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Comprehensive description of the acidic property of effective metallosilicate catalysts by computer simulation

T. Inui *, K. Matsuba, Y. Tanaka

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Abstract

Acidic properties of silica-rich metallosilicates, which are effective for selective hydrocarbon syntheses, were investigated through computer simulations adopting a Monte Carlo method on adsorption of NH_3, methanol, H_2O, and some hydrocarbons. The results of the simulations were compared with experimental data and their validity were confirmed. The unique catalytic performance of different kinds of metallosilicates could be explained according to the microscopic description of their acid sites.

1. Introduction

1.1. Acidic property of metallosilicate measured by NH_3-TPD

The size of a pentasil pore opening of ZSM-5 was delicately modified by isomorphous substitution of other kinds of elements for Al and the amount of incorporated elements [1]. These factors affect the diffusivity of reactants and shape selectivity of the reaction products. However, more evident effects of isomorphous substitution are the change in the acidic property and the exertion of intrinsic metallic and/or metal oxide catalysis [2]. The change in effective diffusivity and the different kinds of catalysis caused by metal incorporation can be observed experimentally.

The acidic property of zeolitic catalysts is usually measured by the NH_3-TPD method, and actually the TPD profiles of different kind of zeolites can be differentiated, as shown in Fig. 1, both in the integral area of profiles and in the shift of peak

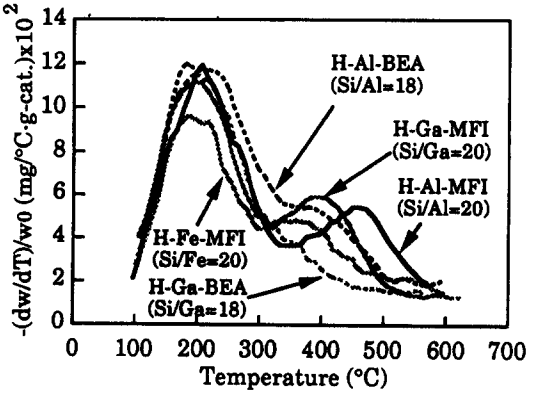

Fig. 1. NH_3-TPD profiles for various metallosilicate catalysts.

temperature. A high-temperature peak above ca. 300–400°C is especially regarded as being due to the desorption from strong acid sites, which are mainly responsible for the acid catalyzed reaction in hydrocarbon synthesis. However, in general, this information persistently remains qualitative, and therefore, so far, the information from the feature of consecutive acid catalyzed reactions such as methanol-to-hydrocarbon conversion via

* Corresponding author.

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dimethyl ether formation, for example, would be the most suggestive tool to determine more precisely the acidic property of zeolitic catalysts [2].

Through the measurements of NH_3-TPD, one can recognize in general, the order of acid strength of the metallosilicates, for example, as in the order of

$$Al \geq Ga > Fe \gg Zn$$

as expressed by the kind of metal incorporated [3]. However, the feature of the reaction indicates a much larger difference than that expected from the qualitative information of the NH_3-TPD.

1.2. New method for evaluation of catalytic property

Teunissen et al. [4,5]. have studied the states of NH_3 or NH_4^+ adsorbed on Al tetrahedral clusters as models cut off the zeolite framework by means of ab initio quantum calculations, and have evaluated a comparison of the computed interaction energies of NH_3 and the experimentally measured heat of adsorption of NH_3. Although good agreement was found in their evaluation, the effects of pressure, temperature and pore-structure remained unknown because of their use of small cluster models.

In order to elucidate more precise differences in the acidic properties of these metallosilicates, we newly investigated the computer simulation of NH_3 adsorption on the acidic sites of different kind of metallosilicates by applying the Monte Carlo method, and estimated the precise position of the adsorption sites and the amount of NH_3 adsorbed. The results were visualized by computer graphics [3,6].

In this presentation, sequential results of NH_3 adsorptions are shown for different kinds of high silica zeolites, MFI (ZSM-5)-type 10 oxygen-member ring metallosilicates and BEA (beta)-type 12 oxygen-member ring metallosilicates were calculated by computer and depicted by computer graphics. The feature of the adsorption pattern of NH_3 is discussed in comparison with the NH_3-TPD profile and the reaction characteristics in some hydrocarbon conversion reactions. Other adsorbates have also been studied.

2. Method of computer simulation

Monte Carlo simulation was carried out for several kinds of metallosilicates, ion-exchanged zeolites, and some conventional zeolites. The potential energies of NH_3 molecules in the metallosilicate were calculated by using the DREIDING II force field [7] developed by Dasgupta and Goddard III. In this force field the interactions (E) consist of bond stretch (E_B, two-body), bond-angle bend (E_A, three-body), dihedral angle torsion (E_T, four-body), inversion (E_I, four-body), van der Waals (E_{vdw}), electrostatic (E_Q), and hydrogen bond (E_{hb}) terms, as in the following equation.

$$E = E_B + E_A + E_T + E_I, + E_{vdw} + E_Q + E_{hb} \quad (1)$$

The fixed pressure (grand canonical) algorithm [8] used in these simulations was as follows:

(1) Creation of a molecule: an ammonia molecule is placed at a random position in the framework domain of the metallosilicate, and whether we accept the configurations or not is judged according to the energy change, i.e. with the probability P expressed as:

$$P = \min[1, \exp\{-DU/kT\} - \ln\{(N+1)kT/pV\}] \quad (2)$$

where DU is the configurational energy change, N is the current number of molecules in the framework of the metallosilicate, p is the pressure of molecules in the gas phase, and V is the cell volume.

(2) Removal of a molecule: a random ammonia molecule located in the framework is chosen, and a new configuration is accepted with the following probability:

$$P = \min[1, \exp\{-DU/kT\} + \ln\{NkT/pV\}] \quad (3)$$

(3) Translation of a molecule: we choose a random molecule in the framework and translate it by a random amount within a cube of size $2d$ ($d=1$ Å), and accept a new configuration with probability P:

$$P=\min[1, \exp\{-DU/kT\}] \quad (4)$$

(4) Rotation of a molecule: a random molecule in the framework is chosen, and a random axis in the framework is chosen and the molecule is rotated by a random amount within the range $-d$ to $+d$ ($d=50°$). A new configuration will be accepted based on the energy change as for Eq. (4).

The amount adsorbed was counted after this cycle and these cycles were repeated 100 000 times. These calculations were carried out at 300 K under 100 kPa by graphics supercomputer TITAN750V (Stardent Inc.). The results of these calculations were investigated with computer graphics.

3. Results and discussion

3.1. Correlation between content of Al and amount of NH_3 adsorbed

The strictly linear relationship between the Al content in H-Al-MFI and the α value, which is regarded as the strength of acidity, was obtained by experiment [9]. However, this relationship has not yet been observed for H-Al-BEA. In order to evaluate the validity of the computer simulation method, the number of NH_3 molecules adsorbed was calculated varying the Al content in the H-Al-MFI framework, and then it was calculated for H-Al-BEA as well.

As shown in Fig. 2, fairly good correlations (lines go through the origins) between the Al content and the average numbers of adsorbed NH_3 on a unit cell of H-Al-MFI and H-Al-BEA and as well as the contents of Al, were observed.

Further, these results explained that the difference of structure between MFI and BEA reflects the strength of acidity of these zeolites. This indicates the validity of the presented simulation method and its potential to predict the amount of adsorbed NH_3 on H-Al-BEAs incorporating different Al contents.

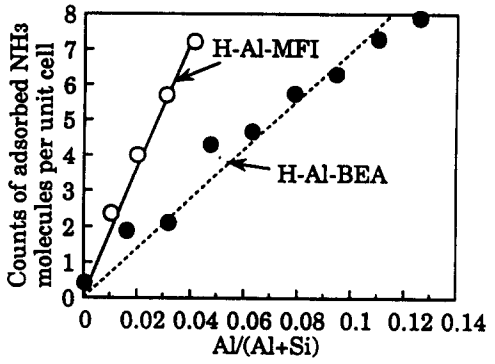

Fig. 2. Relationships between the Al content in silica-rich MFI and BEA and the number of NH_3 molecules adsorbed.

3.2. Simulation of NH_3 adsorption on different kinds of metallosilicates

Twelve kinds of metallosilicates incorporating MFI, BEA, mono- and bi-metallosilicates were treated for the calculations. Fig. 3 shows one of the results obtained for H-Ga-MFI and H-Ga-BEA. The figure shows the geometry of NH_3 adsorbed on the unit cell depicted as A–C coordinate. The average number of adsorbed NH_3 per unit cell is indicated on each upper graph.

The calculated results showed that the order of the amount of adsorbed NH_3 for three kinds of MFI metallosilicates and two kinds of H-Al-silicates having MFI and BEA structure was as follows:

H-Al-MFI > H-Ga-MFI ≫ H-Fe-MFI

and

H-Al-MFI > H-Al-BEA,

H-Ga-MFI > H-Ga-BEA

Reflecting their pore structures, distribution of adsorption sites for NH_3 molecules and concentration of NH_3 adsorbed in MFI structure are much more localized and concentrated, respectively.

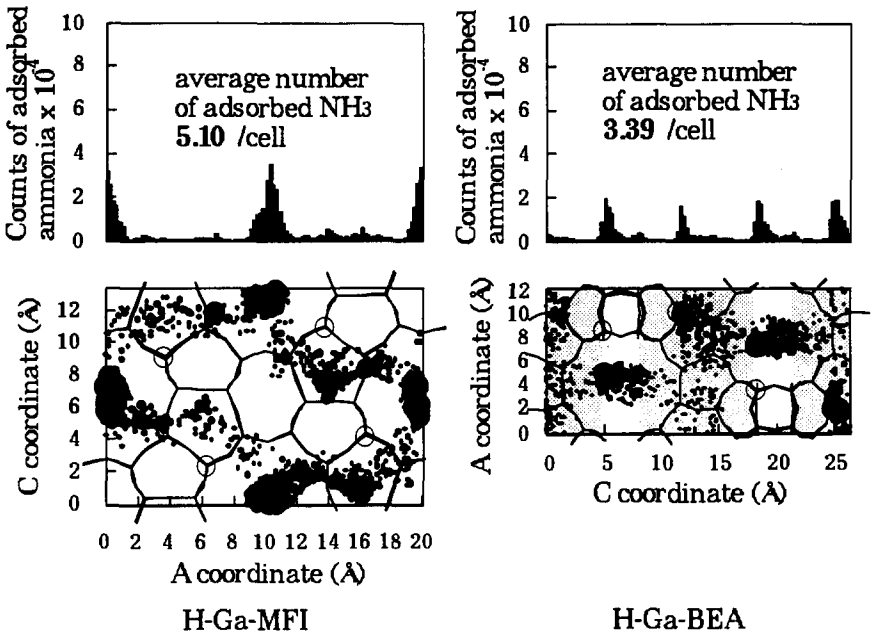

Fig. 3. Distribution and average number of NH_3 adsorbed on H-Ga-MFI and H-Ga-BEA.

These simulation results consistently correspond to the experimental results of NH_3-TPD and the results of hydrocarbon conversion, for example, ethyl benzene conversion [10]. Conversion of ethylbenzene on MFI-metallosilicates was higher than that on BEA-metallosilicates. Conversions of ethylbenzene on both H-Al-MFI and H-Ga-MFI were large, being as high as 90%. therefore, the difference between them is not clear. Catalytic functions rather than acidity are reflected in the reaction results. The Ga ingredient is a function of the hydrogen evolution from the reaction sites to the gas phase, whereas the Al ingredient is a function of the hydrogen shift on the catalyst surface. As a result much heavier aromatics are produced, and conversely light paraffinic hydrocarbons are produced less in Ga-containing metallosilicates.

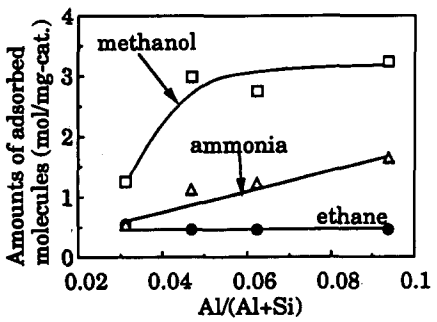

Fig. 4. Effect of Al content in H-Al-BEA on the amount of adsorbates.

In bi-metallosilicates, the amount of NH_3 and the average potential energy of NH_3 were carefully deviated from the simple average of both elements. The calculated results suggest a cause for the marked improvement in the catalytic performance of bi-metallosilicates in the conversion reactions of propane [11] and n-hexane [12].

3.3. Extension of the simulation to the adsorption of related compounds in the catalytic reactions on metallosilicates

The Monte Carlo adsorption method was extended to the simulation of the adsorption of methanol and hydrocarbons. The results of the simulation with methanol and ethane on metallosilicates are shown in Fig. 4.

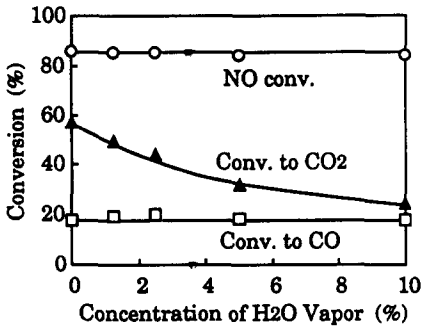

Fig. 5. Effect of H_2O addition on NO conversion on H-Co-silicate. 1000 ppm NO, 10.0% O_2, 3000 ppm n-$C_{16}H_{34}$, 0–10% H_2O, balance N_2, SV = 30 000 h^{-1}, reaction temperature 500°C.

The results for NH_3 are superimposed in the same figure. The amount of adsorbed methanol increased with increasing pressure, while the amount of adsorbed ethane molecules remained constantly at a lower level throughout the whole of the pressure range.

These results coincide with the experimental results that the reactive ability of methanol [3] is higher than those of paraffins such as propane [11].

3.4. Evaluation of water adsorption on different kinds of zeolites

The removal of NO in exhaust gases from diesel engines and other lean-burn combustion facilities has been one of the most important but difficult subjects in catalytic chemistry, because O_2 in the exhaust gas strongly interferes with NO conversion on the catalyst. In our previous work, H-Co-

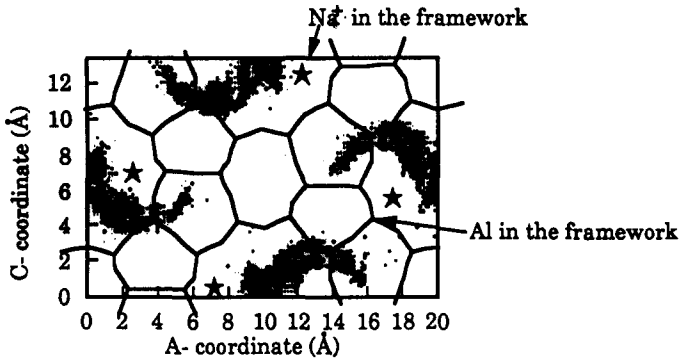

Fig. 6. Distribution of water molecules adsorbed on Na-ZSM-5 at 300 K under 0.1 kPa. Amount: 7.206 m/uc. Energy: −12.46 kcal/mol.

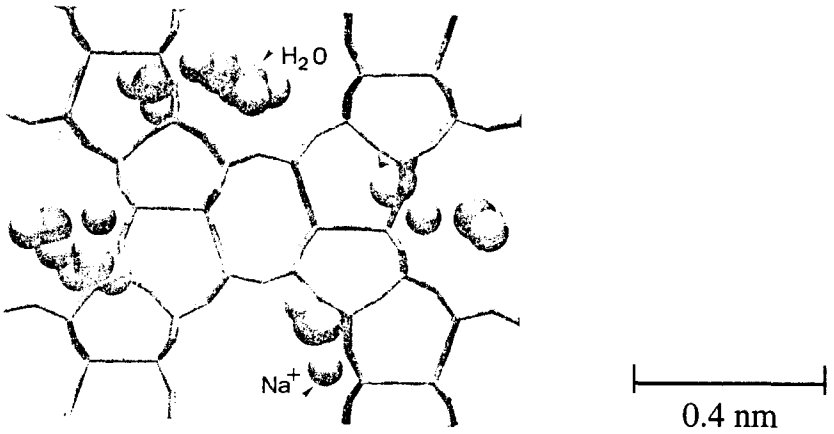

Fig. 7. Computer graphic of water molecules adsorbed on Na-ZSM-5 at 300 K under 0.1 kPa.

Table 1
Amounts and energies of molecules adsorbed on different kinds of MFI-type zeolites at 300 K under 10 kPa

Zeolite	Average energy (kcal/mol)		Adsorbed molecules (m/uc)	
	H_2O	CH_4	H_2O	CH_4
Na-ZSM-5	−11.10	−5.265	15.88	2.345
Fe-ZSM-5	−10.10	−5.373	8.270	2.102
H-ZSM-5	−5.911	−5.283	0.6427	2.458
H-Fe-silicate	−4.304	−5.248	0.2044	2.262

silicate [13] was used and it had a high performance in NO conversion even in the presence of a high concentration (10%) of water vapor as shown in Fig. 5.

The water adsorption property of zeolitic catalysts is usually measured by infrared analysis or nuclear magnetic resonance; however, details about the microscopic states of the water molecules adsorbed has remained ambiguous. The Monte Carlo method was applied to evaluate the high durability of metallosilicate to water vapor.

Fig. 6 shows the distribution of H_2O molecules adsorbed on Na-ZSM-5. Here, H_2O molecules were adsorbed surrounding the Na cations. Each ion was covered with two or three H_2O molecules. Fig. 7 shows a computer graphic of Na-ZSM-5, in which each counter cation is surrounded by two or three water molecules. In the case of Fe-ion-exchanged MFI-type zeolite (i.e. Fe-ZSM-5), the result was quite similar.

On the other hand, water molecules scarcely covered the acid sites in metal-incorporated zeolites even under higher pressure, as shown in Fig. 8. It is thought that the covering causes interference in the contact between reactant molecules and cations in the zeolite. Therefore, the results explain the high tolerance of metallosilicate catalysts to water vapor in a higher temperature range, i.e. H-Co-silicate in the NO conversion reaction [13].

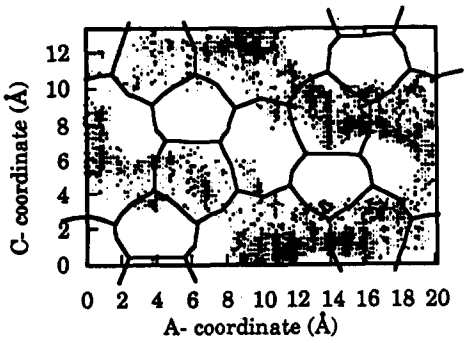

Fig. 8. Distribution of water molecules adsorbed on H-ZSM-5 at 300 K under 20 kPa. Amount: 3.726 m/uc. Energy: −8.761 kcal/mol.

Table 1 shows the amounts of H_2O and CH_4 molecules adsorbed on different kind of MFI-type zeolites.The amounts of H_2O molecules were greatly influenced by the nature of exchanged ion or substituted metal, while all the MFI-type zeolites adsorbed approximately the same amounts of CH_4 molecules. This is because the H_2O molecules were adsorbed on the cation sites, but the CH_4 molecules, which do not have dipole moment, were adsorbed on oxygen atoms inside the pores.

4. Conclusion

The properties of acid sites in metallosilicates can be more precisely depicted by using NH_3 adsorption, calculated by means of the Monte Carlo method. Slight differences in the properties of the acid sites in various kinds of metallosilicates were noticed, and these were used to explain differences in the results of the catalytic reactions of the metallosilicates. We believe that computer simulations will enable us to gain a better understanding into the properties of zeolitic catalysts and that they will have great potential in contributing to the design of zeolite catalysts and catalytic reactions in the future.

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