit cell; [b] percentage of framework iron or aluminum.

developed. Simultaneously, the X-ray diffraction pattern (Fig. 2; for illustration HFeSil(55) is given) and IR spectra of skeletal vibrations indicated a well developed

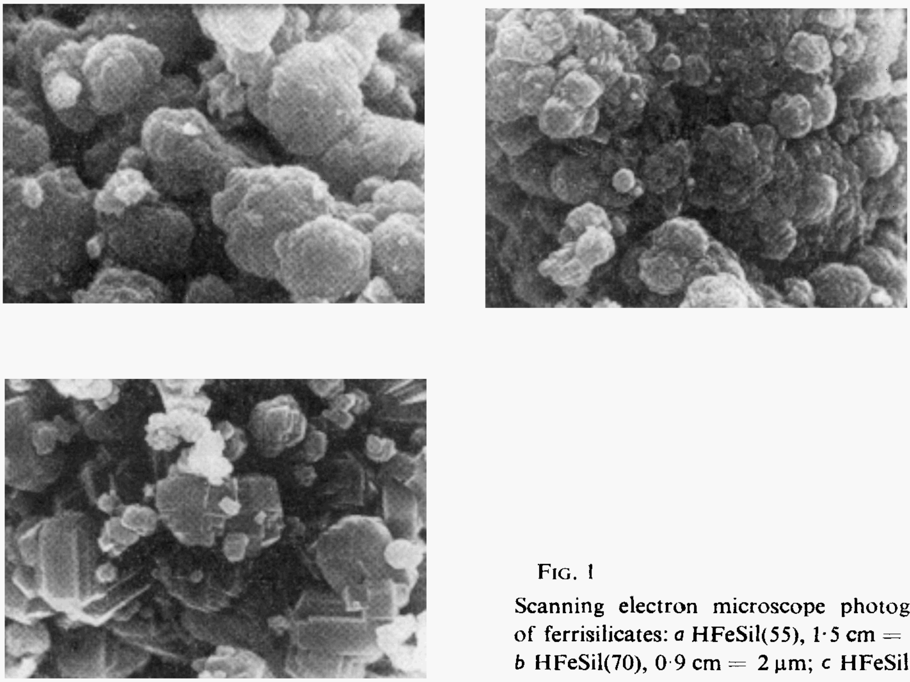

FIG. 1

Scanning electron microscope photographs of ferrisilicates: *a* HFeSil(55), 1·5 cm = 2 μm; *b* HFeSil(70), 0·9 cm = 2 μm; *c* HFeSil(134), 0·9 cm = 2 μm

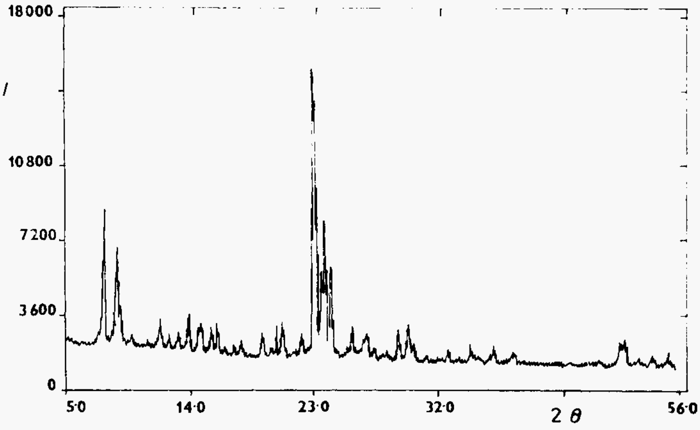

FIG. 2

X-Ray diffraction pattern of HFeSil(55)

MFI structure; moreover, a slight increase in the unit cell volume was observed with increasing number of Fe atoms in the framework (see ref.[19]). The number of Fe framework atoms forming SiOHFe groups (given by TPDA) was in all cases lower than that corresponding to the content of Fe given from the chemical analysis. This indicates that not all Fe atoms in the framework are bonded in tetrahedrally coordinated complexes forming SiOHFe groups; some of them can be located at the extraframework positions. Evidence on the coordination of Fe^{3+} in ferrisilicates were obtained on the basis of ESR spectra. The main signals were observed at g 4·27, ΔH 50 G; g 2·3, ΔH 1 300 G; and g 2·00, ΔH 500 G. Both the signals at g 4·27 and g 2·00 were not possible to remove by an ion-exchange with NH$_4$NO$_3$ solution or by reduction with hydrogen up to 670 K. This indicates that these signals correspond to Fe^{3+} strongly bonded in or to the zeolite framework. According to Vedrine et al.[3] these signals reflect tetrahedrally and tricoordinated iron in the ferrisilicates. It follows that besides SiOHFe groups (exhibiting Broensted acidity) in which Fe^{3+} can be hardly reduced some other non-reducible Fe species are present in ferrisilicates.

As for the acidity of SiOHFe groups the TPDA of ferrisilicates exhibits the high temperature peak maxima at a considerably lower temperature compared to SiOHAl groups in aluminosilicates (Fig. 3). Even though that the temperature of the peak maximum can be used as an indicator of zeolite acidity only with caution[21] a substantially lower temperature determined for Fe-silicates indicates a lower acidity of SiOHFe groups compared to SiOHAl, which is in agreement with literature

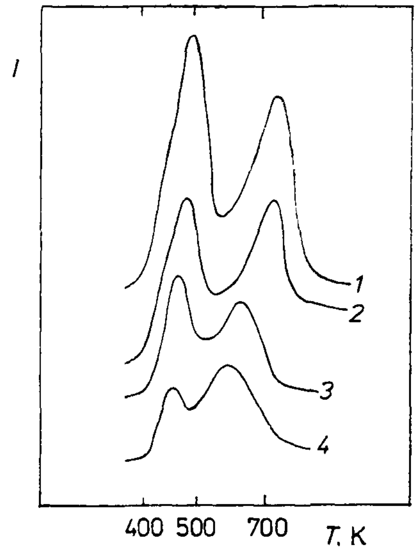

FIG. 3

Temperature programmed desorption curves of ammonia: *1* H-ZSM-5(45), *2* H-ZSM-5-(90), *3* HFeSil(55), *4* HFeSil(70) data[2,5,7]. Similarly, the synthesized Al analogues (ZSM-5 zeolites) exhibit good crystallinity, checked by X-ray diffraction and infrared skeletal vibrations, with a crystal size close to those of ferrisilicates (0·5 – 3·0 μm). The number of framework Al atoms corresponds closely to the overall number of Al given by chemical analysis (see Table I).

The activity and *para*-shape selectivity of Al and Fe-substituted silicates of MFI structure were compared in toluene disproportionation and toluene alkylation with ethylene. It has been found that aluminosilicates exhibit higher conversion of toluene in both reactions (related to the number of strong acid bridging OH groups) than ferrisilicates (Figs 4 – 7). This is in agreement with the lower acidity strength of SiOHFe in comparison with SiOHAl groups (cf. ref.[2]). However, the behaviour of ferrisilicates during time-on-stream in both reactions was different from that of aluminosilicates. While deactivation of the H-form of aluminosilicates was very low (Fig. 8 and cf. refs[14,15]) the ferrisilicates exhibited faster deactivation by coke deposition under the same reaction conditions. The apparent increase in *p*-xylene and *p*-ethyltoluene selectivity in time-on-stream was caused by a decrease in toluene conversion (Figs 9 – 10). It should be noted that with ferrisilicates the upper part of the catalyst bed was completely black and the lower part was white nearly as the original zeolite, in contrast to aluminosilicates, where smaller amount of coke was homogeneously distributed along the catalyst bed.

This clearly indicates that besides SiOHFe groups additional centres of a very high activity should be present in the ferrisilicates which strongly catalyze oligomerization and hydrogen transfer reactions leading to high molecular weight hydrocarbons. Recently, we have found[14,15] that electron-acceptor sites represented by Fe^{3+} or Al^{3+} cations located at cationic sites in the channels of the H-ZSM-5 zeolite contribute to a faster zeolite coking. Such electron-acceptor sites can be represented in ferrisilicates by tricoordinated Fe^{3+} in the framework and/or by some extraframework Fe species.

The values of *para*-selectivity of both the aluminosilicates and ferrisilicates were affected by the toluene conversion values, i.e. by the number and strength of the bridging OH groups. With increasing conversion of toluene the *p*-xylene and *p*-ethyltoluene selectivity approached the equilibrium values (Figs 5, 7). Therefore, for the correct comparison of *para*-selectivity of molecular sieves the relationship of *para*-selectivity on conversion was taken into consideration (Figs 5, 7). This clearly evidences that the *para*-selectivity of ferrisilicates is lower in both reactions than that of Al analogues. Similar results were found also for *m*-xylene isomerization[19]. On the other hand, Fe^{3+} cations located in the H-ZSM-5 channel intersections at cationic sites increased the H-ZSM-5 zeolite *para*-selectivity due to an increase of *para*-isomer formation in the primary alkylation step and/or an increase of differences in diffusivities of individual product isomers (Fig. 7; see also ref.[15]). However, when extraframework cations were located predominantly on the external surface of the zeolite crystals (Fe cations supported on silylated ZSM-5 zeolite, FeSiH-ZSM-5) then they contribute to a substantial decrease in the zeolite *para*-selectivity compared to

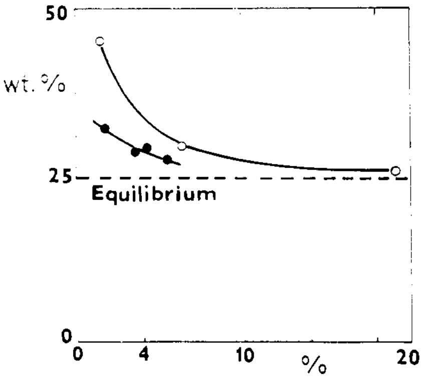

FIG. 4

Dependence of toluene conversion (%) in toluene disproportionation on the number of strong acid OH groups (mmol/g) for aluminosilicates (○) and ferrisilicates (●)

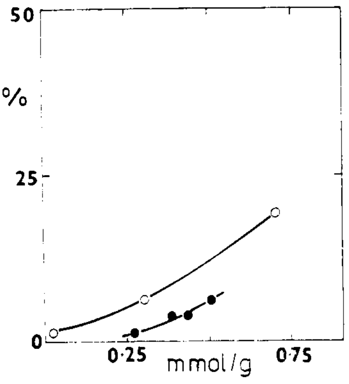

FIG. 5

Dependence of *p*-xylene selectivity on toluene conversion in toluene disproportionation for aluminosilicates (○) and ferrisilicates (●)

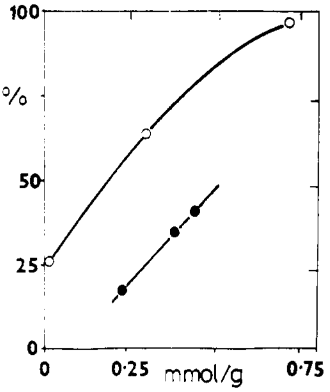

FIG. 6

Dependence of toluene conversion in toluene alkylation with ethylene on the number of strong acid OH groups for aluminosilicates (○) and ferrisilicates (●)

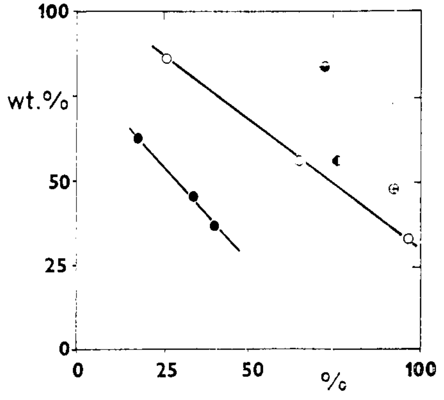

FIG. 7

Dependence of *p*-ethyltoluene selectivity on toluene conversion in toluene alkylation with ethylene for aluminosilicates (○) and ferrisilicates (●), for comparison ⊕ FeH-ZSM-5, ◒ SiH-ZSM-5, ◐ FeSiH-ZSM-5

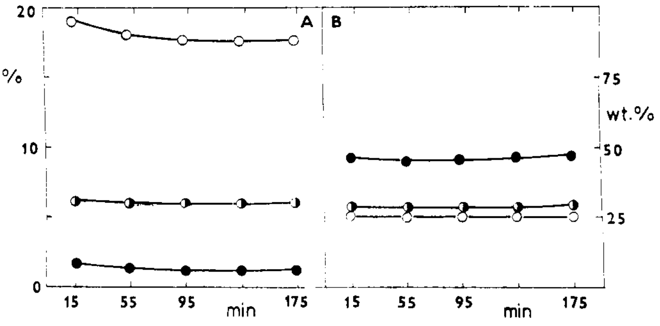

Fig. 8

Time-on-stream dependence of toluene conversion (A) and p-xylene selectivity (B) in toluene disproportionation for aluminosilicates (○ H-ZSM-5(45), ◑ HZSM-5(90), ● HZSM-5(1 200))

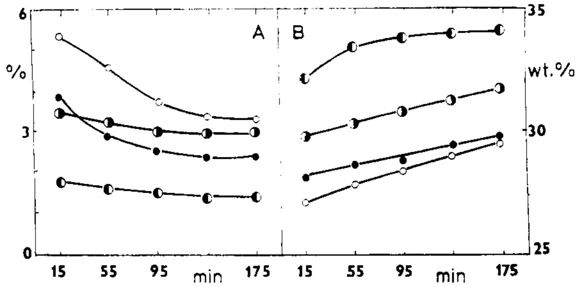

Fig. 9

Time-on-stream dependence of toluene conversion (A) and p-xylene selectivity (B) in toluene disproportionation for ferrisilicates (○ HFeSil(55), ● HFeSil(65), ◑ HFeSil(70), ◐ HFeSil(134)

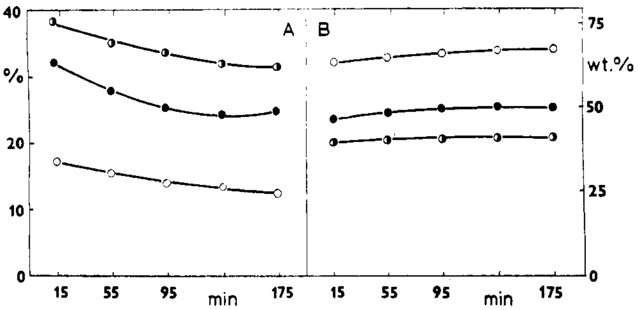

Fig. 10

Time-on-stream dependence of toluene conversion (A) and p-ethyltoluene selectivity (B) in toluene alkylation with ethylene for ferrisilicates (◑ HFeSil(55), ● HFeSil(70), ○ HFeSil(134)) the silylated SiH-ZSM-5 zeolite, likely owing to the enhancement of the isomerization of the *para*-isomer (leaving the zeolite channels) to the *meta*-isomer (see Fig. 7).

Generally, the lower *para*-selectivity of the ferrisilicates compared to aluminosilicates (of a comparable crystal size), can be caused by the differences in the channel diameter and/or in the ratio of the rate of disproportionation and alkylation to isomerization reaction. We believe that one factor which causes the differences in the *para*-shape selectivity as well as in the toluene conversion to desired products (and to high molecular undesired products) between ferrisilicates and aluminosilicates is the presence of tricoordinated iron in the zeolite framework and/or of extraframework Fe cations. The latter species can be located on the outer surface of crystals and thus can contribute to the lower zeolite *para*-selectivity by isomerization of *para*-isomers. However, further studies are in progress to clear up a contribution of a possible different diameter of the ferrisilicate channel system compared to Al analogues which can be given by the larger ion radius of Fe^{3+} cation compared to Al^{3+} cation.

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