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Hydrophilicity of mordenites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio

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Abstract

Hydrophilicity of H-mordenites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (MR) varying in the range from 10 up to 206 was investigated by IR spectroscopy, TPD of ammonia and thermogravimetry methods. It was found that dealuminated mordenite retains affinity for water in the entire MR range, in contrast to published results for synthetic pentasil zeolites. In H-mordenites extra-framework aluminum exists in the form of dimers of aluminum hydroxide, those presumably are stabilized in the channels of mordenite. An inversely proportional correlation between the water content in pores and the concentration of channel Lewis sites was observed.

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1. Introduction

Zeolites are well-known and widely used catalyst supports and adsorbents¹. Between a world of zeolites one can found hydrophilic and hydrophobic moieties. Common opinion is that low-silica zeolites are excellent adsorbents for water and any polar substances, whereas high-silica zeolites converts in hydrophobic and organophilic materials².

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Such dependence make zeolites even more interesting, permitting their simultaneous use in some industrial applications, such as removing of low molecular weight olefins from a water-containing exhaust gases as generated at start-up of an internal combustion engines. This task is proposed to solve by contacting the gas with a hydrophilic material *A* to remove at least some of the water; and then contacting the gas with an olefin-removing agent *B*. In the patent³ both *A* and *B* are proposed to be zeolites, but as an *A* are listed hydrophilic zeolite types, and as *B* are selected the hydrophobic ones. Also, it is proposed that hydrophobicity of zeolite supports will results in reduced effect of moisture on the de-NO_x catalysts and therefore allows purifying of exhaust gases from automobiles running on an oxygen-rich fuel/air mixture⁴. Recent studies that have used hydrophobic Brønsted and Lewis acidic microporous and mesoporous supports in catalytic reactions of biomass conversion in liquid water and biphasic water-organic mixtures demonstrates that both extracrystalline and intracrystalline hydrophobic environments can prevent the condensation of bulk water within internal void spaces and thus alleviate any transport restrictions its presence may cause, while only intracrystalline environments can influence the kinetic effects of molecular water at active sites⁵.

The aim of present work was to study any observable dependence on zeolite-water interaction in a wide range of SiO₂/Al₂O₃ molar ratio (MR). Modern preparative chemistry can produce a wide variety of zeolites with identical geometrical pore structure, but essentially different MR by direct synthesis⁶ or by dealumination/desilication⁷. The mordenite type of zeolite was chosen between different zeolite structures, accessible in wide range of MR, because it has important industrial applications⁸⁻¹⁰.

2. Experimental

Protonated forms of mordenites with SiO₂/Al₂O₃ molar ratios equal to 10, 15, 20, 30, 72, 110, 128 and 206 were supplied by TOSOH Corporation, Tokyo, Japan. Through the article and figures these samples are indicated by the letter M followed by a number, which indicate the molar ratio.

The thermogravimetric analysis in the temperature range from 293 K to 1223 K with a heating rate of 10 K/min was done on a DTA-TGA model STA-780 equipment in a flow of dry air. TPD of ammonia was made on self-constructed equipment. Measurements were carried out on small amount (10 mg) of samples to exclude the influence of re-adsorption of ammonia¹¹. The samples were evacuated at 773 K for 2 h, and exposed to 20 kPa of ammonia at 423 K for 30 min, then evacuated for 1 h and cooled to room temperature. The desorption of ammonia was analyzed under vacuum, using a mass spectrometer, with temperature raised from ambient up to 873 K at 10 K/min.

Samples for IR measurements were pressed into wafers with an average density of about 10 mg/cm². Before measurements they were calcined at 723 K for 1 h in air and then for 1 h directly in vacuum cell at 1.3x10⁻³ Pa. Adsorption of CO and pyridine (Py) was carried out at 163 K and 423 K respectively. CO was adsorbed by pulses of 0.2 mL up to pressure 1.3 kPa. Pyridine was adsorbed for 15 min and evacuated for 30 min to prevent physical adsorption. Spectra were registered maintaining the samples at 163 K in the case of CO and at room temperature in the case of pyridine. The concentration of Brønsted acid sites was calculated from the values of intensity of peaks of OH-groups ($\nu_{OH} = 3610$ and 3720 cm⁻¹) and pyridine ($\nu_{PyH^+} = 1530$ – 1545 cm⁻¹) complex species¹²⁻¹⁴, according to equation:

$$N [\mu\text{mol g}^{-1}] = A [\text{cm}^{-1}] / (A_o [\text{cm} \mu\text{mol}^{-1}] \times \rho [\text{g cm}^{-2}]) \quad (1)$$

where *A* is intensity of band in IR spectrum, *A_o* is coefficient of absorption for IR band taken from¹⁴, and ρ is wafer density.

Concentration of Lewis sites was calculated from intensity of adsorption bands of CO ($\nu_{CO} = 2180$ – 2230 cm⁻¹) and pyridine ($\nu_{PyL} = 1450$ – 1460 cm⁻¹) with eq. (1). Lewis acid site strength was determined from the heat of CO adsorption, calculated by the equation¹⁴:

$$Q_{CO} = 10.5 + 0.5(\nu_{CO} - 2143) \quad (2)$$

where ν_{CO} is wavenumber of maximum of the band of adsorbed CO.

3. Results and discussion

The temperature of maximum of the ammonia desorption peak can be considered as a measure of the strength of acid sites. A decrease of the temperature of peak maximum in the TPD spectra correlates with a decrease in the acid strength¹⁵. The temperature of the desorption peak goes through maximum with MR, see Table 1. Previous studies in our group have shown that the formation of metal clusters and their stability depends on the molar ratio, and also in non-monotonic manner. Island of cluster stability in “molar ratio – temperature of reduction” coordinates was observed firstly for the stabilization of silver clusters in mordenite matrix^{16,17}. Similar dependencies were observed for nickel¹⁸, copper^{19,20} and gold^{21–25} nanoparticles supported on mordenite with wide range of MR. Detailed analysis of the influence of amount and strength of acid sites on H-mordenite with various aluminum concentrations (due to variation of MR) was published in²⁶ (see Figure 4 in the above Ref.). For this current work it is important to mention that total acid amount is proportional to aluminum concentration²⁶.

Calorimetric measurements of ammonia at 423 K on dealuminated mordenites with MR between 14 and 96 show a distinct dependence of the number of strong acid sites on the content of the framework aluminum. Plots of these numbers against the molar fraction of aluminum yield a volcano-shaped curve²⁷. Starting with a low Al content (a high MR), the number of the strong acidic sites increases with increasing Al number of the framework up to 4.6 Al atoms per unit cell (MR of 19) and then decreases. This decrease of the strong acidity above MR=19 may be explained by the appearance of an aluminum atom in the second coordination sphere of the Si—OH—Al group²⁸. For the mordenite set studied in this work, the maximum strength of acid sites is observed for M15. In accordance with literature data in TPD spectra of mordenites with different MR, two separate peaks are found^{29,30}. The low-temperature peak (near 540 K) is practically independent of the degree of dealumination, but the temperature of high-temperature peak decreases (823–758 K) with decreasing of framework Al content ($14 \leq \text{MR} \leq 96$). However, according to^{7, 31}, the method of dealumination of mordenites can influence amount of ammonia TPD peaks and temperature of their maximum. Therefore every set of mordenites, prepared by different methods, can possess slightly different characteristics.

Infrared study of adsorbed carbon monoxide and pyridine revealed that H-mordenites possess four types of Lewis and two types of Brønsted acid centers (Table 1). Concentration of these centers depends on MR in non-monotonic manner.

The concentration of Brønsted sites in accordance with the results of the adsorption of pyridine, and direct measurement of surface-OH species, passes through a maximum as MR changes, peaking for M20 (Table 1), that coincides with literature data on MR dependence of maximum acidity^{27, 28}. Note, that concentration of OH-groups on outer surface ($\text{C}_{\text{OH}(3720)}$) of all mordenites is weakly dependent on MR, while concentration of channel OH-groups ($\text{C}_{\text{OH}(3610)}$) have volcano-shape characteristic, with maximum for M20. Variation of concentration of this type of Brønsted sites is more than 30 times (Table 1). Therefore, the main difference in the properties of the samples is associated with the properties of the inner surface (i.e. surface of the channels) of mordenites with variable MR.

As far as Lewis sites are concerned, the dependence of total concentration of Lewis sites on MR, measured by pyridine adsorption, C_{pyL} , had similar character as that one for Brønsted sites, showing maximum concentration equal to 55 $\mu\text{mol/g}$ for M30 (Table 1). However, the character of dependence of the total Lewis site concentration ΣL_i , measured by CO adsorption, is different (Table 1). For $20 \leq \text{MR} \leq 110$ data of CO and pyridine adsorption practically coincide. On the other hand, Lewis center concentration measured by hydroxyl group concentration, exceed that one measured by pyridine adsorption, about 8 and 4 times, for lower (MR equal to 10 and 15) and higher (MR equal to 128 and 206) molar ratios, respectively.

Calculations in accordance with the eq. (2) showed that Lewis sites L4 are characterized by $Q_{\text{CO}} = 52\text{--}54$ kJ/mol and are the strongest ones. Lewis sites L3 and L2 are of moderate acid strength. For them Q_{CO} is equal to 48–49 and 40–42 kJ/mol, respectively. L1 sites are the weakest ones because of low Q_{CO} (30–34 kJ/mol).

The strongest L4 sites are typical for zeolites^{13, 14}. They can be attributed to clusters of aluminum hydroxide, more probably, to dimers, located on Brønsted sites. Moderate Lewis sites L3 are assigned to dimers, located on Si-OH sites, or to tetramers, located on Si—OH—Al center. Typical for zeolites moderate sites L2 are attributed to large aluminum hydroxide clusters or nucleus of alumina phase. Weak L1 sites, probably, are nucleus of alumina phase, or some kind of defects of alumina phase.

Table 1. Data of ammonia TPD, DTA, DTG, nominal concentration of Al and concentration ($\mu\text{mol/g}$) of acid centers in mordenites with different MR according to IR data.

Sample	M10	M15	M20	M30	M72	M110	M128	M206
T _{ammonia}	633	662	638	622	601	582	580	574
T _{water}	325	382	365	350	336	335	327	326
Wt loss, %	6.2	15.1	11.8	10.7	12.7	9.9	9.4	7.8
C _{Al}	2800	2000	1540	1050	450	300	260	160
C _{L1}	111	107	-	-	-	-	-	-
C _{L2}	33	40	25	35	18	26	46	40
C _{L3}	19	-	-	-	-	22	55	45
C _{L4}	-	42	15	37	9	-	-	-
ΣL_i (i=1-4)	163	189	40	72	27	48	101	85
C _{Al-IR}	197	419	575	480	217	191	252	200
C _{PyH⁺}	31	260	350	260	117	115	88	60
C _{PyL}	18	27	48	55	25	45	25	21
C _{OH(3610)}	13 (280)	210 (290)	475 (290)	330 (300)	120 (300)	75 (300)	88 (300)	45 (300)
C _{OH(3720)}	21 (260)	20 (260)	60 (260)	78 (250)	70 (260)	68 (260)	63 (260)	70 (250)

T_{ammonia} – temperature of maximum in the TPD spectra of ammonia desorption;

T_{water} – temperature of maximum on the DTA curve of water desorption;

Wt loss, % – amount of water loss in DTG experiment;

C_{Al} – nominal concentration of Al species according to MR;

C_{L1} – concentration of Lewis site characterized by $\nu_{\text{CO}} = 2182\text{--}2190\text{ cm}^{-1}$;

C_{L2} – concentration of Lewis site characterized by $\nu_{\text{CO}} = 2200\text{--}2205\text{ cm}^{-1}$;

C_{L3} – concentration of Lewis site characterized by $\nu_{\text{CO}} = 2218\text{--}2220\text{ cm}^{-1}$;

C_{L4} – concentration of Lewis site characterized by $\nu_{\text{CO}} = 2225\text{--}2230\text{ cm}^{-1}$.

ΣL_i – total concentration of all types of Lewis acid sites;

C_{Al-IR} – Al concentration from IR data for CO and OH-groups;

C_{PyH⁺} – concentration of pyridinium ions ($\nu = 1535\text{--}1545\text{ cm}^{-1}$);

C_{PyL} – concentration of complexes of pyridine and Lewis site ($\nu = 1450\text{--}1460\text{ cm}^{-1}$);

C_{OH(3610)} – concentration of channel OH-groups ($\nu_{\text{OH}} = 3605\text{--}3615\text{ cm}^{-1}$); in parentheses $\Delta\nu$ - shift of ν_{OH} for adsorbed CO;

C_{OH(3720)} – concentration of OH-groups on outer surface ($\nu_{\text{OH}} = 3720\text{--}3725\text{ cm}^{-1}$); in parentheses $\Delta\nu$ - shift of ν_{OH} for adsorbed CO;

“-” – concentration is lower than the sensitivity limit ($10\text{ }\mu\text{mol g}^{-1}$).

Two types of Brønsted sites were identified due to their characteristic frequencies in the spectra of OH groups. The first type, characterized by the band $3615\text{--}3605\text{ cm}^{-1}$, is assigned to OH-groups into zeolite channels¹⁴. After CO adsorption this band is shifted ($\Delta\nu=280\text{--}300\text{ cm}^{-1}$) to low frequency. Larger shift, and consequently, stronger channel Brønsted sites were observed for mordenites with $\text{MR}\geq 30$ (Table 1). The second type of Brønsted sites is characterized by the band at $3760\text{--}3725\text{ cm}^{-1}$. This band corresponds to bridge Si—OH—Al groups on the outside surface of zeolite crystallites¹⁴. The second type of Brønsted sites is weaker than channel OH-groups ($\Delta\nu=250\text{--}260\text{ cm}^{-1}$).

As can be seen in the Table 1, stabilization of the smallest Lewis sites L4 (dimer of aluminum hydroxide) occurs in the MR range 15–72. It is interesting that, in spite of the difference of the chemical nature of dimer of aluminum hydroxide and metal clusters and nanoparticles, they are stabilized in the same MR region^{16–20}. This MR region corresponds to maximal contribution and strength of channel Brønsted centers. It suggests that dimer of aluminum hydroxide and metal nanoparticles are stabilized on the same centers (channel Brønsted sites).

The highest temperature of maximum of desorption peak of ammonia (663 K) was observed for M15 (Table 1). For other samples, position of peak maximum was shifted to lower temperatures (the lowest was 573 K for M206). The peak always had complex shape and consisted of several peaks. According to thermogravimetry data, peak of water desorption for all mordenites was observed at $\sim 323\text{--}383\text{ K}$. The temperature of the maximum of DTA peak position due to water removing, and weight loss of samples were maximal for M15 also (Table 1).

The expected value of water weight loss on the basis of available mordenite pore volume $0.14 \text{ cm}^3/\text{g}$ ³² is equal to 14 wt.%. The results of thermogravimetric study permitted to check the hypothesis about diminishing of hydrophilicity with increasing of MR. This statement is based on the observed facts that high-silica zeolites like silicalites, zeolite beta and ZSM-5 with high MR are hydrophobic³³⁻³⁶. In our case, the data of IR and thermogravimetry methods are correlated (Table 1). An inversely proportional correlation between the amount of desorbed water and total concentration of Lewis sites is observed. It implies that the more the total concentration of Lewis sites the less water amount is adsorbed by the mordenite. This correlation disapproves the hypothesis about change of mordenite hydrophilic properties with MR. There is no direct relation between MR and amount of desorbed water for mordenites, while it exists for ZSM-5^{35,36}. It is known, that silicalites are hydrophobic³³. In spite of the fact that the concentration of Al in M206 is very low, less than 1/2 of Al atom per unit cell, it still has hydrophilic properties and adsorbs even more water than the M10 sample (Table 1). In agreement with IR data, very small amount of water can be desorbed from M10 because of occupying of pores by large weak Lewis sites L1, L2 and L3 in this mordenite sample.

According to the definition, a hydrophilic material is a material, which has high affinity to water^{37,38}. There is an opinion that the quantity of adsorbed water by a zeolite is proportional to the framework aluminum content due to acidic protons (Brønsted centers) associated with the framework aluminum atoms³⁹. In general, it is true, but for many systems such regularity is broken. Data presented in this work shows the absence of direct relation between hydrophilicity and MR of this set of mordenites. It makes the challenge in the rationalization of zeolitic materials. As the geometrical, physical and chemical characteristics of zeolite frameworks affect the performances of the resulting materials¹⁰, the future perspective on the rational synthesis of materials with desired functions and structures need better understanding of factors that determine the properties of target materials. Predictable changes in reactivity of zeolite matrix can be caused by impurities which are present in very small quantities⁵, but can be generated purposefully by appropriate treatment. Different types of defects, silanol nests and extra-framework aluminum clusters formed during dealumination treatment apparently are responsible for the enhancement of water adsorption by these high-silica mordenites (Table 1). Also, it was reported that not only the concentration, but the distribution of generated moieties can be important for final properties of obtained material². It concerns the Brønsted acid sites (BAS) in the zeolite micropores. In the Ref.⁴⁰ was demonstrated that the acid sites are distributed quite evenly between oxygen atoms in different crystallographic positions. The accessibility of BAS depend on their local environment, so it is important to know the number and locations of BAS. Our data demonstrates the correlation between BAS located in the mordenite voids and cluster stabilization, dependent on $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Hydrophilicity of this set of mordenite is important factor for applying them as the nanoparticle supports.

4. Conclusions

It was obtained an inversely proportional correlation between the water content in pores and the concentration of channel Lewis sites for all studied mordenites except of M15. This correlation permits to conclude that mordenites keeps hydrophilic properties in the range of MR from 10 to 206 in contrast to published results for silicalite and ZSM zeolites. The Lewis sites occupy some part of channel volume, diminishing water volume in the channels. Stabilization of clusters of different chemical nature (metal clusters and non-framework aluminum hydroxide dimers) was found to occur in mordenites possessing high concentration of accessible Brønsted channel sites and high strength of acid sites.

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