Preparation of Metallosilicates with ZSM-5 Type Structure by Atom-Planting Method

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(Received October 18, 1990)

Aluminosilicates, gallosilicates, and indosilicates with the ZSM-5 type structure were prepared by the "Atom-Planting method". The introduction of metal cations into the framework of highly siliceous ZSM-5 zeolites was confirmed by IR and unit cell volume measurements. The acidic properties of these metallosilicates were examined by pyridine-IR and NH_3-temperature programmed desorption spectroscopies. The increasing order of the acid strengths of the metallosilicates is indosilicate<gallosilicate<aluminosilicate.

The framework composition of molecular-sieve materials is an important factor which can affect the physical and chemical properties of these materials. An aluminosilicate zeolite offers the ion-exchange properties, high acidity, and shape-selective structural features desired by those working in the areas of adsorption and catalysis. However, modifications and subsequent improvements of these properties have served as a driving force for changing the composition of the zeolites. There have been many studies in which silicon or aluminium in the framework of synthetic zeolites were replaced by some elements such as B, Be, Cr, Ge, Fe, Ga, P, Ti, V, Zr, etc.[1] These molecular sieves are generally synthesized hydrothermally. Jacobs et al. have discussed the probability of an isomorphous substitution of an element on the basis of a simplified version of Pauling's minimum radius ratio; they concluded that molecular sieves having elements with ionic radii between 0.020 and 0.061 nm can be obtained.[2] Since trivalent ions, such as aluminium ions, replace tetravalent silicium ions at the tetrahedral framework positions, the framework bears a net negative charge, which must be compensated for by counter cations. Brønsted acid sites occur in metallosilicates when the cations balancing the framework anionic charge are protons. Chu and Chang have reported that the strength of Brønsted acid sites on a series of the metallosilicates with the ZSM-5 type structure increases according to $B(OH)Si \ll Fe(OH)Si < Ga(OH)Si < Al(OH)Si$.[3]

It has been reported that aluminium atoms are introduced into the framework of a highly siliceous ZSM-5 zeolite by alumination with $AlCl_3$ vapor at elevated temperatures,[4—10] and that not only Brønsted acid sites, but also Lewis acid sites, are generated.[6—9] For the introduction of aluminium into the framework, Chang et al. have reported that aluminium atoms can be introduced by the reaction of four terminal SiOH groups, the so-called "hydroxyl nest", with $AlCl_3$.[4] We have also discussed the mechanism for alumination, suggesting that aluminium atoms can be introduced into defect sites (including the hydroxyl nests) of the framework.[9,10] Kraushaar et al. have carried out a silylation of the highly siliceous ZSM-5 with trimethylchlorosilane, analyzed the products by ^{29}Si cross polarization MAS NMR, and proposed the existence of hydroxyl nests in the zeolitic framework.[11]

If some atoms other than silicon and aluminium can be introduced into the defect sites of the framework by treatments with metal chloride at elevated temperature, it will be possible to obtain metallosilicates. We call the preparation method the "Atom-Planting method". We have succeeded in obtaining an antimonosilicate with the ZSM-5 type structure by means of this atom-planting method.[12] The antimonosilicate has never been synthesized hydrothermally, probably because the antimony(III) cation is too large (0.090 nm). In a similar way, Kraushaar and van Hooff have reported that titanosilicate can be prepared by a subsequent dealumination of a ZSM-5 zeolite having a relatively high aluminium content with hydrochloric acid and reaction with titanium tetrachloride vapor at high temperatures.[13]

In this paper, we report that the preparation of not only aluminosilicate, but also gallosilicate and indosilicate, with the ZSM-5 type structure by the atom-planting method. Moreover, we discuss the acidic properties of these metallosilicates.

Experimental

Materials. High-purity grade gallium trichloride and indium trichloride were used without further purification. Aluminium trichloride was sublimed in order to remove any impurities. High-purity grade pyridine was thoroughly degassed several times by condensing with liquid nitrogen, and then evacuated and melted before use.

The parent highly siliceous ZSM-5 zeolite was prepared in the laboratory as previously described.[14] The Si/Al atomic ratio of the parent ZSM-5 zeolite was 870.

Atom-Planting Procedure. A 2 g sample of the parent highly siliceous ZSM-5 zeolite (powder form) was placed in a vertical quartz tube reactor and dehydrated for 4 h at 773 K in a stream of dry helium. After dehydration, the temperature was brought to an atom-planting temperature, 923 K; dry helium was then passed through a metal chloride container. The metal chloride container was heated to achieve a vapor pressure of 11 kPa. The gas line between the container and the reactor was heated to prevent vapor condensation. The parent ZSM-5 was treated with metal chloride for 2 h and then purged with dry helium at the atom-planting temperature for 1 h to remove any residual metal chloride. The samples, thus treated, were then cooled to room temperature in dry helium stream. These samples were transformed into the NH_4^+-form by a cation-exchange procedure with 0.1 M NH_4NO_3 at 343 K for 36 h (1 M=1 mol dm^{-3}), washed with a large amount of deionized water and then dried in air at 383 K for 16 h.

Analysis of Samples. The amounts of metals in the bulk phase were determined by atomic absorption spectrophotometry. X-Ray diffraction was used to determine the crystallinity and unit-cell volumes of samples. Lead nitrate was used as an internal standard for the determination of the unit-cell volumes. The surface area of the samples were determined by applying the N_2 adsorption method at 77 K.

Infrared Measurements. Infrared spectra were measured at 4 cm^{-1} resolution on a JASCO IR-810 Spectrometer. The IR cell used was fitted with KBr windows and connected to a high-vacuum system. A 20 mg sample of the zeolite powder was accurately weighed, and then pressed into a 15 mm-diameter self-supported wafer. This wafer was placed in the IR cell and evacuated at 773 K for 1.5 h before measurements. In observations of adsorbed pyridine on samples, a wafer evacuated at 773 K for 1.5 h was exposed to pyridine vapor (1.3 kPa) at 423 K for 1 h; the IR cell was then evacuated at 423 K for 1 h, followed by desorption succesively at 523, 623, 673, 723, 773 K for 1 h in each case. All IR spectra were recorded at room temperature.

Temperature Programmed Desorption (TPD) of Ammonia. Ammonia-TPD experiments were performed using a conventional static-adsorption system connected to a quadrupole mass spectrometer through a high-vacuum line. Samples evacuated at 773 K for 1 h were exposed to a 21 kPa of ammonia gas at 423 K for 0.5 h, evacuated for 1 h at 423 K, and then cooled to room temperature. Spectra were obtained at a heating rate of 10 K min^{-1} from 314 to 848 K.

Results and Discussion

Preparation of Metallosilicates. The amounts of metals in the bulk phase of the atom-planted samples are shown in Table 1. The samples planted with aluminium, gallium, and indium are denoted by AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z, respectively. The order of the amounts of introduced metals in the bulk phase were AP(Al)-Z>AP(Ga)-Z>AP(In)-Z, when these samples were prepared under the same conditions. Samples treated with metal chlorides were rinsed with 0.1 M NH_4NO_3. Therefore, the introduced metals existed in the framework sites of the ZSM-5 zeolite and/or non-framework sites except ion-exchange sites. These atom-planted sample were checked by powder X-ray diffraction for crystallinity, which was uniformly good. Moreover, the surface areas of the atom-planted samples were almost the same as that of the parent ZSM-5, as shown in Table 1. Consequently, the structure of the ZSM-5 zeolite was not destroyed by the atom-planting method.

Since trivalent ions are introduced into the tetrahedral framework sites, acidic OH groups responsible for the Brønsted acid sites should be generated. In addition, the frequency of the acidic OH groups in the IR spectra can be varied by substitution with Me^{3+} of different nature. The IR spectra in the hydroxyl stretching region for the parent highly siliceous ZSM-5 (Si/Al=870) and the atom-planted samples [AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z] are depicted in Fig. 1. The parent ZSM-5 (spectrum a) showed only one band at 3740 cm^{-1} due to non-acidic silanol groups.[15] The IR

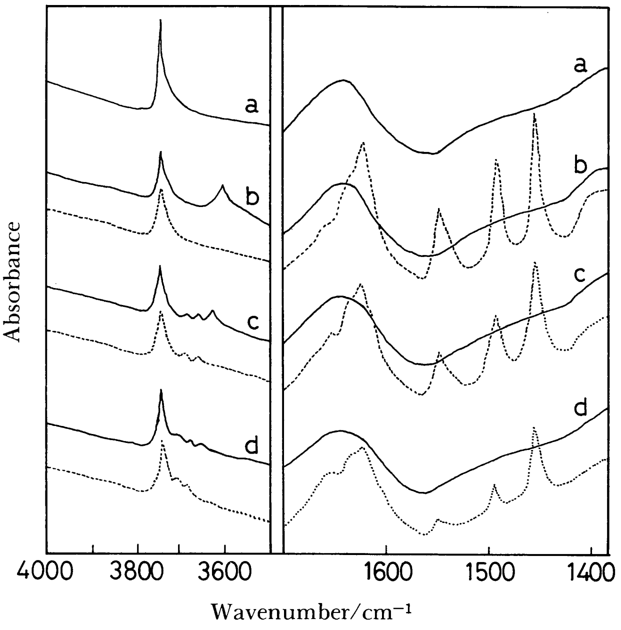

Fig. 1. Infrared spectra in the hydroxyl stretching region for parent ZSM-5 and the atom-planted samples: (a) parent (Si/Al=870), (b) AP(Al)-Z, (c) AP(Ga)-Z, (d) AP(In)-Z. Dotted lines show IR spectra following pyridine adsorption.

Table 1. Chemical and Physical Properties of the Samples Investigated

Sample	Metal concn	Surface area	Unit-cell				Amount of acid sites/mmol g^{-1}
			Dimensions/Å			Vol/Å^3	
	mmol g^{-1}	m^2 g^{-1}	a	b	c		
Parent ZSM-5	0.02 (Al)	448	20.22	20.11	13.08	5320	0.01
AP(Al)-Z	0.74 (Al)	415	20.28	20.18	13.04	5336	0.29
AP(Ga)-Z	0.30 (Ga)	422	20.32	20.10	13.11	5354	0.16
AP(In)-Z	0.24 (In)	431	20.40	20.09	13.13	5382	0.14

spectrum for the AP(Al)-Z exhibited a new band at 3610 cm^{-1} together with the band at 3740 cm^{-1}. The 3610 cm^{-1} band is attributed to the framework Al(OH)Si groups responsible for Brønsted acid sites.[15] In the IR spectrum of pyridine adsorbed on AP(Al)-Z, we observed an absorption band at 1545 cm^{-1}, which was attributed to pyridinium ion;[16] the absorption band at 3610 cm^{-1} disappeared. These facts show the introduction of the Al^{3+} into the framework by the atom-planting method.

The IR spectrum for the AP(Ga)-Z exhibited new bands at 3625, 3660, and 3690 cm^{-1} together with the band at 3740 cm^{-1}. On the IR spectrum of pyridine adsorbed on the AP(Ga)-Z, we observed the 1545 cm^{-1} band; the band at 3625 cm^{-1} disappeared. Chu and Change have demonstrated that in a gallosilicate with the ZSM-5 type (MFI) structure, the H^+ form has a characteristic band at 3620 cm^{-1} attributable to the framework Si(OH)Ga.[3] These facts indicate the introduction of Ga^{3+} into framework by the atom-planting method.

The spectrum of the AP(In)-Z exhibited new bands at 3650, 3680, and 3705 cm^{-1}, together with the 3740 cm^{-1} band. In the IR spectrum of pyridine adsorbed on the AP(In)-Z, we observed the 1545 cm^{-1} band; the 3650 cm^{-1} band disappeared. This fact suggests that the introduction of In^{3+} into the framework by the atom-planting method.

When aluminium, gallium, and indium atoms are introduced into the framework of the parent ZSM-5, the unit-cell volumes of the atom-planted samples should become more than that of the parent ZSM-5, because the ionic radii of Al^{3+} (0.053 nm), Ga^{3+} (0.061 nm), and In^{3+} (0.076 nm) are larger than that of Si^{4+} (0.040 nm). As shown in Table 1, the unit-cell volumes of these atom-planted samples were more than that of the parent ZSM-5. These facts also suggest that aluminium, gallium, and indium are introduced into the framework. From these results, it is apparent that aluminosilicate, gallosilicate, and indosilicate with the ZSM-5 type structure can be prepared by the atom-planting method.

The bands at 3660 and 3690 cm^{-1} for the AP(Ga)-Z, and at 3680 and 3705 cm^{-1} for the AP(In)-Z were attributed to non-acidic OH groups, since these bands were not affected by the adsorption of pyridine. Metal atoms may be introduced not only into the framework sites, but also into the non-framework sites, as was observed in the case of the aluminium-planting.[9] The bands responsible for the non-acidic OH groups may be due to some hydroxylated metal-containing species in the non-framework. In the spectra of the pyridine adsorbed on the AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z, we also observed the adsorption band of the pyridine coordinated with Lewis acid sites at 1455 cm^{-1}.[16] These facts indicate that not only Brønsted acid sites but also Lewis acid sites are generated by the atom-planting method. A part of metal introduced into the non-framework sites may be responsible for the Lewis acid sites.

We have discussed the mechanism for alumination (Al-planting) of the highly siliceous ZSM-5 with $AlCl_3$, and suggested that aluminium atoms are introduced into defect sites of the highly siliceous ZSM-5.[9,10] The amount of defect sites in the framework of highly siliceous ZSM-5 can be changed by controlling the synthetic conditions of the zeolites.[10,17] The amount of defect sites was measured through the exchange of oxygen isotopes between the zeolitic framework and $C^{18}O_2$.[10,17,18] When the plantings of gallium and indium into the highly siliceous ZSM-5 with a very small amount of the defect sites were carried out at 923 K, the adsorption bands attributed to the acidic OH groups could not be detected. Hence, gallium and indium could be poorly introduced into the framework of the highly siliceous ZSM-5 with a very small amount of the defect sites. Endoh et al. have reported the galliation of the highly siliceous ZSM-5 by a treatment with NaOH solution containing gallium ions, and concluded that the reactivity of the zeolite for the galliation may depend upon the amount of the defect sites.[18] Consequently, for the mechanism of the planting of gallium and indium atoms in the zeolitic framework, we suggest that gallium and indium atoms are planted solely in the defect sites of the zeolite.

We have also reported that a considerable amount of aluminium is introduced into the non-framework sites by alumination, and that the introduction of aluminium into the non-framework occurs by a reaction of the terminal SiOH groups on the external surface and/or non-intact Si–O–Si bonds with $AlCl_3$.[9,10] In the IR spectra, changes in the terminal SiOH region may provide information related to the mechanism of the introduction of atoms into the non-framework sites. We have reported that the band at 3740 cm^{-1} can be attributed not to hydroxyl nests (defect sites), but to both isolated SiOH groups on the external surface and intracrystalline isolated SiOH groups.[17] Due to the atom-planting, the intensity of the 3740 cm^{-1} band decreased. This fact suggests that a part of the metal atoms in the non-framework sites is caused by a reaction of the terminal SiOH groups on the external surfaces with metal chlorides.

The amount of the Brønsted acid sites may correspond to the amount of the metal in the framework sites. The relative amount of the Brønsted acid sites was roughly estimated on the basis of the integrated absorbances of the acidic OH bands. The area of the Al(OH)Si band for the AP(Al)-Z was about 2 times as much as that of the Ga(OH)Si band for the AP(Ga)-Z, and was about 5 times as much as that of the In(OH)Si band for the AP(In)-Z. These facts suggest the order of the amonts of metal atoms introduced into the framework were AP(Al)-Z>AP(Ga)-Z>AP(In)-Z, although each parent ZSM-5 has the same amount of defect sites. This order may be explained as follows: the larger radius of metal cation corresponds to the lower thermostability of the metallosilicate or to the less amount of defect sites available for the atom planting.

Acidic Properties of Metallosilicates. The acidic properties of metallosilicates AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z were examined from the infrared spectra of the adsorbed pyridine and the spectra of temperature-programmed desorption for ammonia. In the IR spectra in the OH stretching region, we observed a band at 3610 cm^{-1} due to Al(OH)Si, a band at 3625 cm^{-1} due to Ga(OH)Si, and a band at 3650 cm^{-1} due to In(OH)Si. The fact that the 3625 cm^{-1} band due to Ga(OH)Si and the 3650 cm^{-1} band due to In(OH)Si appear at higher frequencies than the 3610 cm^{-1} band due to Al(OH)Si indicates that the OH bonds in the Ga(OH)Si and In(OH)Si are more covalent than those in the Al(OH)Si and, hence, less acidic.

The strength distribution of Brønsted and Lewis acid sites can be measured from the thermodesorption of pyridine. On IR spectra of pyridine adsorbed on metallosilicates, we can observe the absorption bands of pyridinium ion (PyH$^+$) at 1545 cm^{-1} and of the pyridine coordinated with Lewis acid sites (PyL) at 1455 cm^{-1}. As the desorption temperature increases, only pyridine molecules adsorbed on stronger sites will remain. Figure 2 shows the absorbances of the PyH$^+$ and PyL bands for the AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z after pyridine was desorbed at progressively higher temperatures. As shown in Fig. 2a, it is apparent that the order of the acid strength of Brønsted acid sites are In(OH)Si<Ga(OH)Si<Al(OH)Si. These results are consistent with the hypothesis from the IR spectra in the OH stretching region. In addition, as shown in Fig. 2b, it is apparent that these metallosilicates prepared by the atom-planting method have a large amount of Lewis acid sites, and that the order of the acid strength of Lewis acid sites are AP(In)-Z< AP(Ga)-Z<AP(Al)-Z.

The ammonia-TPD spectra for the AP(Al)-Z, AP(Ga)-A, and AP(In)-Z are depicted in Fig. 3. The spectrum for the AP(Al)-Z had not only a main peak at 543 K but also a shoulder peak at 643 K. We have reported that AP(Al)-Z has stronger acid sites than those on ZSM-5 zeolites, which are prepared by hydrothermal synthesis. The shoulder peak at 643 K indicates that the strong acid sites are generated by the

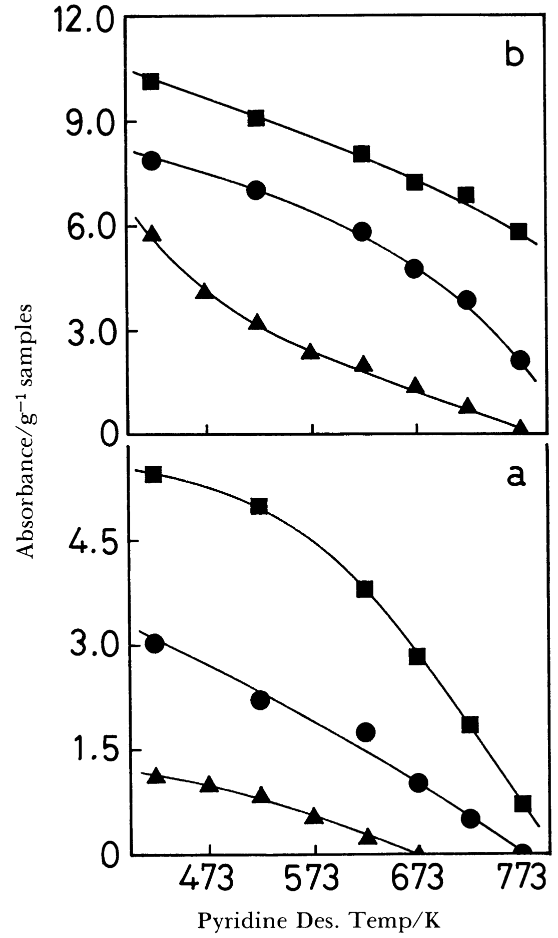

Fig. 2. Absorbance per gram of the AP(Al)-Z (■), the AP(Ga)-Z (●), and the AP(In)-Z (▲) on Brønsted acid sites (band at 1545 cm^{-1}); (a), and Lewis acid sites (band at 1455 cm^{-1}); (b), after desorption at 423—773 K.

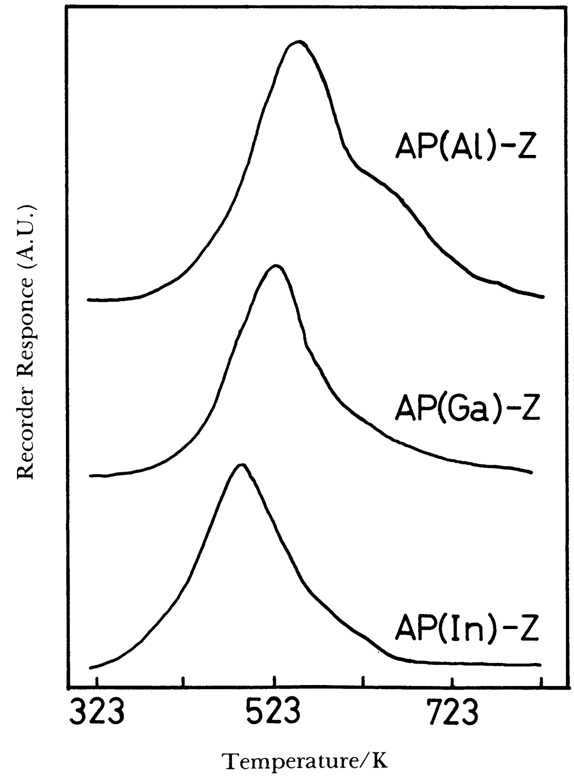

Fig. 3. NH$_3$-TPD spectra for the AP(Al)-Z, AP(Ga)-Z, and AP(In)-Z.

Al-planting. The spectra for the AP(Ga)-Z and for the AP(In)-Z had a single peak at 523 K and a single peak at 483 K, respectively. These facts indicate that the acid strength of the metallosilicates is ordered as follows: AP(In)-Z<AP(Ga)-Z<AP(Al)-Z.

The amount of acid sites was evaluated from the amount of ammonia desorbed during the TPD measurements. The evaluated amounts of acid sites on the metallosilicates are given in Table 1, together with the amounts of bulk metals. The amount of metal in the bulk phase was 1.7—2.5 times as much as that of the acid sites. Therefore, a part of the introduced metals does not contribute to the generation of the Brønsted or Lewis acid sites.

References

1) R. M. Barrer, "Hydrothermal Chemistry of Zeolites," Academic Press, London (1982), p. 251.

2) N. Tielen, M. Geelen, and P. A. Jacobs, *Acta Phys. Chem.*, **31**, 1 (1985).

3) C. T. -W. Chu and C. D. Chang, *J. Phys. Chem.*, **89**, 1569 (1985).

4) C. D. Change, C. T. -W. Chu, J. N. Miale, R. F. Bridger, and R. B. Calvent, *J. Am. Chem. Soc.*, **106**, 8143 (1984).

5) R. M. Dessau and G. T. Kerr, *Zeolites*, **4**, 315 (1984).

6) M. W. Auderson, J. Klinowski, and L. Xinsheng, *J. Chem. Soc., Chem. Commun.*, **1984**, 1596.

7) S. Namba, K. Yamagishi, and T. Yashima, *Chem. Lett.*, **1987**, 1109.

8) T. Yashima, K. Yamagishi, S. Namba, S. Nakata, and S. Asaoka, *Stud. Surf. Sci. Catal.*, **37**, 175 (1988).

9) K. Yamagishi, S. Namba, and T. Yashima, *J. Catal.*, **121**, 47 (1990).

10) K. Yamagishi, S. Namba, and T. Yashima, *Shokubai*, **30**, 440 (1988).

11) B. Kraushaar, L. J. M. Van de Ven, J. W. De Haan, and J. H. C. Van Hooff, *Stud. Surf. Sci. Catal.*, **37**, 167 (1988).

12) K. Yamagishi, S. Namba, and T. Yashima, *Stud. Surf. Sci. Catal.*, **48**, 459 (1989).

13) B. Kraushaar and J. H. C. Van Hooff, *Catal. Lett.*, **1**, 81 (1988).

14) T. Yashima, Y. Sakaguchi, and S. Namba, *Stud. Surf. Sci. Catal.*, **7**, 739 (1980).

15) P. A. Jacobs and R. Von Ballmoos, *J. Phys. Chem.*, **86**, 3050 (1982).

16) E. P. Parry, *J. Catal.*, **2**, 371 (1963).

17) K. Yamagishi, S. Namba, and T. Yashima, *J. Phys. Chem.*, **95**, 872 (1991).

18) A. Endoh, K. Nishimiya, K. Tsutsumi, and T. Takaishi, *Stud. Surf. Sci. Catal.*, **46**, 779 (1989).