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Selective alkylation of aniline with methanol over metallosilicates

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The selective alkylation of aniline with methanol was investigated over various metallosilicates synthesized in two different media: alkaline medium (NaOH) and fluorine medium (NH_4F). Through the elemental analysis, XRD, and ^{29}Si MAS NMR, it was thought that all the metallosilicates had MFI zeolite structure and the metals were incorporated in metallosilicate framework successfully. Temperature programmed desorption (TPD) of NH_3 and aniline alkylation suggested that the selectivity for N,N-dimethylaniline (NNDMA) is high when the metallosilicates have a large number of medium acid sites (567–673 K), which means that the medium acid sites play an important role in the production of NNDMA. It was also known that metallosilicates synthesized in fluorine medium have strong acid sites (>773 K) and were deactivated more rapidly than those synthesized in alkaline medium.

Keywords: aniline alkylation; metallosilicate; acidity; NNDMA selectivity

1. Introduction

Toluidine (T), N-methylaniline (NMA), and N,N-dimethylaniline (NNDMA) are the major products in the alkylation of aniline with methanol. They are important intermediates in the manufacture of dyes, plastics and explosives. The liquid phase alkylation process commercialized in 1866 has been extensively used in industry to prepare NNDMA [1]. However, this process had severe corrosion problems due to the use of strong acid as a catalyst at high temperature and pressure. Though the liquid phase reaction gives higher yields than the gas phase reaction, it has many undesired by-products. The gas phase reaction gives NMA [2,3] and NNDMA [4] as major products. In recent years, gas phase alkylation of aniline with NaX, NaY and ZSM-5 was reported [5,6]. Previous studies indicated that the major factors influencing the activity and selectivity of gas phase aniline alkylation are the acid–base property and shape selectivity of the solid catalyst. Through the

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correlation of acidity of ZSM-5, [B]ZSM-5 and ion-exchanged [B]ZSM-5 with the selectivity towards methylated anilines, Woo et al. [7] suggested that strong acid sites, medium acid sites, and weak acid sites are active sites to produce C-alkylate and coke, NNDMA and N-methyltoluidine (NMT), and NMA, respectively. In this study, various metallosilicates having the MFI structure were prepared to investigate the catalytic properties for the alkylation of aniline with methanol. A metallosilicate is a structure-modified zeolite in which the Si^{4+} site is substituted isomorphously by such metal ions as Ga, Fe, Ti and Zr metal ions [8–10]. Such substitution can bring changes in the lattice parameters of the unit cell and acid–base properties.

2. Experimental

2.1. SYNTHESIS OF (M)ZSM-5(*x*)

M(ZMS)-5(x) (M is the kind of isomorphously substituted metal ion and x is the atomic ratio of Si/M) was prepared by hydrothermal crystallization at 150°C for 3 days from a mixture containing colloidal silica, metal source, TPABr and NH_4F according to Guth's method [11] (or NaOH instead of NH_4F according to Howden's method [12]). Detailed information on the preparation of (M)ZSM-5s is shown in table 1. When NaOH is used as a charge balancing cation, (M)ZSM-5s were ion exchanged with 0.1 M NH_4OH at room temperature and then calcined at 550°C for 5 h to obtain the H-form. However, using NH_4F as charge balancing cation, the H-form was obtained directly by calcining at 550°C for 5 h. The pres-

Table 1
Preparation conditions of metallosilicates

Sample	Metal source	Mole ratios of reactant mixture					pH of reactant mixture
		Si	M	F^-	TPA^+	H_2O	
silicalite	–	40	0	40	6	1600	8.0
[Ge]ZSM-5	$Ge(OC_2H_5)_4$	40	1	40	6	1600	8.0
[B]ZSM-5	H_3BO_3	40	1	40	6	1600	8.1
[Al]ZSM-5	AlO(OH)	40	1	40	6	1600	7.9
[Ga]ZSM-5	$Ga(NO_3)_3{\cdot}9H_2O$	40	1	40	6	1600	7.6
[Ti]ZSM-5	$Ti(OC_2H_5)_4$	40	1	40	6	1600	8.0
[V]ZSM-5	$VOSO_4$	40	1	40	6	1600	7.5
[Fe]ZSM-5	$Fe(NO_3)_3{\cdot}9H_2O$	40	1	40	6	1600	7.8
[Ni]ZSM-5	$Ni(NO_3)_2{\cdot}6H_2O$	40	1	40	6	1600	7.9
[Zr]ZSM-5	$Zr(OC_2H_5)_4$	40	1	40	6	1600	7.9
silicalite [a]	–	40	0	40	6	1600	11.4
[Al]ZSM-5 [a]	AlO(OH)	40	1	40	6	1600	12.8
[B]ZSM-5 [a]	H_3BO_3	40	1	40	6	1600	10.4

[a] Synthesized in alkaline medium (NaOH) instead of fluorine medium (NH_4F) and F^- mole ratio reveals Na^+ mole ratio.

ence of metal in the ZSM-5 framework was confirmed by solid state ^{29}Si MAS NMR and XRD techniques [13,14].

2.2. CHARACTERIZATION OF METALLOSILICATES

Synthesized metallosilicates were characterized by elemental analysis, XRD and ^{29}Si NMR. Elemental analyses were done by atomic absorption spectroscopy. X-ray diffraction patterns were taken on a Rigaku D/Max II-A diffractometer using Ni-filtered Cu Kα radiation. The ^{29}Si MAS NMR spectra were obtained on a Bruker AM-200 high resolution solid state NMR spectrometer operating at the field of 4.7 T with a standard magic angle spinning (MAS) probe. MAS was at 3.8 kHz using an Andew-Beam single bearing rotor. Chemical shifts were determined from TMS used as an external reference. BET surface areas of prepared metallosilicates were measured by Micromeritics Digisorb 2600.

2.3. REACTION AND NH_3 TPD

For NH_3 TPD, 0.2 g of sample was put in a quartz reactor and purged with He at 550°C for 2 h. NH_3 was adsorbed at 25°C for 30 min, then purged with 100 ml/min He. TPD spectra were obtained by raising the temperature at a rate of 10°C/min in the 60 ml/min flow of He.

The vapor phase alkylation of aniline with methanol was carried out in a differential tubular reactor at 300–450°C. The reactant was fed by a liquid syringe pump and then vaporized in a pre-heater at 250°C. The products were analyzed with Varian 1400 GC using a 10% carbowax 20M on Chromosorb W-HP(80/100) column.

3. Results and discussion

3.1. CHARACTERIZATION

3.1.1. Elemental analysis and surface area

Various metallosilicates were synthesized from the reaction mixtures described in table 1. The final compositions and the surface areas of metallosilicates prepared in fluorine medium are summarized in table 2. The surface area reveals that metallosilicates are highly porous and have surface area of 300–400 m^2/g. The Si/metal ratios of all metallosilicates were about 40–70 except for [V]ZSM-5 and [Zr]ZSM-5. In case of [V]ZSM-5 and [Zr]ZSM-5, only one fourth of vanadium and one fifth of zirconium in the reactant mixtures were incorporated in zeolite. Table 2 also shows that large amount of fluoride ion existed in the metallosilicates after synthesis.

3.1.2. XRD

All of the metallosilicates showed X-ray diffraction patterns of ZSM-5 [15] having characteristic peaks at $2\theta = 6$–11°, 22.5–23.5°, and 45–46° as shown in fig. 1.

Table 2
Elemental analysis and surface area of metallosilicates prepared in fluorine medium (NH_4F)

Sample	Atomic ratios of product			BET surface area (m^2/g) (N_2 absorbed)
	Si/M	Si/F	M/F	
silicalite	–	36.0	–	384
[Ge]ZSM-5	51.4	34.3	0.67	299
[B]ZSM-5	60.2	40.4	0.67	302
[Al]ZSM-5	51.4	32.3	0.63	321
[Ga]ZSM-5	43.5	70.1	1.61	329
[Ti]ZSM-5	69.5	24.8	0.36	365
[V]ZSM-5	152.4	31.1	0.59	407
[Fe]ZSM-5	44.4	65.4	1.47	324
[Ni]ZSM-5	72.4	47.6	0.66	360
[Zr]ZSM-5	205.2	36.0	0.52	336

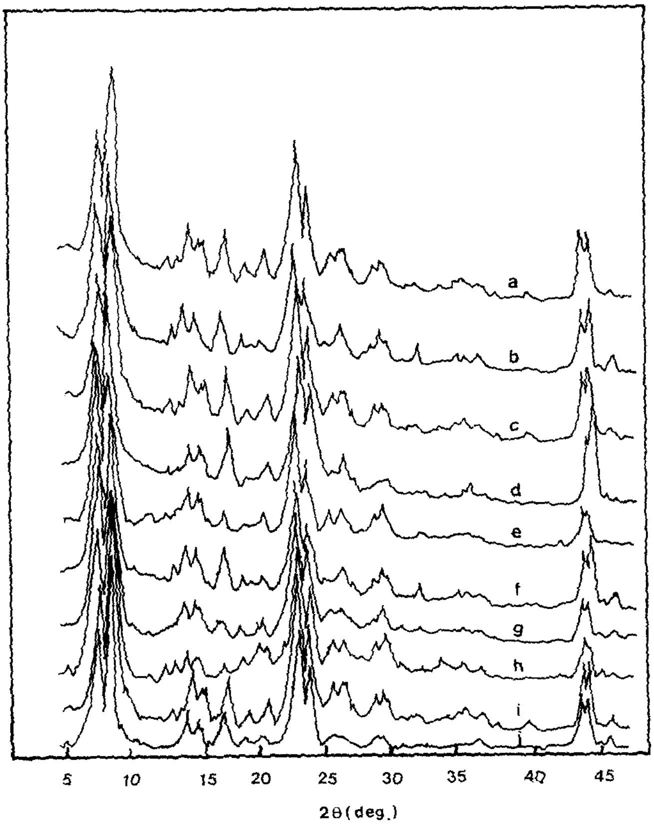

Fig. 1. X-ray pattern of metallosilicates: (a) silicalite, (b) [Ge]ZSM-5, (c) [B]ZSM-5, (d) [Al]ZSM-5, (e) [Ga]ZSM-5, (f) [Ti]ZSM-5, (g) [V]ZSM-5, (h) [Fe]ZSM-5, (i) [Ni]ZSM-5, (j) [Zr]ZSM-5.

3.1.3. ^{29}Si MAS NMR

In order to see the incorporation of the metal in the zeolite framework, the chemical shifts of prepared metallosilicates were measured by ^{29}Si MAS NMR with TMS as the external reference. The results are summarized in table 3. Silicalite having no added metal showed a single ^{29}Si NMR band (strong, half-band width = 330 Hz) at −111.5 ppm without any shoulder. This band was assigned to the tetrahedral Si(4Si) structure of silicalite from the results of Ball et al. [13] and Hayashi et al. [14]. However, other metallosilicates having added metal showed two NMR bands: a sharp and strong band between −109 and −112 ppm and a small shoulder between −102 and −105 ppm. The small shoulder was assigned to the Si(1M, 3Si) structure, where one of the four adjacent tetrahedral sites is substituted by M. From this result, it is thought that the metal components are incorporated in metallosilicate framework.

It was also observed that there is band broadening in the NMR spectra of metallosilicates having paramagnetic components such as Fe and V (table 3). Ball et al. [13] reported that the half-band width of ^{29}Si NMR band increased with the increase in the paramagnetic ion content in the tetrahedral sites of ZSM-5.

3.1.4. Thermogravimetric analysis (TGA)

TGA was carried out by raising the temperature at a rate of 5°C/min as shown in fig. 2. TGA analysis indicated that TPA$^+$ ions entrapped in the cage of metallosilicates decomposed at two different temperatures of 420 and 470°C, respectively. The result is similar to that of Soulard and Parker [16,17]. The differences in decomposition temperature are due to the two different states of TPA$^+$ ion in the zeolite

Table 3
Assignment of ^{29}Si MAS NMR band of metallosilicates prepared in fluorine medium (NH_4F)

Sample	Chemical shift [a] (ppm from TMS)	Half-band width (Hz)	Tentative assignment
silicalite	−111.5(s)	330	Si(4Si)
[Ge]ZSM-5	−112.5(s)	320	Si(4Si)
	−105.0(sh)	320	Si(1Ge, 3Si)
[Ga]ZSM-5	−108.7(s)	270	Si(4Si)
	−102.0(sh)	270	Si(1Ga, 3Si)
[Ti]ZSM-5	−112.5(s)	330	Si(4Si)
	−104.0(sh)	330	Si(1Ti, 3Si)
[V]ZSM-5	−109.5(s)	330	Si(4Si)
	−105.0(sh)	380	Si(1V, 3Si)
[Fe]ZSM-5	−109.3(s)	380	Si(4Si)
	−102.0(sh)		Si(1Fe, 3Si)
[Ni]ZSM-5	−109.1(s)	340	Si(4Si)
	−103.6(sh)	340	Si(1Ni, 3Si)
[Zr]ZSM-5	−112.5(s)	340	Si(4Si)
	−104.0(sh)		Si(1Zr, 3Si)

[a] s = strong; sh = shoulder.

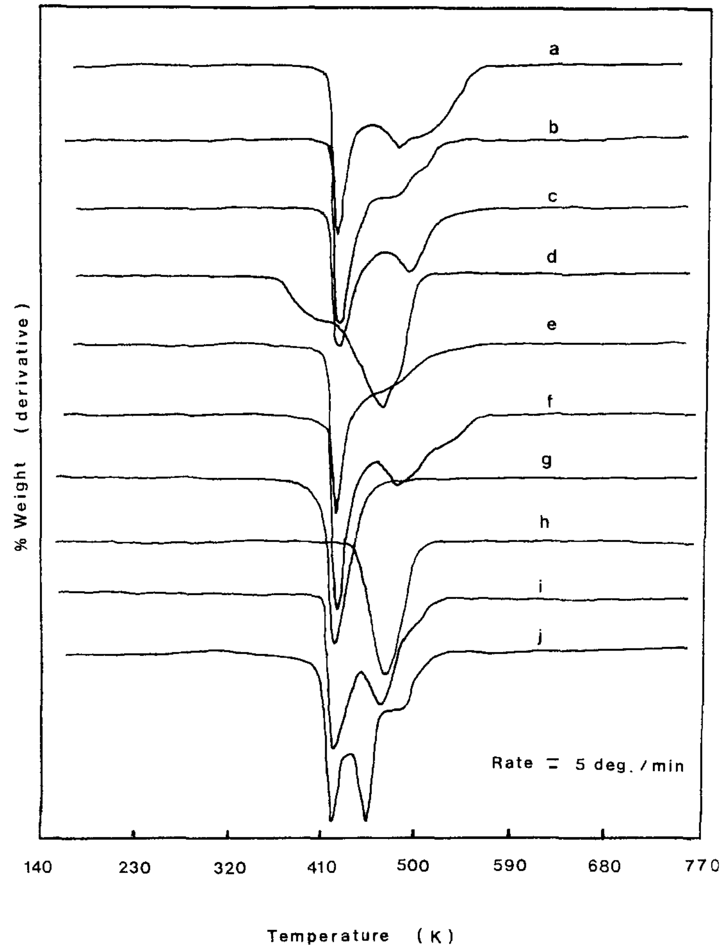

Fig. 2. Thermogravimetric analysis of metallosilicates: (a) silicalite, (b) [Ge]ZSM-5, (c) [B]ZSM-5, (d) [Al]ZSM-5, (e) [Ga]ZSM-5, (f) [Ti]ZSM-5, (g) [V]ZSM-5, (h) [Fe]ZSM-5, (i) [Ni]ZSM-5, (j) [Zr]ZSM-5.

pore, which are a TPA ion pair (TPAF or TPAOH) and a charge balancing cation (TPA^+) for isomorphously substituted metal ion. The TPA^+ ion pair decomposed at low temperature (420°C) and the charge balancing cation (TPA^+) decomposed at high temperature (470°C). Compared with the results of aniline alkylation as shown in table 4, the metallosilicates having a high temperature peak (470°C) showed high activity for aniline alkylation.

3.1.5. NH_3 TPD

Fig. 3 shows NH_3 TPD spectra of metallosilicates synthesized with two different charge balancing cations. Metallosilicates prepared in fluorine medium (NH_4F) showed a strong acid peak above 773 K which did not exist in metallosilicates prepared in alkaline medium (NaOH). Other peaks are similar in both media. Chapman

Table 4
Product distribution in aniline alkylation over the various metallosilicates [a]

Catalyst	Conversion (%)	Selectivity (%)				NNDMA/ NMA	C-alkyl/ N-alkyl
		NMA	NNDMA	NNDMT	toluidine		
silicalite	3.2	87.6	12.4	0.	0.	0.14	0.
[Ge]ZSM-5	17.0	90.4	9.6	0.	0.	0.11	0.
[B]ZSM-5	12.6	97.3	2.7	0.	0.	0.30	0.
[Al]ZSM-5	71.4	51.7	36.8	4.5	7.0	0.71	0.13
[Ga]ZSM-5	5.7	100	0.	0.	0.	0.	0.
[Ti]ZSM-5	8.3	89.9	8.3	1.8	0.	0.09	0.02
[V]ZSM-5	5.0	100	0.	0.	0.	0.	0.
[Fe]ZSM-5	30.1	79.1	15.1	5.8	0.	0.19	0.06
[Ni]ZSM-5	33.7	57.1	39.7	0.	0.	0.70	0.03
[Zr]ZSM-5	66.3	78.7	19.8	1.5	0.	0.25	0.02

[a] Reaction condition: temp., 400°C; LHSV = 4.3, time on stream = 1 h, feed composition: aniline: methanol: N_2 = 1 : 3 : 23.

and Yoshida [18,19] explained that this strong acidity was caused by the influence of fluoride ions which substituted terminal hydroxyl groups of the zeolite. This explanation is adequate because large amounts of fluoride remained in metallosilicates after synthesis as shown in table 2.

NH_3 TPD was performed on all of the metallosilicates as shown in fig. 4. There are three peaks; weak (373–473 K), medium (567–673 K) and strong (>773 K) acidities. The peak area varied according to the kind of substituted metals.

3.2. ANILINE ALKYLATION WITH METHANOL

Until now, various catalysts such as silica gel [20], alumina [3], ZSM-5 [6] and

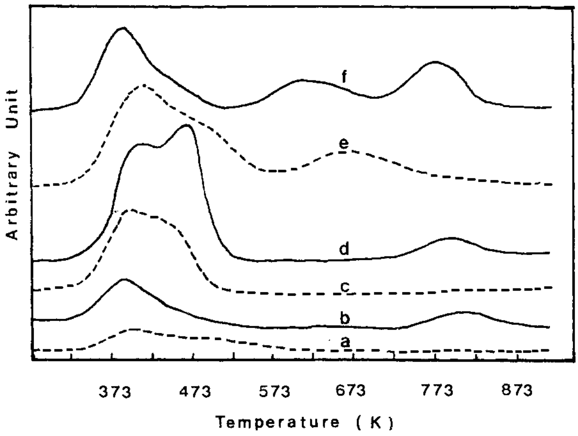

Fig. 3. NH_3 temperature programmed desorption of metallosilicates prepared by two different methods ((—) alkaline medium, (- - -) fluorine medium): (a), (b) [Al]ZSM-5, (c), (d) [B]ZSM-5, (e), (f) silicalite.

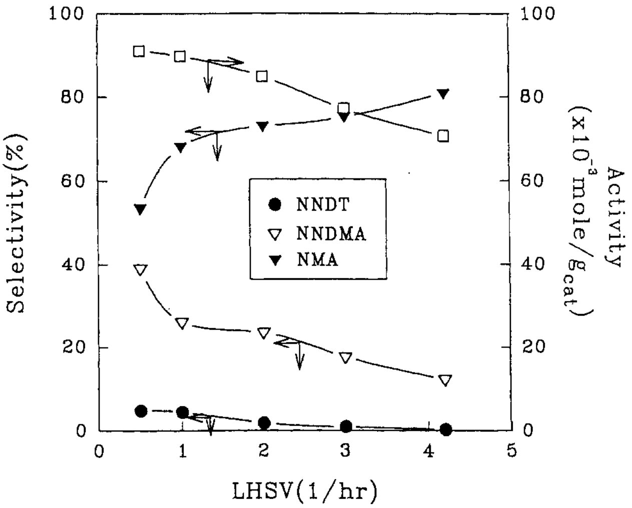

Fig. 4. NH_4 temperature programmed desorption of metallosilicates: (a) silicalite, (b) [Ge]ZSM-5, (c) [B]ZSM-5, (d) [Al]ZSM-5, (e) [Ga]ZSM-5, (f) [Ti]ZSM-5, (g) [V]ZSM-5, (h) [Fe]ZSM-5, (i) [Ni]ZSM-5, (j) [Zr]ZSM-5.

[B]ZSM-5 [7] were tested for aniline alkylation. It was reported that for selective N-alkylation of aniline acid and base properties of the catalyst are important.

3.2.1. Effect of contact time

[Zr]ZSM-5 was used to investigate the effect of contact time on the activity and the product distribution as shown in fig. 5. The aniline conversion increased linearly up to 80% with contact time, which indicates that there are no external mass

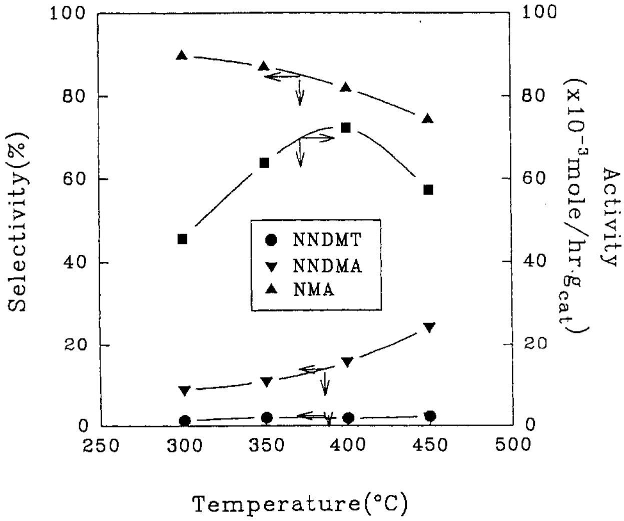

Fig. 5. Effect of contact time on the activity and selectivity over [Zr]ZSM-5 (N_2 : MeOH : aniline = 23 : 3 : 1, temp. = 400°C, time on stream = 1 h).

transfer limitations. As the contact time increased, the selectivity of NMA decreased but that of NNDMA and NMT increased. This is due to the further alkylation of NMA to NNDMA and NMT.

3.2.2. Effect of temperature

The activity reached its maximum at 400°C and decreased as the temperature was increased as shown in fig. 6. This apparently resulted from the deactivation caused by coke formation due to strong acid sites [7]. The selectivities changed with reaction temperature. As the temperature increased, the selectivity to NMA steadily decreased and selectivity to NNDMA increased. The selectivity towards N,N-dimethyltoluidine (NNDMT) increased a little bit above 350°C. From the data on contact time and temperature it can be concluded that the reaction path is aniline → NMA → NNDMA → NNDMT.

3.2.3. Deactivation

The deactivation behaviour is shown in fig. 7 for the aniline alkylation reaction over [Al]ZSM-5 and [B]ZSM-5 prepared by two different methods (alkaline medium and fluorine medium as shown in table 1). [Al]ZSM-5 and [B]ZSM-5 prepared in fluorine medium deactivated more rapidly than those prepared in alkaline medium. After 5 h, the activity decreased to 30% of the initial catalytic activity. It is suggested that the more rapid deactivation in case of fluorine medium is due to the strong acid sites associated with terminal fluoride ions (fig. 3).

3.2.4. Comparison of the product distribution over metallosilicates

Table 4 shows the activities and selectivities of aniline alkylation reaction with various metallosilicates. The effect of framework metal was analyzed based on

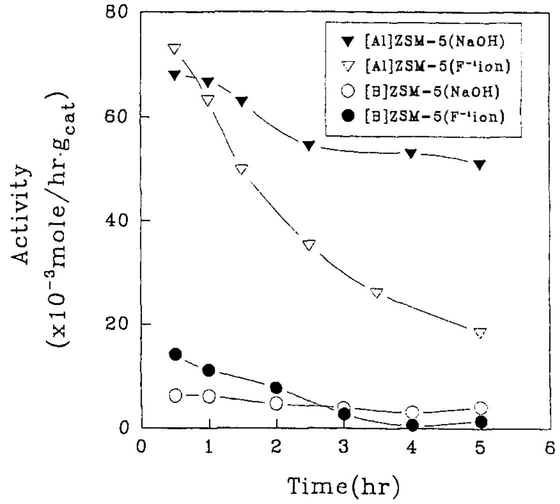

Fig. 6. Effect of temperature on the activity and selectivity over [Zr]ZSM-5 (N_2 : MeOH : aniline = 23 : 3 : 1, temp. = 400°C, LHSV = 4.3, time on stream = 1 h).

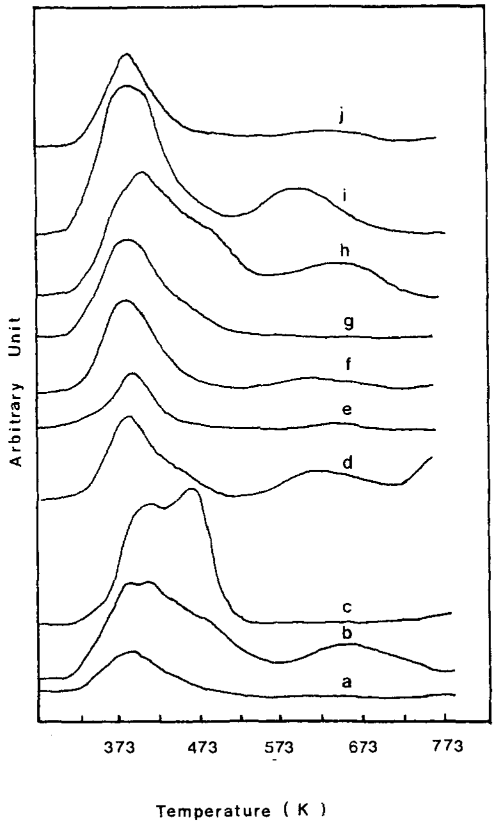

Fig. 7. Deactivation mode of [Al]ZSM-5 and [B]ZSM-5 prepared by two different methods (N_2 : MeOH : aniline = 23 : 3 : 1, temp. = 400°C, LHSV = 4.3).

metals from groups IIIA (B, Al, Ga) and IVA (Si, Ge) and transition metals (Ti, V, Fe, Ni, Zr). Among B, Al and Ga metallosilicates of IIIA group metals, [Al]ZSM-5 showed the highest activity (71.4%) and selectivity for NNDMA (36.8%). In IVA group silicalite and [Ge]ZSM-5, [Ge]ZSM-5 showed higher activity (17%) than silicalite (3.2%) but no apparent difference in selectivities. In the transition metals Ti, V, Fe, Ni and Zr, [Ni]ZSM-5 showed the highest selectivity (39.7%). The effect of framework metal on selectivity of aniline alkylation was related closely with the medium acid sites (567–673 K) as shown in fig. 8. The peak area was calculated from the area of NH_3 TPD peak between 567 and 673 K. This correlation suggests that the medium acidity plays an important role for NNDMA selectivity.

4. Conclusions

Metallosilicates were synthesized in fluorine medium (NH_4F) and alkaline medium (NaOH), respectively. Through the elemental analysis, XRD, and ^{29}Si MAS

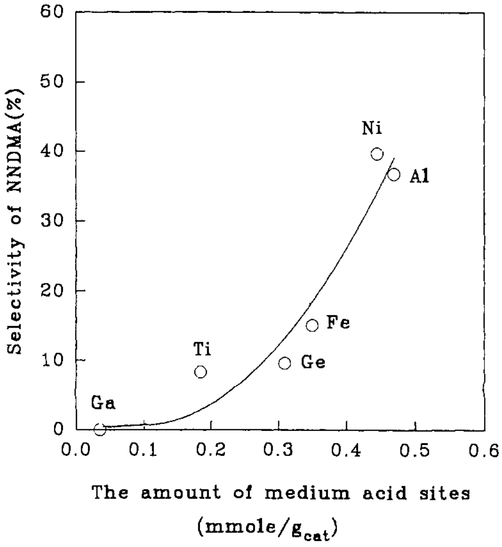

Fig. 8. Relation between selectivity of NNDMA and amount of medium acid site (567–673 K).

NMR methods, metal sources were shown to be incorporated in metallosilicate framework. NH_3 TPD spectra showed that metallosilicates synthesized in NH_4F medium had a stronger acid site (773 K) and deactivated more rapidly than that in NaOH medium. Aniline alkylation reaction indicated that the selectivity for NNDMA is higher when metallosilicates have large amount of medium acid sites (567–673 K), which means that medium acid sites play an important role in the production of NNDMA.

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References

[1] L.K. Doraiswamy, G.R.W. Krishnan and S.P. Mukherjee, Chem. Eng. 88 (1981) 78.
[2] M. Onaka, K. Ishikawa and Y. Isumi, Chem. Lett. (1983) 1783.
[3] A.G. Hill, J.H. Shipp and A.J. Hill, Ind. Eng. Chem. 43 (1951) 1579.
[4] J.M. Parera, A. Gonzalez and M.A. Barral, I&EC Prod. Res. Dev. 7 (1968) 59.
[5] G.O. Chivadze and L.Z. Chkheidze, Iz. Akad. Nauk Gruz. SSR, Ser. Khim 10 (1984) 232.
[6] P.Y. Chen, M.C. Chen, H.Y. Chu, N.S. Chang and T.K. Chuang, *Proc. 7th Int. Conf. on Zeolites*, Tokyo (1986) p. 739.

[7] S.I. Woo, J.K. Lee, S.B. Hong, Y.K. Park and Y.S. Uh, Stud. Surf. Sci. Catal. 49 (1989) 1905.
[8] K.G. Ione and L.A. Vostrikova, Russian Chem. Rev. 56 (1987).
[9] K.G. Ione, L.A. Vostrikova and V.M. Mastikhin, J. Mol. Catal. 31 (1985) 355.
[10] T. Inui, O. Tamase, K. Hukuda, A. Itoh and J. Tarumoto et al., *Proc. 8th Int. Congr. on Catalysis*, Berlin, Vol. 3 (1984) p. 569.
[11] J.L. Guth, H. Kessler and R. Wey, *Proc. 7th Int. Conf. on Zeolites*, Tokyo (1986) p. 121.
[12] M.G. Howden, Zeolites 5 (1985) 334.
[13] J.W. Ball, J. Dwyer, A.A. Garforth and W.J. Smith, *Proc. 7th Int. Conf. on Zeolites*, Tokyo (1986) p. 137.
[14] S. Hayashi, K. Suzuki, S. Shin, K. Haymizu and O. Yamamoto, Bull. Chem. Soc. Japan 58 (1985) 52.
[15] L.M. Bibby, L.P. Aldridge and N.B. Milestone, J. Catal. 72 (1981) 373.
[16] M. Soulard, S. Bilgerm, H. Kessler and J.L. Guth, Zeolites 7 (1984) 463.
[17] L.M. Parker, D.M. Bibby and J.E. Patterson, Zeolites 4 (1984) 168.
[18] I.D. Chapman and M.L. Hair, J. Catal. 2 (1963) 145.
[19] S. Yoshida, S. Tai and K. Tarama, J. Catal. 45 (1976) 242.
[20] A.B. Brown and E.E. Reid, J. Am. Chem. Soc. 46 (1924) 1836.