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Acidity and Catalytic Properties of Realuminated Zeolite Y

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We have compared the acidity and the catalytic properties of (i) zeolite H-Y, (ii) H-Y dealuminated by hydrothermal treatment (H-US-Y), and (iii) H-US-Y realuminated by the KOH treatment (H-Real-US-Y). Quantitative IR measurements of pyridine sorption show that the concentration of "3460 cm^{-1} hydroxyl groups", the Brønsted acid sites active in many catalytic reactions, is slightly lower in sample H-Real-US-Y than in H-Y. This demonstrates that most of the 3460 cm^{-1} hydroxyl groups, present in the parent material and subsequently destroyed by dealumination, are restored by realumination and the K^+/H^+ exchange. The turnover frequency of the realuminated zeolite in *m*-xylene reactions is higher than in the parent sample, as a result of the higher strength of the acid sites, caused by the higher population of the most strongly acidic $Si_3\mathbf{Si{-}OH{-}Al}Si_3$ groupings. Dealumination and realumination also alter the selectivity in the transformation of *m*-xylene. Disproportionation of xylenes to toluene and trimethylbenzenes, which involves bulky transition step complexes, is hindered in the dealuminated zeolite, where the channels are partly blocked by the extra-framework Al species, but is restored in the realuminated material, in which the extra-framework species are re-inserted into the framework.

Introduction

The Brønsted acidity of zeolites arises from the presence in their hydrogen forms (usually prepared by the calcination of the ammonium forms) of Si−OH−Al groups ("bridging hydroxyl groups"). Much attention has therefore been devoted to the determination of their number and structure. It is clear that the framework aluminum content must affect the population and the strength of these acid sites, responsible for the catalytic activity in many important reactions. The Si/Al ratio can be controlled either during crystallization or via various postsynthesis treatments. Zeolites X and Y (synthetic equivalents of the rare mineral faujasite) can be synthesized with a very limited range of Si/Al ratios (ca. 1.0 to ca. 3.4).[1] The use of crown ethers in the course of synthesis increases the upper limit to ca. 4.9.[2] A number of methods aimed at increasing the Si/Al ratio of zeolite Y have been developed.[3,4] However, the most common procedure is hydrothermal treatment at elevated temperatures. Calcination of the ammonium form of zeolite Y, either under deep bed conditions (self-steaming) or under controlled atmosphere (steam, ammonia, etc.) yields a more siliceous framework. Solid-state NMR monitors the chemical status of aluminum expelled into the extra-framework positions[5] during such treatment (known as "ultrastabilization") and shows that the resulting framework vacancies are reoccupied by silicon. The presence of steam facilities the process. Materials prepared in this way have valuable catalytic properties, and the majority of fluid catalytic cracking catalysts (FCC) are manufactured by steam treatment of zeolite Y.[6]

The dealumination/realumination process can be regarded as the isomorphous substitution of the type $[Si^{4+}, Al^{3+}]_F \leftrightarrow [Si^{4+}]_F + [Al^{3+}]_{EF}$, where the subscripts F and EF denote framework and extra-framework atoms, respectively. The forward reaction (i.e., dealumination) has been studied extensively.[3,4] By contrast, the reverse process, whereby the extra-framework aluminum is re-inserted into the tetrahedral framework, has been described only relatively recently in a handful papers.[7−15] It has been shown that treatment of dealuminated zeolite Y with dilute aqueous solutions of bases (preferably KOH), yields samples with an enhanced content of framework aluminum. ^{29}Si and ^{27}Al magic-angle spinning (MAS) NMR, IR, and X-ray and neutron diffraction show that, depending on the conditions, most of the extra-framework aluminum can be re-inserted.[7,8,13,15]

Infrared spectra of hydrogen forms of as-prepared and dealuminated zeolite Y (Si/Al > 2.00) contain two distinct bands: from $Si{-}O_1H{-}Al$ hydroxyls (3631−3647 cm^{-1}) and $Si{-}O_3H{-}Al$ hydroxyls (ca. 3550 cm^{-1}), where the subscripts refer to the various crystallographically inequivalent kinds of oxygen atoms in the faujasite framework. Although the precise IR frequency of the former band depends somewhat on the Si/Al ratio, we shall refer to it as the "3640 cm^{-1} band". Our recent IR study revealed[16] that the same two bands appear in the spectra of realuminated zeolite Y. This indicates that the bridging hydroxyl groups destroyed by the hydrothermal treatment are restored upon realumination with KOH followed by the $K^+ \rightarrow H^+$ ion exchange. Most interestingly, benzene sorption shows that the acid *strength* of the 3640 cm^{-1} OH groups in realuminated H-Y is higher than before dealumination. We have explained this in terms of the presence of different kinds of bridging hydroxyl groups with respect to the number of aluminum atoms connected, via oxygens, to the silicon involved in an acidic hydroxyl. There are thus $Si_3\mathbf{Si{-}OH{-}Al}Si_3$, $AlSi_2\mathbf{Si{-}OH{-}Al}Si_3$, and $Al_2Si\mathbf{Si{-}OH{-}Al}Si_3$ hydroxyls. In the "Si(*n*Al) notation" used in the NMR spectroscopy of zeolites ($n \leq 4$ is the number of aluminum connected to a silicon) these correspond to Si(1Al), Si(2Al), and Si(3Al) environments, respectively. ^{29}Si MAS NMR reveals that the contribution of Si(1Al) species increases as a result of the dealumination−realumination cycle, which means that the population of the

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most acidic Si_3**Si**−**OH**−**Al**Si_3 protons and the average acid strength of the 3640 cm^{-1} hydroxyl groups, have increased.

The aim of this work is to examine the acidity and catalytic activity of bridging hydroxyl groups. It is particularly important to know whether all the 3640 cm^{-1} hydroxyl groups in zeolite H-Y prior to dealumination could be restored upon realumination and to clarify the effect of the dealumination−realumination cycle on the catalytic properties. We have therefore determined the concentration of 3640 cm^{-1} hydroxyl groups in zeolite Y by quantitative IR studies of pyridine sorption.

Catalytic activity of the samples was tested in isomerization and disproportionation of *m*-xylene, an industrially important process used as a test reaction for shape-selective catalysts.[20−24] Two important reactions involving xylene isomers are catalyzed by acid sites: isomerization (*o*-xylene ↔ *m*-xylene ↔ *p*-xylene) and disproportionation (2 xylene ↔ toluene + trimethylbenzenes). The latter “transalkylation reaction” frequently occurs on acid catalysts. Isomerization may proceed according to a unimolecular (by consecutive 1,2-methyl shifts) or a bimolecular mechanism.[25,26] Bimolecular disproportionation of alkylaromatic molecules is mostly governed by the channel structure[27] and proceeds much more easily in large-pore zeolites such as zeolites Y, L, and beta, where the bulky transition-state complexes can be accommodated, than in zeolites with narrow pores, such as ZSM-5, ZSM-35, or NU-10. The selectivity for xylene transformation reflects therefore the intrinsic properties of the catalyst. In addition to isomerization and disproportionation, a third pathway involves dealkylation of alkylaromatics, producing toluene, benzene, and light paraffins.

We have followed the effect of the dealumination and realumination on the catalytic behavior of zeolite H-Y in the reactions of *m*-xylene. The catalytic activity of 3640 cm^{-1} groups in the parent, dealuminated, and realuminated samples has been monitored in terms of the relative values of turnover numbers. The effect of dealumination and realumination on the intrinsic properties of the zeolite was monitored by measuring the selectivity in the transformation of *m*-xylene.

Experimental Procedures

Catalyst Preparation. The ultrastable sample H-Y was prepared by hydrothermal treatment[17,18] of highly crystalline synthetic zeolite Na-Y with Si/Al = 2.47 and Na/Al = 1.09 (as determined by atomic absorption). The 78% ammonium-exchanged form, prepared by stirring Na-Y twice with 10 wt% NH_4Cl at 368 K for 1 h, had the lattice parameter $a_o = 2.466$ nm. The ammonium form was heated in a vertical quartz reactor at 823 K for 18 h, with water being injected at a rate of 12 mL/h so that the partial pressure of H_2O above the sample was 1 atm. The hydrothermally dealuminated form H-US-Y had the lattice parameter $a_o = 2.451$ nm.

A 2 g portion of H-US-Y was realuminated by stirring with 100 mL of 0.25 M aqueous solution of KOH at 353 K for 25 h. The product was washed with water and dried. KOH rather than NaOH was used because synthetic faujasites cannot recrystallize from potassium-bearing solutions.[19] Since after realumination the sample was in the potassium form, it was exchanged four times with ammonium nitrate to yield NH_4-Real-US-Y ($a_o = 2.463$ nm). Thermal treatment of this sample gave H-Real-US-Y, suitable for catalytic testing.

X-ray Diffraction. Powder X-ray diffraction patterns were acquired on Dron-2 and Philips diffractometers using Ni-filtered Cu Kα radiation. All samples were hydrated over saturated aqueous calcium nitrate prior to measurement. Silicon powder was used as an internal standard for lattice parameter calculations.

TABLE 1: Concentrations of 3640 cm^{-1} Hydroxyl Groups (in μmol/g) in the Parent Sample H-Y and the Realuminated Sample H-Real-US-Y As Determined by Pyridine Sorption, and the Turnover Frequency Number (TOF) in the Transformation of *m*-Xylene[a]

sample	concentration of 3640 cm^{-1} hydroxyl groups (μmol/g)	TOF (s^{-1})
H-Y (parent)	1290	0.064
H-Real-US-Y	950	0.081

[a] We estimate the experimental error at less than ±5% of each value.

Infrared Spectroscopy. For IR studies, the zeolites were pressed into thin wafers (3−8 mg/cm^2 and activated in situ in the IR cell at 720 K in vacuum for 1 h. The spectra were recorded with a Bruker 48 PC spectrometer equipped with an MCT detector.

Catalytic Tests. Zeolite crystals were pressed into binder-free wafers, crushed and sieved to 30−60 mesh. A 50 mg sample was diluted with 0.5 mL inactive glass spheres and packed into a stainless steel down-flow microreactor (10 mm i.d.) placed in a tubular furnace. Additional amounts of glass spheres (0.5 mL) were placed on top of the catalyst bed. The catalyst was heated to 723 K at a rate of 100 K/h and activated in a nitrogen flow of 50 mL/min for 3 h. Measurements were performed in the pulse mode, in order to avoid coke formation which can obscure the intrinsic activity and selectivity of the catalysts. All reaction parameters were kept constant during the test to maintain maximum reproducibility. The products were analyzed with a GCHF gas chromatograph equipped with a TCD detector and a 3 m column packed with Bentone-34, didecyl phthalate, and silicon oil A on Chromosorb W (30−60 mesh). We estimate the error involved in product analysis at less than 0.1 mol%.

Results and Discussion

Brønsted Acidity. We have monitored the concentration of 3640 cm^{-1} hydroxyl groups (projecting into supercage and thus accessible to the reacting molecules) by measuring the sorption of pyridine. In the parent sample H-Y this gives rise to a band from pyridinium ions PyH^+ (1545 cm^{-1}) and decreases the intensity of the 3640 cm^{-1} band. Small portions of pyridine were adsorbed quantitatively at 420 K, and the extinction coefficient was then calculated from the linear dependence of intensity of the 1545 cm^{-1} band versus the amount of pyridine sorbed. The resulting value of 0.085 cm^2 μmol was used to determine the concentration of pyridinium ions in samples in which all the high-frequency OH groups are neutralized by pyridine. The results were 1290 μmol/g for the parent sample H-Y and 950 μmol/g for the realuminated sample H-Real-US-Y (Table 1). We estimate the experimental error at less than ±5% of each value. The decrease in concentration after the completion of the dealumination−realumination cycle is caused by not all aluminum atoms reentering the framework.

Catalytic Activity. The parent sample H-Y is highly active in the transformation of *m*-xylene (Table 2). Toluene and trimethylbenzenes (TMB) are formed in addition to the products of isomerization. Toluene is produced by disproportionation and dealkylation of xylene isomers. The contribution of these two parallel reactions, with higher energy of activation than that required for isomerization, increases with temperature. In sample H-Y the concentration ratio of the products of isomerization (*p*-xylene + *o*-xylene) to that of disproportionation (toluene + TMB) decreases with temperature from 3.85 to 673 K to 1.50 to 723 K. The *p*-xylene/*o*-xylene concentration ratio remains essentially constant (0.64−0.68) in this temperature

TABLE 2: Transformation of *m*-Xylene on Parent Zeolite H-Y, Dealuminated (Ultrastable) Sample H-US-Y, and the Hydrogen Form of Realuminated Sample (H-Real-US-Y)[a]

	673 K			698 K			723 K		
product	H-Y	H-US-Y	H-Real-US-Y	H-Y	H-US-Y	H-Real-US-Y	H-Y	H-US-Y	H-Real-US-Y
benzene	0.74	0.45	4.42	1.76	0.82	5.73	3.16	1.39	7.56
toluene	11.26	8.83	24.15	20.35	12.67	25.55	26.54	15.38	28.84
ethylbenzene	0.74	0.90	0.11	0.04	0.78	0.11	0.01	0.77	0.33
p-xylene	11.24	2.05	6.35	10.48	2.28	6.41	8.87	2.84	6.09
m-xylene	55.95	80.01	51.50	45.45	77.25	48.32	40.08	69.06	43.27
o-xylene	16.47	5.86	8.86	15.48	5.49	9.22	13.79	9.36	8.19
1,3,5-TMB	0.76	0.13	1.22	1.30	0.18	1.59	1.55	0.29	1.21
1,2,4-TMB	2.46	1.17	3.39	4.28	0.53	3.07	5.14	0.91	4.51
1,2,3-TMB	0.38	traces	traces	0.86	traces	traces	0.86	traces	traces
$\sum$TMB	3.60	1.30	4.61	6.44	0.71	4.66	7.55	1.20	5.72
p-xylene + *o*-xylene	27.71	7.91	15.21	25.96	7.77	15.63	22.66	12.20	14.28
p-xylene/*o*-xylene	0.68	0.35	0.72	0.68	0.42	0.70	0.64	0.30	0.74
I/D	3.85	3.04	1.65	2.02	5.47	1.68	1.50	5.08	1.25

[a] Product distribution is given in mol%. TMB = trimethylbenzene, I = isomerization, D = disproportionation, and I/D = (*p*-xylene + *o*-xylene)/2$\sum$TMB. The number of toluene molecules formed via transalkylation is equal to the sum of trimethylbenzene isomers. We estimate the error involved in product analysis at less than 0.1 mol %.

range. We note that the experimentally observed distribution of trimethylbenzenes is close to that required by thermodynamic equilibrium arguments.[28] Finally, small amounts of benzene (0.74−3.16%) are formed as a result of consecutive reactions: dealkylation of toluene and transalkylation of toluene and xylene isomers.

The conversion of *m*-xylene on the dealuminated sample H-US-Y is much lower (20−30%) than on parent H-Y. This is in agreement with the IR studies, which show a distinct concentration decrease of the catalytically active 3640 cm^{-1} hydroxyl groups in the former sample.[16] Dealkylation and disproportionation are hindered, so that the contribution of isomerization is higher. The isomerization/disproportionation ratio (3.04−5.08) shows a smaller contribution of the disproportionation route, demanding a bimolecular transition state. It is therefore clear that the aluminum species in the extra-framework positions decrease the void space available for the reactants.

The overall conversion of *m*-xylene rises significantly upon realumination and is essentially the same in H-Real-US-Y as in H-Y (Table 2), despite the lower concentration of acid centres available for the reactant on the realuminated catalyst (Table 1). We also note that the amounts of TMB in sample H-Real-US-Y are close to that found for H-Y, while more toluene is formed. The isomerization/disproportionation (I/D) ratio is only 1.25−1.65 (Table 2). In other words, the contribution of the space-demanding bimolecular transalkylation of *m*-xylene increases again after realumination, and the relative contributions of the two reaction pathways become similar to that observed for the parent H-Y. As extra-framework aluminum re-enters the framework, the contribution of isomerization decreases at the expense of transalkylation route. Finally, shape selectivity, expressed in terms of the *p*-xylene/*o*-xylene ratio, remains the same within the experimental error, and recalls that of the parent sample H-Y. No steric restrictions operate therefore in the realuminated sample, which supports the proposed mechanism of realumination.[7] The I/D ratio thus appears as a very useful tool for the characterization of modified zeolite catalysts.

Having determined the concentration of the active acid sites (3640 cm^{-1} hydroxyl groups), we can make a quantitative comparison of the catalytic performance of the samples. The turnover frequency (TOF) of *m*-xylene transformation calculated taking into account the number of proton sites accessible for reacting molecules, is 25% higher for the realuminated sample (Table 1). This indicates a higher acid strength of the catalytically active hydroxyl groups, in agreement with the results of our study of benzene sorption.[16] Finally, the TOF values are close to the value of 0.074 s^{-1} measured by Corma et al.[29] for zeolite H-Y the Si/Al = 4.3. We conclude that the increased acid strength of bridging hydroxyl groups[16] in the realuminated material is indeed caused by the higher population of the Si(1Al) groups (and thus of the $\mathrm{Si_3}\mathbf{Si{-}OH{-}Al}\mathrm{Si_3}$ hydroxyls) in comparison with sample H-Y, as monitored by ^{29}Si MAS NMR.[7]

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References and Notes

(1) Kacirek, H.; Lechert, H. *J. Phys. Chem.* **1976**, *80*, 1291.

(2) Delprato, F.; Delmotte, L.; Guth, J. L.; Huve, L. *Zeolites* **1990**, *10*, 546.

(3) Scherzer, J. In *Catalytic Materials: Relationship between Structure and Reactivity*; Whyte, T. E., Jr., Dalla Betta, R. A., Derouane, E. G., Baker, R. T. K., Eds.; ACS Symposium Series 248: American Chemical Society: Washington, DC, 198; p 157.

(4) Sulikowski, B. *Heterog. Chem. Rev.* **1996**, *3*, 203 and references therein.

(5) Klinowski, J.; Thomas, J. M.; Fyfe, C. A.; Gobi, G. C. *Nature* **1982**, *296*, 533.

(6) Rabo, J. A.; Pellet, R. J.; Risch, A. P.; Blackwell, C. S. Presented at the Katalistiks' 8th Annual Fluid Cat Cracking Symposium, June 1−4, 1987, Budapest, Hungary.

(7) Hamdan, H.; Sulikowski, B.; Klinowski, J. *J. Phys. Chem.* **1989**, *93*, 350.

(8) Sulikowski, B.; Rakoczy, J.; Hamdan, H.; Klinowski, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1542.

(9) Chang, C. D.; Chu, C. T.-W.; Miale, J. N.; Bridger, R. F.; Calvert, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 8143.

(10) Anderson, M. W.; Klinowski, J.; Liu, X. *J. Chem. Soc., Chem. Commun.* **1984**, 1596.

(11) Liu, X.; Klinowski, J.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 582.

(12) Man, P. P.; Klinowski, J. *J. Chem. Phys. Lett.* **1988**, *147*, 581.

(13) Hamdan, H.; Klinowski, J. In *Zeolite Synthesis*; Occelli, M. L., Robson, H. E., Eds.; 196th National Meeting of the American Chemical Society, Los Angeles, CA, September 25−30, 1988; ACS Symposium Series 398; American Chemical Society: Washington, DC, 1989; p 448.

(14) Hamdan, H.; Klinowski, J. *ACS Symp. Ser.* **1989**, *398*, 465.

(15) Barrie, P. J.; Gladden, L. F.; Klinowski, J. *J. Chem. Soc., Chem. Commun.* **1991**, 592.

(16) Datka, J.; Sulikowski, B.; Gil, B. *J. Phys. Chem.* **1996**, *100*, 11242.

(17) McDaniel, C. V.; Maher, P. K. In *Molecular Sieves*; Society of Chemical Industry: London, 1968; p 186.

(18) Kerr, G. T.; Shipman, G. F. *J. Phys. Chem.* **1968**, *72*, 3071.

(19) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982.

(20) Sulikowski, B. *React. Kinet. Catal. Lett.* **1981**, *16*, 39.

(21) Mavrodinova, V.; Penchev, V.; Lohse, U.; Stach, H. *Zeolites* **1989**, *9*, 197.

(22) Dewing, J. *J. Mol. Catal.* **1984**, *27*, 25.

(23) Richter, M.; Fiebig, W.; Jerschkewitz, H. G.; Lischke, G.; Öhlmann, G. *Zeolites* **1989**, *9*, 238.

(24) Datka, J.; Piwowarska, Z.; Rakoczy, J.; Sulikowski, B. *Zeolites* **1988**, *8*, 199.

(25) Karge, H. G.; Ladebeck, J.; Sarbak, Z.; Hatada, K. *Zeolites* **1982**, *2*, 94.

(26) Corma, A.; Sastre, E. *J. Chem. Soc., Chem. Commun.* **1991**, 594.

(27) Martens, J. A.; Perez-Pariente, J.; Sastre, E.; Corma, A.; Jacobs, P. A. *Appl. Catal.* **1988**, *45*, 85.

(28) Taylor, W. J.; Wagman, D. D.; Williams, M. G.; Pitzer, K. S.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1946**, *37*, 95.

(29) Corma, A.; Llopis, F.; Monton, J. B. In *New Frontiers in Catalysis*, Proc. 10th Intern. Congress on Catalysis, Budapest, July 19−24, 1992; Guczi, L., Solymosi, F., Tétényi, P., Eds.; Akadémiai Kiadó: Budapest, 1993; Part B, p 1145.