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Liquid Phase Reaction of Acetaldehyde over Various ZSM-5 Zeolites

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Acetaldehyde reacted over various ion-exchanged ZSM-5 zeolites at 15±0.5 °C under a nitrogen pressure of 1×10^5 Pa. The main products of the reaction were $2\alpha,4\alpha,6\alpha$-trimethyl-1,3,5-trioxane (*cis*-paraldehyde) and its isomer, $2\alpha,4\alpha,6\beta$-trimethyl-1,3,5-trioxane (*trans*-paraldehyde). Several rare earth ZSM-5 (REZSM-5) and M/HZSM-5 (partially proton exchanged ZSM-5) catalysts exhibited high activities for *trans*-paraldehyde formation. The reaction appeared to proceed by the following scheme: *cis*-paraldehyde ← acetaldehyde →*trans*-paraldehyde. A comparison of the catalytic activity with the IR intensity of acidic OH groups over the catalyst suggested that the active site for *cis*-paraldehyde formation was the Brönsted acidic site, while the active site for *trans*-paraldehyde formation was a Brönsted acid site in the neighborhood of an M^{n+} site in the ZSM-5 zeolite pore.

The characteristic molecular shape selectivities of the ZSM-5 zeolite have attracted world-wide attention, and many papers[1)] reporting on the catalysis of the ZSM-5 zeolite have been published. However, most of the reactions which have been studied were gas-phase reactions. Information concerning liquid-phase catalysis over the ZSM-5 zeolite is still scarce in the literature, though, Izumi et al.[2—5)] studied certain organic reactions in solutions using other kinds of catalysts (zeolite, alumina, and clay).

Hitherto, the present authors[6—11)] have clarified various aspects of the adsorption characteristics of ion-exchanged ZSM-5 zeolites. In this work. the authors directed their attention to the catalytic properties of ion-exchanged ZSM-5 zeolites. Thus, acetaldehyde was reacted over the ZSM-5 catalyst in the liquid phase, and the effects of the ion exchange upon the activity and selectivity were studied. The results of an IR study of the catalysts are also presented for consideration.

Experimental

1 Catalysts and Substrate. The catalysts used in the present study can be classified into three groups, as shown in Table 1. The group-I catalysts were prepared from NaZSM-5 using an ordinary ion-exchange method. Since details concerning the ion-exchange procedure have already been reported elsewhere,[7,8)] only a short description of the ion-exchange is given in the table. Regarding group-I catalysts, the REZSM-5 (RE=La, Ce, Nd, Y) catalysts are worth considering. Namely, these catalysts were found to contain considerable amounts of Na^+, indicating that RE cations can exchange only part of the Na^+ cation contained in the starting NaZSM-5. It can therefore be expected that if HZSM-5 is used as the starting zeolite, only some of the contained protons would be exchanged by RE^{3+}, i. e. a catalyst containing both RE^{3+} and H^+ would be obtainable. Thus, group-II catalysts (RE/HZSM-5) were designed and prepared. Group-III catalysts contain both H^+ and M^+ (M=Li, Na, Cs). The degree of ion-exchange has been determined by analyzing samples using either atomic absorption spectroscopy (Hitachi 180-80) or X-ray fluorescence spectroscopy (JEOL JSX-60X).

Acetaldehyde was commercially obtained (E. Merck A. G.) and used as a reactant after the treatment described in the following section.

2 Apparatus and Procedure. Figure 1 shows the apparatus used in the catalytic study. It is made of Pyrex glass and consists of an evacuation system and a reaction system. The former system is capable of evacuating the entire system to below 1 Pa. The latter system (reaction system) comprises an acetaldehyde reservoir (A), a reaction vessel (B), nitrogen reservoir (C), and sampler (E). A side tube (B′) was attached in order to restrain the magnetic stirrer (S) from heating conditions during the catalyst pretreatment in B. A greaseless stopcock (D) was placed in the glass line connecting A and B.

Prior to each catalytic run, an appropriate amount (10

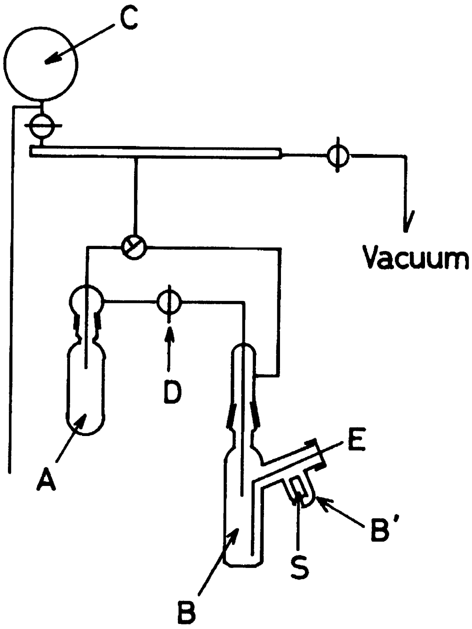

Fig. 1. Experimental set up for catalytic runs: A: acetaldehyde reservoir, B: reaction vessel, B′: side tube, C: nitrogen reservoir, D: greaseless stopcock, E: sampler, S: stirrer.

Table 1. Catalyst Used in the Present Study

Catalyst	Contents of cations [a]		Solution		Outline of preparation procedure	Group
	M^{n+}/Al_{flame}	H^+/Al_{flame}	mol dm^{-3}			
NaZSM-5[b]	1.0	0.0	—		Original	I
HZSM-5	0.0	1.0	HCl	(0.1)		
LiZSM-5	1.18	0.20	LiCl	(0.3)		
KZSM-5	0.94	0.0	KCl	(1.0)		
CsZSM-5	1.19	0.0	CsCl	(0.3)		
MgZSM-5	0.6	0.32	$Mg(NO_3)_2$	(0.4)		
CaZSM-5	0.54	0.08	$CaCl_2$	(0.6)	Parent NaZSM-5 was treated 7 times (each at 343 K for 8 h) by the solution indicated here, then the product was thoroughly washed with distilled water and dried overnight at about 110 °C.	
SrZSM-5	0.64	0.05	$Sr(NO_3)_2$	(0.3)		
BaZSM-5	0.58	0.04	$BaCl_2$	(0.4)		
MnZSM-5	0.51	0.42	$MnCl_2$	(0.3)		
ZnZSM-5	0.55	0.48	$Zn(NO_3)_2$	(0.5)		
NiZSM-5	0.56	0.57	$NiCl_2$	(0.5)		
CoZSM-5	0.34	0.60	$CoCl_2$	(0.5)		
CuZSM-5	0.73	0.89	$CuSO_4$	(0.5)		
CrZSM-5	0.11	1.02	$CrCl_3$	(0.2)		
AlZSM-5	0.09	1.01	$Al_2(SO_4)_3$	(0.5)		
LaZSM-5	0.11	0.12	$La(NO_3)_3$	(0.3)		
CeZSM-5	0.10	0.19	$CeCl_3$	(0.1)		
NdZSM-5	0.08	0.05	$NdCl_3$	(0.1)		
YZSM-5	0.04	0.06	$Y(NO_3)_3$	(0.1)		
La/HZSM-5[c]	0.08	0.86	$La(NO_3)_3$	(0.3)	Form HZSM-5	II
Ce/HZSM-5[c]	0.04	0.93	$CeCl_3$	(0.1)	Form HZSM-5	
Nd/HZSM-5[c]	0.04	0.97	$NdCl_3$	(0.1)	Form HZSM-5	
Li/HZSM-5[c]	—		$LiCl+NH_4Cl$	(0.1)	Form LiZSM-5	III
Na/HZSM-5[d]	—		$NaCl+NH_4Cl$	(0.1)	Form NaZSM-5	
Cs/HZSM-5[d]	—		$CsCl+NH_4Cl$	(0.1)	Form NH_4ZSM-5	

a) Cation contents in the table, atomic ratios of a cation to aluminum in ZSM-5 framework (where M^{n+} is a metal ion introduced by ion exchange), were obtained by X-ray fluorescence spectroscopy or atomic absorption spectroscopy (for concentration of metal ion) and IR absorption of acidic OH-vibration (for concentration of proton). b) Kindly presented by Chem. Res. Lab. Tosoh Co., Ltd., $SiO_2/Al_2O_3=23.3$ in mole ratio. c) Part of proton in the HZSM-5 was exchanged by RE^{3+}. The HZSM-5 used was prepared in advance by treating NaZSM-5 with a NH_4Cl solution. d) M′ZSM-5 (M′=Li, Na, or NH_4) was immersed in a mixed solution of NH_4Cl and MCl (M=Li, Na, or Cs; total cation concentration=0.1 mol dm^{-3}, 70 °C, 8 h) and washed with distilled water several times to remove Cl^- ion. By varying the ratio of MCl to NH_4Cl, two samples for Li/HZSM-5, ten samples for Na/HZSM-5, and five samples for Cs/HZSM-5 were prepared. Finally, the zeolite was calcined at 500 °C under an N_2 atmosphere to decompose NH_4^+ to H^+.

ml) of acetaldehyde taken in A was degassed by repeated evacuation at liquid nitrogen temperature and warming to ambient temperature. The desired amount (about 0.2 g) of the catalyst was then taken into B and degassed at 350 °C. After degassing for 4 h, the reaction vessel (B) was cooled to a predetermined reaction temperature (15 °C). The stopcock (D) was then opened and A was warmed to about 50 °C. When an appropriate amount of acetaldehyde was evaporated from A and condensed in B, the stopcock (D) was closed and 1×10^5 Pa of nitrogen was introduced into the reaction vessel (B). The stirrer (S) was then magnetically carried from B′ to B.

The reaction was initiated by driving the stirrer. During the reaction, a small amount of the reacting liquid was withdrawn from B with a syringe, and served for gas chromatography (Hitachi 163 instrument). The conditions of the gas chromatographic analysis were as follows: column=PEG 20-M 2m; temperature=50 °C, and raised to 180 °C at a rate of 5 °C min^{-1} after 13 min from sample injection; injection temperature=230 °C; carrier gas=He (30 ml min^{-1}), and detector=FID. The chromatographic analysis was supplemented by gas chromatography-mass spectrometry (JEOL JMS-D300 instrument).

3 Characterization of Catalyst. The IR spectra of the catalysts were recorded on a JEOL JIR-100 FT-IR spectrometer. For this experiment, the catalyst powder was pressed into a disk (13 mm in diameter and about 100 µm in thickness) and placed in an IR cell (reported in earlier papers[6,7]). The sample disk was heated at 300 °C for 8 h under a vacuum of 1×10^{-3} Pa, the IR spectra were then recorded at room temperature and under the same vacuum condition. In addition, acid and base properties were investigated concerning some of the catalysts; measurements of the IR spectra of the adsorbed pyridine and the adsorbed CO_2 were also undertaken.

Results and Discussion

1 Reaction Products. The main products of the reaction were (2α,4α,6α)-trimethyl-1,3,5-trioxane (*cis*-paraldehyde; Fig. 2-I) and its isomer, (2α,4α,6β)-trimethyl-1,3,5-trioxane (*trans*-paraldehyde; Fig. 2-II).

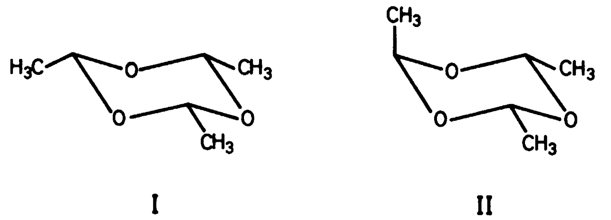

Fig. 2. Molecular structure of paraldehyde; I: 2α,4α, 6α-trimethyl-1,3,5-trioxane (*cis*-paraldehyde), II: 2α, 4α,6β-trimethyl-1,3,5-trioxane (*trans*-paraldehyde).

Although metaldehyde was also produced, its content in the products was negligibly small.

Table 2 summarizes the conversions (weight basis) of acetaldehyde to *cis*-paraldehyde (I) and to the *trans*-paraldehyde (II) during a reaction period of 500 min. This table also includes the integrated intensity of the IR band of the acidic OH of the catalyst. It can be seen that not only the degree of acetaldehyde conversion, but also the product selectivity were strongly affected by the cation species incorporated in the catalyst: The acetaldehyde conversion was very high and the *cis*-paraldehyde selectivity was almost 100% for every reaction over HZSM-5, AlZSM-5, CrZSM-5, and CuZSM-5; although the aldehyde conversion was relatively small, the *trans*-paraldehyde selectivity was measurable in reactions over MgZSM-5, SrZSM-5, MnZSM-5, CoZSM-5, NiZSM-5, and ZnZSM-5, as well as over REZSM-5 (RE = a rare earth element). Neither *cis*-paraldehyde nor *trans*-paraldehyde was formed over AZSM-5 (A = an alkaline metal element), expect for LiZSM-5, which gave small, but measurable, conversions to *cis*-paraldehyde and *trans*-paraldehyde.

Interestingly, the RE/HZSM-5 (RE = La, Ce, or Nd) catalysts exhibited a higher activity for *trans*-paraldehyde formation than did the REZSM-5 catalysts. This appears to be worth noting. The former catalyst contains RE^{3+} and H^+ while the latter catalyst contains RE^{3+} and Na^+ as described in Experimental Section. It is strongly suggested that the acid-base properties of the zeolite surface determine the (*cis*-paraldehyde/*trans*-paraldehyde) ratio in the acetaldehyde reaction.

It appears that *trans*-paraldehyde and *cis*-paraldehyde were produced via the following parallel reaction pathway:

cis-paraldehyde ← acetaldehyde → *trans*-paraldehyde.

A consecutive reaction pathway (acetaldehyde→*cis*-paraldehyde→*trans*-paraldehyde) is unlikely, since *cis*-paraldehyde is thermodynamically much more stable than *trans*-paraldehyde;[12)] the standard free energy change for the trans–cis isomerization is $-10\ \mathrm{kJ\,mol^{-1}}$, and the corresponding equilibrium constant is 66 at 15 °C. The experimental results shown in Fig. 3 justify the above-mentioned point of view. Both the *cis*-paraldehyde and the *trans*-paraldehyde contents can be extrapolated to their respective initial values, less than 1 and larger than 0 at zero conversion ($X = 0$). The experimental results given in Fig. 3 show another aspect of the activity of the catalyst used. Namely, type-I catalysts appear to have little activity for converting *trans*- to *cis*-paraldehyde. If this was not the case, the *trans*-paraldehyde fraction (II) should rapidly decrease upon increasing the conversion (X).

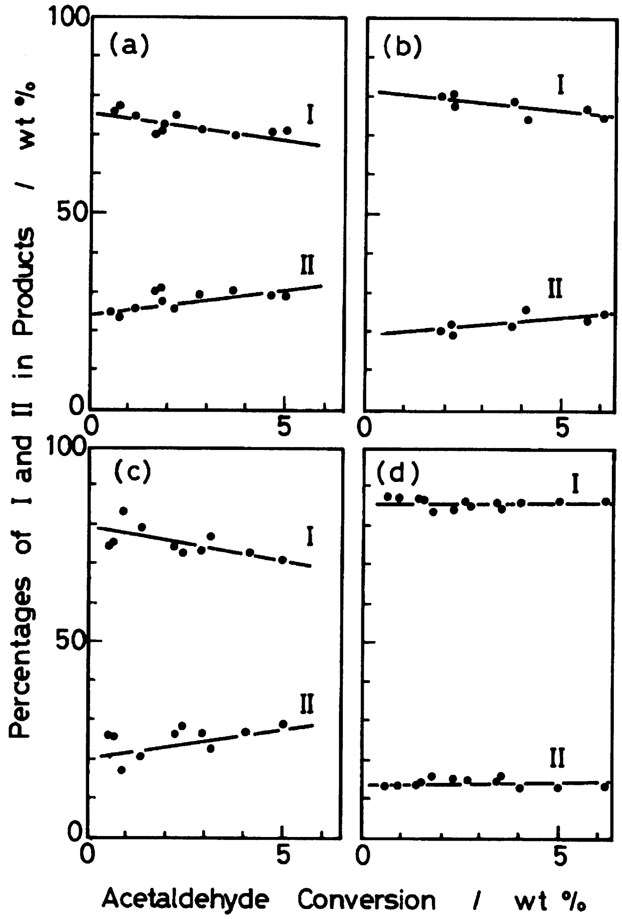

Fig. 3. Product compositions (I/[I+II], II/[I+II]) as a function of acetaldehyde conversion (I represents *cis*-paradehyde, II represents *trans*-paraldehyde); (a): LaZSM-5, (b): CeZSM-5, (c): NdZSM-5, (d): CoZSM-5.

On the other hand, type-II catalyts (RE/HZSM-5) appear to have activities for converting *trans*- to *cis*-paraldehyde, as shown in Fig. 4. The Brönsted acid sites in the RE/HZSM-5 were suspected of causing the trans- to cis- reaction. A test reaction was thus carried out; namely, an acetaldehyde solution containing 25% *cis*-paraldehyde and 7% of *trans*-paraldehyde (68% acetaldehyde) was contacted with an HZSM-5 catalyst. The result shown in Fig. 5 proves that the Brönsted sites really catalyze the trans to cis reaction.

2 Catalytic Activity and Acid-Base Properties of Catalysts. The preceding ideas (Sect. 1) led the authors to a comparison of the catalytic property to the acid-base property of the catalyst. For this purpose, the

Table 2. Results of Catalytic Runs of 500 min

Catalyst	Conversion to I[a]	II[a]	Composition of products II/I	IR intensity of acidic OH
	wt %		weight ratio	cm^{-1} mg^{-1}
HZSM-5	89.4	0	0	1.68
LiZSM-5	0.21	0.11	0.52	(0.38)
NaZSM-5	0	0	—	0.00
KZSM-5	0	0	—	0.00
CsZSM-5	0	0	—	0.00
MgZSM-5	1.06	0.18	0.17	0.60
CaZSM-5	0	0	—	0.15
SrZSM-5	0.13	0.04	0.31	0.09
BaZSM-5	0	0	—	0.08
MnZSM-5	1.40	0.35	0.25	0.79
ZnZSM-5	7.11	0.66	0.09	0.91
NiZSM-5	1.35	0.29	0.21	1.08
CoZSM-5	4.34	0.63	0.15	1.13
CuZSM-5	87.0	0	0	1.68
CrZSM-5	94.3	0	0	1.93
AlZSM-5	89.2	0	0	1.91
LaZSM-5	3.48	1.43	0.41	0.23
CeZSM-5	6.62	2.23	0.34	0.36
NdZSM-5	3.55	1.45	0.41	0.09
YZSM-5	2.13	0.66	0.31	0.11
La/HZSM-5	40.9	6.83	0.17	1.62
Ce/HZSM-5	86.6	0.00	0.00	1.76
Nd/HZSM-5	72.5	3.29	0.05	1.83
Na/HZSM-5	0.87	0.21	0.24	0.03
Na/HZSM-5	1.78	0.33	0.18	0.06
Na/HZSM-5	4.37	1.11	0.25	0.09
Na/HZSM-5	17.0	2.85	0.17	0.25
Na/HZSM-5	23.2	4.65	0.20	0.45
Na/HZSM-5	30.4	5.24	0.17	0.49
Na/HZSM-5	54.8	6.67	0.12	0.92
Na/HZSM-5	57.3	6.48	0.11	1.03
Na/HZSM-5	66.5	6.26	0.09	1.69
Na/HZSM-5	76.5	3.57	0.05	1.98
Cs/HZSM-5	0.63	0.25	0.39	0.05
Cs/HZSM-5	9.78	3.47	0.36	0.20
Cs/HZSM-5	15.9	6.33	0.40	0.19
Cs/HZSM-5	32.9	6.83	0.21	0.39
Cs/HZSM-5	60.5	5.74	0.09	1.24
Li/HZSM-5	75.3	2.91	0.04	0.72
Li/HZSM-5	74.8	3.87	0.05	1.36

a) I represents *cis*-paraldehyde and II represents *trans*-paraldehyde.

intensity of the IR absorption band at 3610 cm^{-1} was used as a measure of the Brönstead acidity.[9,13]

The result given in Fig. 6a provides information concerning the relation between the surface acidity and the selectivity (ratio of the weight fraction of *trans*-paraldehyde to that of *cis*-paraldehyde in the products; trans/cis) of the catalyst. The selectivity of the *trans*-paraldehyde formation decreases as the surface acidity increases, though the data points exhibit considerable scattering.

Figure 6b reveals another aspect of the catalysis of the acid site of ZSM-5. Namely, an increase in the surface acidity above a critical value (ca. 1.3 cm^{-1} g^{-1}) causes an abrupt increase in *cis*-paraldehyde formation. It must be noted, however, that conversion to the *cis*-isomer is measurable, even for a catalyst with a surface acidity smaller than the critical value. Although the non-linear relation between the acidity and the activity shown in Fig. 6b is interesting, the purpose of the present discussion is not to give an analysis of the relation described in the figure. Here, it is sufficient to say that although a high concentration of the Brönsted acid site favors the *cis*-paraldehyde formation, it does not favor *trans*-paraldehyde formation.

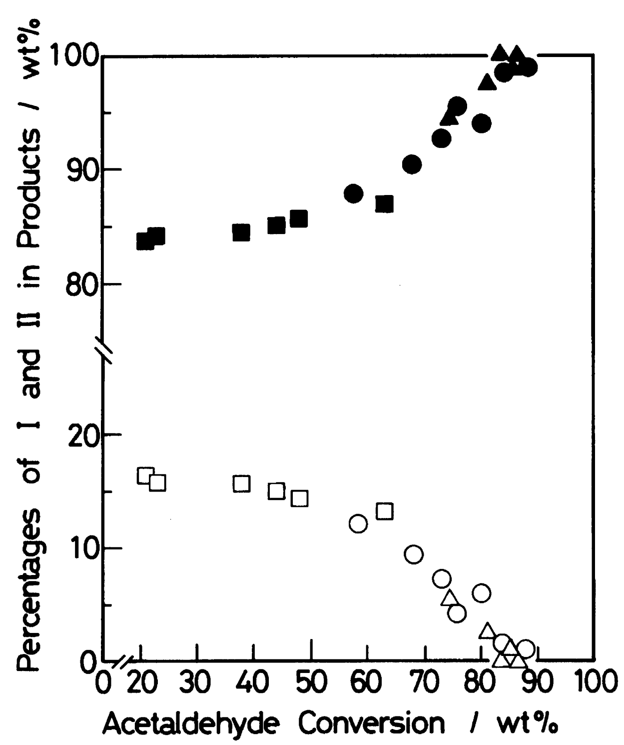

Fig. 4. Product compositions (I/[I+II] : closed symbols and II/[I+II] : open symbols) as a function of acetaldehyde conversion (I represents *cis*-paraldehyde, II represents *trans*-paraldehyde); La/HZSM-5 (□, ■), Ce/HZSM-5 (○, ●), Nd/HZSM-5 (△, ▲).

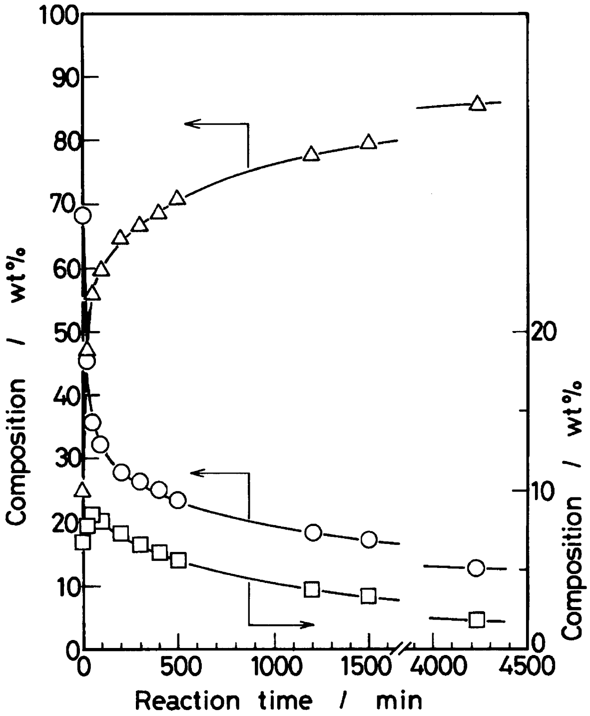

Fig. 5. *trans*-Paraldehyde concentration over an HZSM-5 catalyst as a function of the reaction time; the composition of the starting solution was as follows: acetaldehyde (68%), *cis*-paraldehyde (25%), and *trans*-paraldehyde (7%)); ○ : acetaldehyde, △ : *cis*-paraldehyde, □ : *trans*-paraldehyde.

It has been reported that *trans*-paraldehyde can be synthesized from acetaldehyde in a dilute Na_2CO_3 solution.[14] The surface basicity of the catalyst was therefore suspected of catalyzing *trans*-paraldehyde formation. Unfortunately, however, the surface basicity obtained by a CO_2 adsorption method[15] failded to correlate with the catalytic activity. Furthermore, the La/HZSM-5 catalyst, which was more acidic than LaZSM-5, exhibited a higher activity for *trans*-paraldehyde formation then did the latter catalyst (Table 2). In addition, AZSM-5 (A = an alkali metal ion) zeolites catalysts, which were expected to act as base catalysts, were inactive for *trans*-paraldehyde formation. All of the experimented results described above indicate that *trans*-paraldehyde formation cannot be simply related with the surface basicity.

3 Activation of AZSM-5 Catalysts. As shown in Table 2, neither *cis*-paraldehyde nor *trans*-paraldehyde was formed over AZSM-5 (A = an alkali metal ion) catalysts, i. e. the AZSM-5 catalysts were inactive. These catalysts were found to be activated by introducing proton sites, as shown in Fig. 7. The conversion of acetaldehyde monotonously increased with an increase in the number of acid sites introduced, and no abrupt activity change was found. Such critial acidity, as observed for the polyvalent cation exchanged ZSM-5 series (Fig. 6b), did not exist. Interestingly, however, catalysts activated by the acid sites promoted *trans*-paraldehyde formation. As shown in Fig. 7b, the activity for the *trans*-paraldehyde formation increased upon introducing the Brönsted acid sites, and became maximum at 50% of the proton-exchange. This result probably indicates that a Brönsted acid site in the neighbohood of a metal ion site is required for *trans*-paraldehyde formation. Other explantions are not applicable. For instance, if an isomerization of *trans*-paraldehyde to *cis*-paraldehyde is promoted by a Brönsted acid site, the *trans*-paradehyde formation profile (Fig. 7b) may result. However, this would not be the case due to the following reasons: 1) Isomerization of *trans*-paraldehyde to *cis*-paraldehyde was slow, as shown in Fig. 6; 2) *trans*-Paraldehyde was not detected in the reaction over HZSM-5 catalysts, even at the earliest sampling time (100 min). We can therefore infer that the metal ion existing in the vicinity of the Brönsted site supresses the formation of *cis*-paraldehyde, though details of the function of the metal ion site are not clear at the present stage.

In the present work, the surface concentration of the Lewis acid site in a group-III catalyst was also determined by the pyridine adsorption method.[16] The surface concentration of Lewis acid sites in group-III catalysts increases with an increase in the concentration of Brönsted acid sites; the amounts were fairly smaller than those of the Brönstead acid sites (1/2—1/5). The

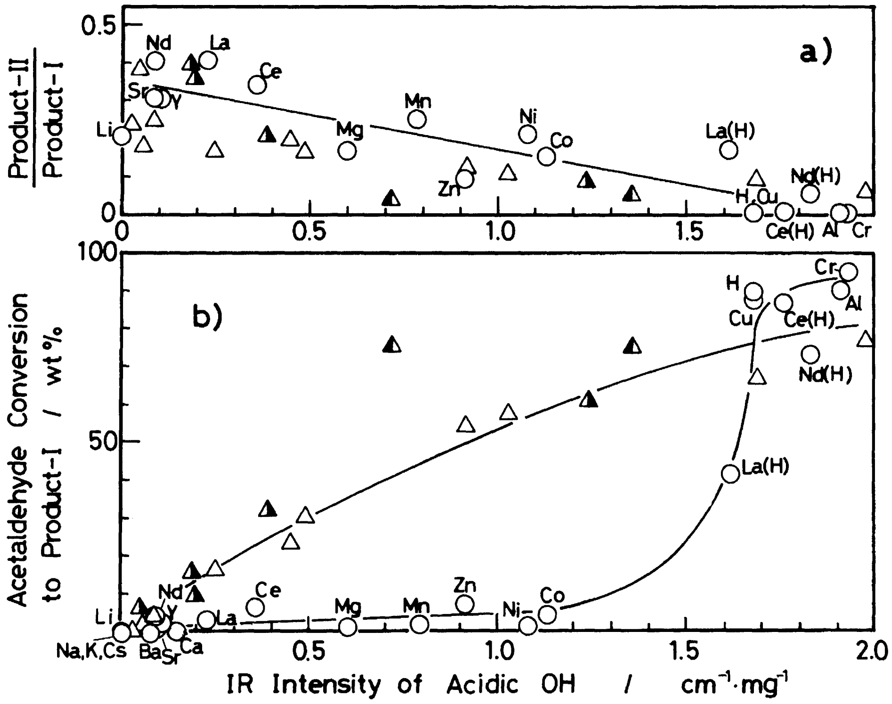

Fig. 6. Effects of the concentration of OH site upon acetaldehyde reaction; (a) : effects upon product composition (trans/cis ratio), (b) : effects upon *cis*-paraldehyde formation; ▲ : Li/HZSM-5, △ : Na/HZSM-5, ▲ : Cs/HZSM-5.

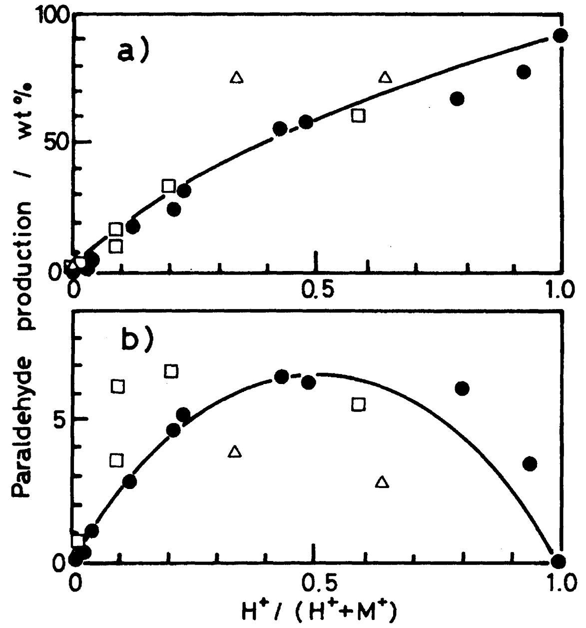

Fig. 7. Effects of the proton site concentration upon *cis*-paraldehyde (a) and *trans*-paraldehyde (b) formation at 500 min of the reaction period; △ : Li/HZSM-5, ● : Na/HZSM-5, □ : Cs/HZSM-5.

results could therefore not be related to the catalytic activity for *trans*-paraldehyde formation.

Conclusion

Reactions of acetaldehyde in the liquid phase were carried out using various ion-exchanged ZSM-5 catalysts. The obtained important results can be summarized as follows: 1) The main products were 2α,4α,6α-trimethyl-1,3,5-trioxane and its isomer, 2α,4α,6β-trimethyl-1,3,5-trioxane. 2) Over most of the catalysts, the reaction proceeds via a parallel pathway, i. e. *cis*-paraldehyde ← acetaldehyde →*trans*-paraldehyde. 3) The active site for *cis*-paraldehyde formation would be the Brönsted acidic site; the active site for *trans*-paraldehyde formation would be the Brönsted acid site in the neighborhood of the M^{n+} site produced over ZSM-5.

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