NO abatement with CH_4 in the presence of O_2 on H-ZSM5 with Si/Al = 15–200: the dependence of activity on the proton concentration

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The abatement of NO with methane in the presence of oxygen was studied on commercial H-ZSM5 samples with Si/Al = 15–200 in a conventional flow apparatus. H-ZSM5 samples were used in the acid form or after exchanging protons with sodium ions to various extents. Their catalytic activity was compared with that of commercial H-mordenite and H-Y. On all H-ZSM5 catalysts, reaction rates R_{NO} and R_{CH_4} (molecules $s^{-1}\,g^{-1}$) increased proportionally to the proton concentration, showing that either all protons or a constant fraction of them were equally active. On sodium-exchanged H-ZSM5 samples with Si/Al = 15–17, both R_{NO} and R_{CH_4} nearly exponentially increased with the proton concentration. Conversely, on sodium-exchanged H-ZSM5 with Si/Al = 50, both R_{NO} and R_{CH_4} linearly increased with the proton concentration. At lower Si/Al ratios, replacing the H-ZSM5 protons with sodium ions partly inactivated the remaining protons.

Keywords: NO abatement, H-ZSM5 zeolites, Brønsted acid sites

1. Introduction

The catalytic activity of zeolites for hydrocarbon conversion reactions (hexane or cumene cracking, propylene polymerization, xylene isomerization, and toluene disproportionation) depends on their acid strength and the proton concentration [1–7].

Acid zeolites are also active for NO or NO_2 abatement with hydrocarbons in the presence of oxygen [8–15]. Whether the catalytic activity for this reaction is dependent on the acid strength and the proton concentration remains less clear. With propane or propene as the reducing agent, Hamada et al. [8] found that H-mordenite (H-MOR) was more active than H-ZSM5 and far more active than H-Y, and that H-ZSM5 was far more active than Na-ZSM5. With methane, Campa et al. [9] found that H-ZSM5 was much more active than Na-ZSM5, in agreement with the results of Li and Armor [10,11]. With methane, Yogo et al. [12] found that H-ZSM5, H-MOR, and H-ferrierite were active for NO abatement, H-ZSM5 being the most active at 773 K. With propene or methane, Miller et al. [13] found that the catalytic activity for NO_2 reduction increased with increasing the acid strength of zeolites. With both hydrocarbons, the activity increased in the order $SiO_2–Al_2O_3 < \text{H-USY} < \text{H-ZSM5} < \text{H-MOR}$ [13]. With propene, on H-ZSM5 with various Si/Al ratios, Satsuma et al. [14] found that the NO to N_2 conversion increased with the proton concentration. Analogously, with propene on H-MOR with various Si/Al ratios, Gerlach et al. [15] recently found that the catalytic activity for NO_2 reduction increased with the proton concentration.

To gain more information about the dependence of the catalytic activity of zeolites for NO abatement on the acid strength and the proton concentration, we studied H-ZSM5 samples with Si/Al ratios from 15 to 200, H-ZSM5 samples exchanged to various extents with sodium ions, and we compared their activity with that of H-MOR and H-Y. Because preliminary tests with propene showed that carbon formation poisoned the catalysts, as the reducing agent for our study we used methane rather than higher hydrocarbons.

2. Experimental

2.1. Catalysts

H-ZSM5 zeolites with different Si/Al ratios (15–200) were used as such or after exchange with sodium to various extents. ZSM5 samples, kindly supplied by P.Q. Corporation, EKA Chemicals, Enichem Anic, and Süd Chemie AG, were all in the acidic form, except the Na-ZSM5 sample supplied by Enichem Anic (table 1).

Sodium-exchanged catalysts were prepared by contacting at 323–338 K a weighted amount of H-ZSM5 with aqueous solutions of sodium acetate at various concentrations (0.01–2 M). After sodium exchange the samples were thoroughly washed with distilled water and dried overnight at 383 K. The sodium content in the dried samples was determined by atomic absorption (Varian SpectrAA-30),

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Table 1
Catalysts.

Zeolite	Na exchange (%)	E_{NO} (kJ mol^{-1})	E_{CH_4} (kJ mol^{-1})
H-ZSM5-15 (PQ)[a]	0	75 ± 4	81 ± 4
	25	75 ± 4	81 ± 4
	65	74 ± 4	100 ± 4
H-ZSM5-16 (EKA)[b]	0	79 ± 4	87 ± 4
	10	75 ± 4	85 ± 4
	55	71 ± 4	92 ± 4
H-ZSM5-17 (ENI)[c]	0	91 ± 4	117 ± 4
	10	93 ± 4	127 ± 4
Na-ZSM5-14 (ENI)[c]	100	75 ± 4	80 ± 4
H-ZSM5-50 (SC)[d]	0	73 ± 4	86 ± 4
	16	65 ± 4	100 ± 4
	30	65 ± 4	100 ± 4
	65	65 ± 4	111 ± 4
	84	65 ± 4	98 ± 4
H-ZSM5-120 (SC)[d]	0	92 ± 4	107 ± 4
H-ZSM5-200 (SC)[d]	0	90 ± 4	100 ± 4
H-MOR-25 (SC)[d]	0	90 ± 4	110 ± 4
	100	–	–
H-Y-2.5 (Linde)[e]	6	88 ± 4	101 ± 4
	83		

[a] P.Q. Corporation (CBV 3024G, lot no. 1822-54).
[b] Eka Chemicals (EZ 472, lot no. 145-94-011).
[c] Enichem Anic (a portion of the same batch used in references).
[d] Süd-Chemie AG (287 H/96).
[e] Linde (LZ-Y62, lot no. 0955000).

and expressed as percent of exchange (the exchange extent was calculated assuming that *one* Na corresponds to *one* Al atom). Samples are labelled as H-ZSM5, followed by two figures, the first specifying the Si/Al ratio, and the second the analytical sodium-exchange extent. In parentheses, the zeolite suppliers are specified (table 1). H-ZSM5-17 (ENI) and Na-ZSM5-14 (ENI) samples, prepared and characterised by Enichem Anic [16,17], were portions of samples previously used as starting materials for the preparation of Cu-ZSM5 [18], Co-ZSM5 [9] and Mn-ZSM5 [19] catalysts.

IR spectra of all ZSM5 samples were run on an FTIR spectrometer (Perkin–Elmer 2000) at a resolution of 4 cm^{-1}. The powdered samples were pelleted in self-supporting disks of ca. 10 mg cm^{-2}, and put in an IR cell which allowed thermal treatments in vacuum or in a controlled atmosphere. Before IR spectra were run, samples were heated with O_2 at 793 K for 1 h and evacuated at the same temperature for 1 h. FTIR spectra of all samples consisted of a narrow and intense band at 3747 cm^{-1}, assigned to the OH stretching mode of silanols, and a band at 3620 cm^{-1}, assigned to the stretching mode of the acidic bridged hydroxy groups. The intensity of the band at 3620 cm^{-1} increased with the Al content, and decreased with the Na-exchange extent, showing that protons of the acidic hydroxy group were replaced by sodium ions. Accordingly, the band at 3620 cm^{-1} was absent in the sample Na-ZSM5-14 (ENI). In addition to the foregoing bands, in the H-ZSM5-17 (ENI) and H-ZSM5-16 (EKA) samples, we detected an extremely weak band at 3665 cm^{-1}, assigned to OH groups associated with extraframework aluminium, the intensity of which was $\leqslant 10\%$ of that of the band at 3620 cm^{-1}. None of the other samples contained this band. All the assignments given above are the same as those previously reported for ZSM5 samples [16,17]. Based on the IR characterisation, in the following we will assume that *one* Al atom of the ZSM5 sample corresponds to *one* proton.

2.2. Catalytic experiments

The catalytic activity was measured in a flow apparatus at atmospheric pressure. The apparatus included a feeding section where four gas streams (He, 3% NO in He, 2% CH_4 in He, and 10% O_2 in He) were regulated by means of independent mass flow controller-meters (MKS model 1259, driven by a four-channel unit MKS model 247 c) and mixed in a glass ampoule before entering the reactor. Gas mixtures were purchased from Rivoira and were used without further purification. The reactor was made of silica with an internal sintered frit of about 12 mm diameter supporting the powdered catalyst (0.1–0.4 g). The reactor was vertically positioned in an electrical heater, with a thermocouple touching the external wall of the reactor at the middle of the catalyst bed. Reactants and products were analysed by gas chromatography (Varian model 6000 gas chromatograph, equipped with an Alltech CTR 1 column kept at 308 K). A thermal conductivity detector (TCD) was used for detecting N_2, N_2O, CO, CO_2, and a flame ionization detector (FID) for CH_4. Peak areas were evaluated by electronic integration.

A fresh portion of catalyst was treated in a flow of 2% O_2/He mixture, while heating the reactor from room temperature to 773 K in about 2 h and then isothermally at 773 K for 45 min. After this treatment, the reactor was bypassed and the temperature adjusted to the desired value. Catalysis was generally run with equimolar mixtures of NO and CH_4 containing 4000 ppm v/v of either reactant, $O_2 = 2\%$, with He as balance. The reaction temperature or mixture composition were changed without intermediate activation treatment. The total flow rate was generally maintained at 50 cm^3 STP min^{-1}. Space velocities (GHSV) in the range 3750–15000 h^{-1} (based on the apparent density of samples $= 0.5$ g cm^{-3}) were obtained by changing the mass of catalyst.

Kinetic parameters were evaluated as reported previously [9,19]. In particular, reaction rates were calculated from the following equations:

$$CH_4 + 2NO + O_2 \rightleftharpoons N_2 + 2H_2O + CO_2 \tag{1}$$

$$CH_4 + 2NO + \tfrac{3}{2}O_2 \rightleftharpoons N_2O + 2H_2O + CO_2 \tag{2}$$

$$CH_4 + 2O_2 \rightleftharpoons 2H_2O + CO_2 \tag{3}$$

$$CH_4 + \tfrac{3}{2}O_2 \rightleftharpoons 2H_2O + CO \tag{4}$$

The rate of NO abatement, R_{NO} (molecules $s^{-1}\,g^{-1}$), was calculated from $N_2 + N_2O$ molecules produced in equations (1) and (2). The rate of CH_4 consumption, R_{CH_4} (molecules $s^{-1}\,g^{-1}$), was calculated from $CO_2 + CO$ molecules produced in equations (1)–(4). All rates were evaluated from experiments in which conversion never exceeded 30%. Apparent activation energies, E_{NO}, were calculated from $\log R_{NO}$ vs. $1/T$ Arrhenius plots, and E_{CH_4} from $\log R_{CH_4}$ vs. $1/T$.

The percent selectivities, SCR (NO reduction rather than CH_4 combustion), S_{N_2} (N_2 rather than N_2O), and S_{CO_2} (CO_2 rather than CO) were calculated as: $SCR = (R_{NO}/R_{CH_4}) \times 100$; $S_{N_2} = (r_1/R_{NO}) \times 100$; $S_{CO_2} = [(r_2 + R_{NO})/R_{CH_4}] \times 100$, where r_1 is the rate of N_2 formation in equation (1), and r_2 is the rate of CO_2 formation in equation (3).

3. Results and discussion

3.1. The activity of H-ZSM5

The dependence of catalytic activity on temperature was studied with the reactant mixture containing 4000 ppm of NO, 4000 ppm of CH_4 and 2% of O_2. For all catalysts, in experiments lasting several hours, R_{NO} and R_{CH_4} remained constant with time on stream. Table 1 lists the apparent activation energies E_{NO} and E_{CH_4}, calculated from the linear part of the relevant Arrhenius plots (figure 1 (a) and (b)).

On all catalysts, R_{NO} increased with temperature and showed activity bending at about 753 K. That activity bending was real was confirmed by our observation that the R_{CH_4} vs. T curves never showed bending but R_{CH_4} increased exponentially as a function of temperature, over the whole temperature range. According to Li and Armor [20], the bending of the R_{NO} vs. T curves depends on the specific catalyst and is caused by the decrease in either adsorbed NO_2 or gas-phase CH_4.

For all H-ZSM5 catalysts, as the temperature increased from 648 to 773 K, SCR decreased to 50%, S_{N_2} increased from 70 to 100% and S_{CO_2} decreased to 60–85%.

The dependence of reaction rates on the composition of the reactant mixture was studied on the H-ZSM5-50 sample at 673 K. In particular, the dependence of R_{NO} and R_{CH_4} on the oxygen content was studied with a mixture containing O_2 from 0 to 2.0%, with $NO = CH_4 = 4000$ ppm. R_{NO} increased with increasing O_2 up to 0.5%, and remained nearly constant thereafter, whereas R_{CH_4} increased in the whole O_2 concentration range (figure 2(a)). As the O_2 content increased, SCR monotonically decreased (from 100 to 50%), S_{N_2} slightly decreased (from 100 to 90%), and S_{CO_2} remained nearly constant (ca. 60%) in the oxygen range 0.5–2.0%.

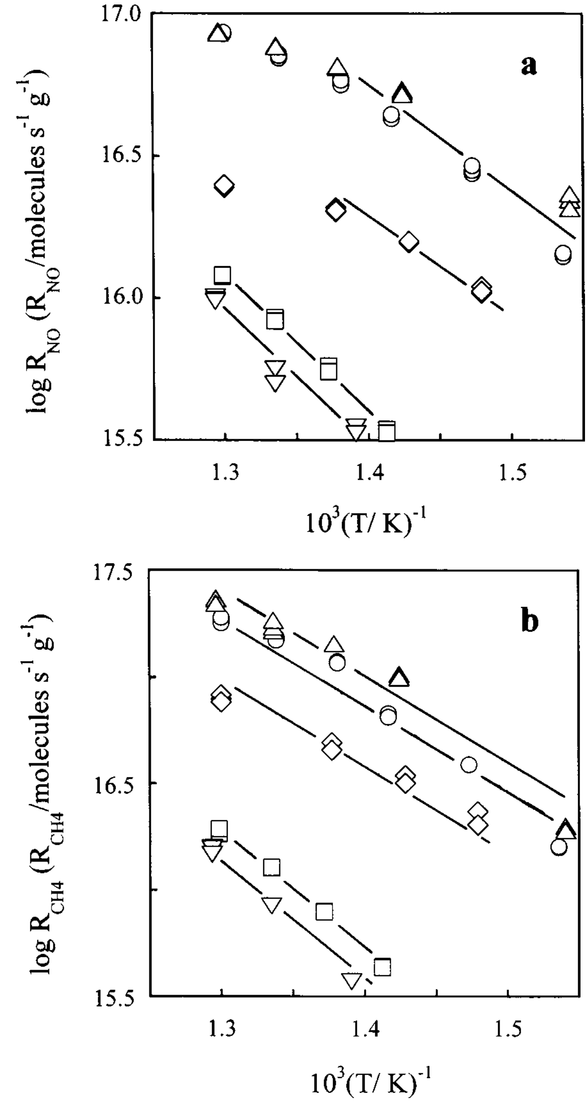

Figure 1. Catalytic activity of H-ZSM5: (a) $\log R_{NO}$ vs. $1/T$ and (b) $\log R_{CH_4}$ vs. $1/T$. Catalysts: (△) H-ZSM5-15, (○) H-ZSM5-16, (◇) H-ZSM5-50, (□) H-ZSM5-120, and (▽) H-ZSM5-200. Reactant mixture: $NO = CH_4 = 4000$ ppm, $O_2 = 2\%$.

The dependence of R_{NO} and R_{CH_4} on the nitric oxide content was studied with a mixture containing NO from 0 to 0.4%, with $CH_4 = 4000$ ppm and $O_2 = 2\%$. With increasing NO content, R_{NO} monotonically increased, and R_{CH_4} steeply increased with 0.02% of NO and then increased more slowly (figure 2(b)). With increasing the NO pressure, SCR increased to 50%, S_{N_2} decreased from 100 to 90%, and S_{CO_2} decreased to 20% with $NO = 0.03\%$ and increased to 60% with $NO = 0.3\%$.

The dependence of R_{NO} and R_{CH_4} on the methane content was studied with a mixture containing CH_4 from 0 to 0.4%, with $NO = 4000$ ppm and $O_2 = 2\%$. Both R_{NO} and R_{CH_4} monotonically increased with increasing methane content (figure 2(c)). As the CH_4 content increased, SCR decreased from 70 to 50%, S_{N_2} remained nearly constant (90%) throughout the CH_4 concentration range and S_{CO_2} decreased from 85 to 60%.

The Arrhenius plot illustrates the dependence of R_{NO} and R_{CH_4} on the Si/Al ratio (figure 1). At all temperatures, R_{NO} and R_{CH_4} markedly decreased with increasing the Si/Al ratio. Specifically, at 723 K both R_{NO} and R_{CH_4} linearly increased with the proton concentration, showing that protons play an important role in determining the cat-

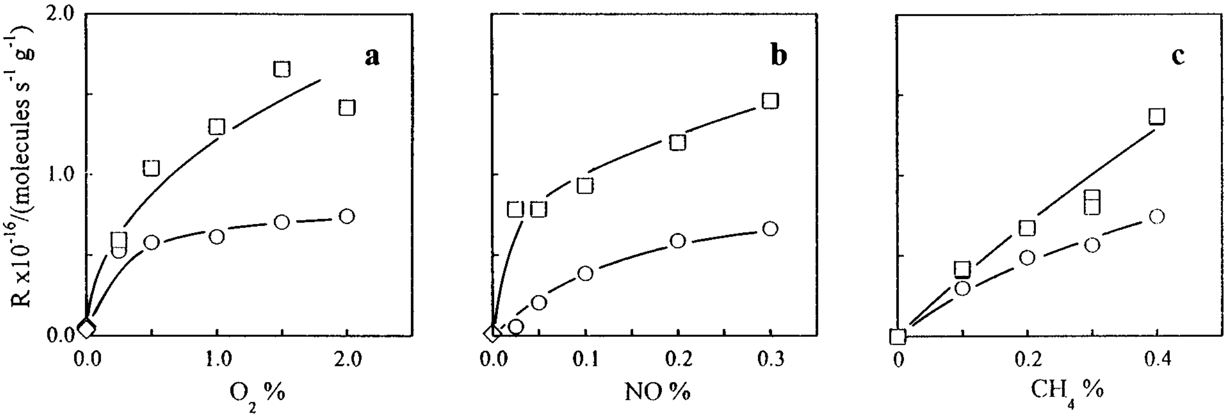

Figure 2. Dependence of catalytic activity on reactant concentration. Catalyst H-ZSM5-50 (SC). (a) Reactant mixture NO = CH$_4$ = 4000 ppm with O$_2$ as indicated; R_{NO} (○) and R_{CH_4} (□) vs. O$_2$ content, at 673 K. In the absence of oxygen, the rates R_{NO} and R_{CH_4} (◇) were calculated from $CH_4 + 4NO \rightleftharpoons 2N_2 + 2H_2O + CO_2$ and $CH_4 + 8NO \rightleftharpoons 4N_2O + 2H_2O + CO_2$. (b) Reactant mixture CH$_4$ = 4000 ppm, O$_2$ = 2% and NO as indicated; R_{NO} (○) and R_{CH_4} (□) vs. NO content, at 673 K. In the absence of NO, the rate R_{CH_4} (◇) was calculated from the combustion reactions (equations (3) and (4)). (c) Reactant mixture NO = 4000 ppm, O$_2$ = 2% and CH$_4$ as indicated; R_{NO} (○) and R_{CH_4} (□) vs. CH$_4$ content, at 673 K.

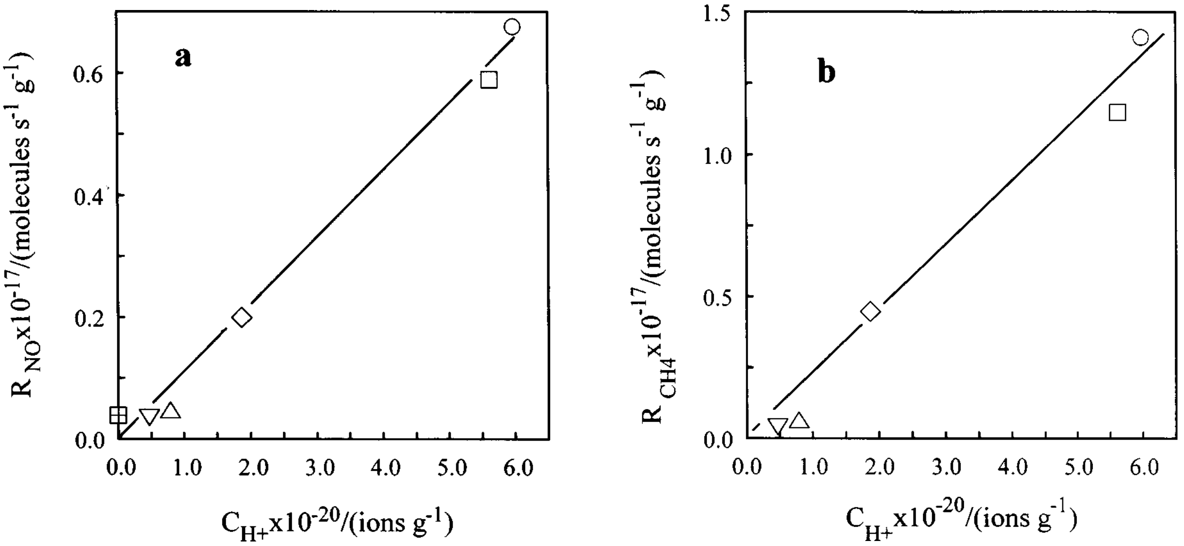

Figure 3. Catalytic activity of H-ZSM5 as a function of proton content, at 723 K: (a) R_{NO} vs. C_{H+} and (b) R_{CH_4} vs. C_{H+}. Catalysts: (⊞) Na-ZSM5, (○) H-ZSM5-15, (□) H-ZSM5-16, (◇) H-ZSM5-50, (△) H-ZSM5-120, and (▽) H-ZSM5-200.

alytic activity of H-ZSM5. We suggest that protons are the active sites for both NO abatement and CH$_4$ combustion (figure 3 (a) and (b)). Under this hypothesis, the observed linearity shows that either all protons or a constant fraction of them are equally active for both reactions.

3.2. The activity of sodium-exchanged H-ZSM5

At a given Si/Al ratio, on all Na-exchanged H-ZSM5 catalysts, both R_{NO} and R_{CH_4} decreased with increasing Na-exchange extent, so that on the Na-ZSM5-14 sample they were extremely small. Selectivity values (SCR, S_{N_2}, and S_{CO_2}), and apparent activation energies (E_{NO} and E_{CH_4}, table 1) of sodium-exchanged H-ZSM5 approximated the corresponding H-ZSM5 values. Because all these results indicated that sodium ions contributed little or nothing to the catalytic activity, we were able to analyse the dependence of catalytic activity on the proton concentration also for the sodium-exchanged samples. As illustrated below, we identified two distinct trends, depending on the Si/Al ratio.

On samples with the lowest Si/Al ratio (Si/Al = 15–17), both R_{NO} and R_{CH_4} markedly and nearly exponentially increased as a function of the proton concentration. H-ZSM5 samples in which 35% of the protons, or higher percentages, were exchanged with sodium showed extremely low catalytic activity (figure 4(a), data for R_{CH_4} not shown). On samples with a higher Si/Al ratio (Si/Al = 50), both R_{NO} and R_{CH_4} nearly linearly increased as a function of the proton concentration (figure 4(b), data for R_{CH_4} not shown).

Owing to the equivalence of all protons in H-ZSM5 with Si/Al $\geqslant$ 10 [21,22], the explanation for the linear increase in R_{NO} and R_{CH_4} with increasing the proton concentration in samples with Si/Al = 50 is straightforward. That is, the replacement of active protons with inactive sodium progressively and linearly depresses the catalytic activity. In agreement, Kotrel et al. [5] studying the effect of proton replacement with sodium ions on the activity for hexane cracking of H-ZSM5 with Si/Al = 35, found a linear dependence of the catalytic activity on the sodium percent exchange up to 60–80%. Hence, they suggested that the effect of sodium was a local phenomenon [5].

Conversely, explaining why the activity dropped to zero when about 35% of protons were replaced by sodium in samples with Si/Al = 15–17 is inevitably more complex. A possible explanation follows the reasoning of Baba et al. [4] when explaining an analogous activity drop on H-ZSM5 samples with Si/Al = 21. In particular, to explain the activity drop for the cyclopropane isomerization occurring when 20% of H-ZSM5 protons were replaced with sodium, and for the hexane cracking when 35% protons were replaced, Baba et al. [4] suggested that the presence of sodium exerted a long-range inductive effect causing the remaining protons to become less active. The absence of the inductive effect in samples with a higher Si/Al ratio, possibly depends on the larger distance among framework Al species.

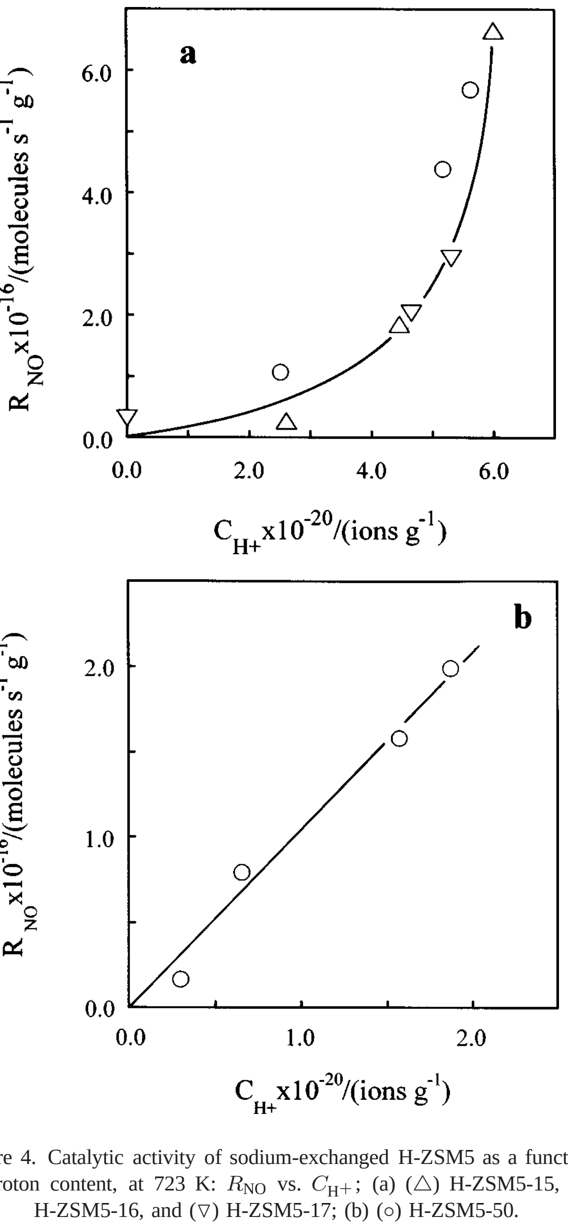

Figure 4. Catalytic activity of sodium-exchanged H-ZSM5 as a function of proton content, at 723 K: R_{NO} vs. C_{H+}; (a) (△) H-ZSM5-15, (○) H-ZSM5-16, and (▽) H-ZSM5-17; (b) (○) H-ZSM5-50.

3.3. *The activity of mordenite and Y zeolites: a comparison with ZSM5*

On H-MOR, R_{NO} was thirteen times higher and R_{CH_4} four times higher than the relevant values on Na-MOR. On H-MOR, SCR was 70–80%, S_{N_2} 80–90% and S_{CO_2} remained at 100% throughout the whole temperature range. On Na-MOR, SCR was 20–25%, resulting substantially lower than the relevant value on H-MOR. Analogously, Na-Y was substantially less active than H-Y. On H-Y, as the temperature increased from 680 to 773 K, SCR decreased from 85 to 60%, S_{N_2} increased from 90 to 100%, and S_{CO_2} decreased from 100 to 80%.

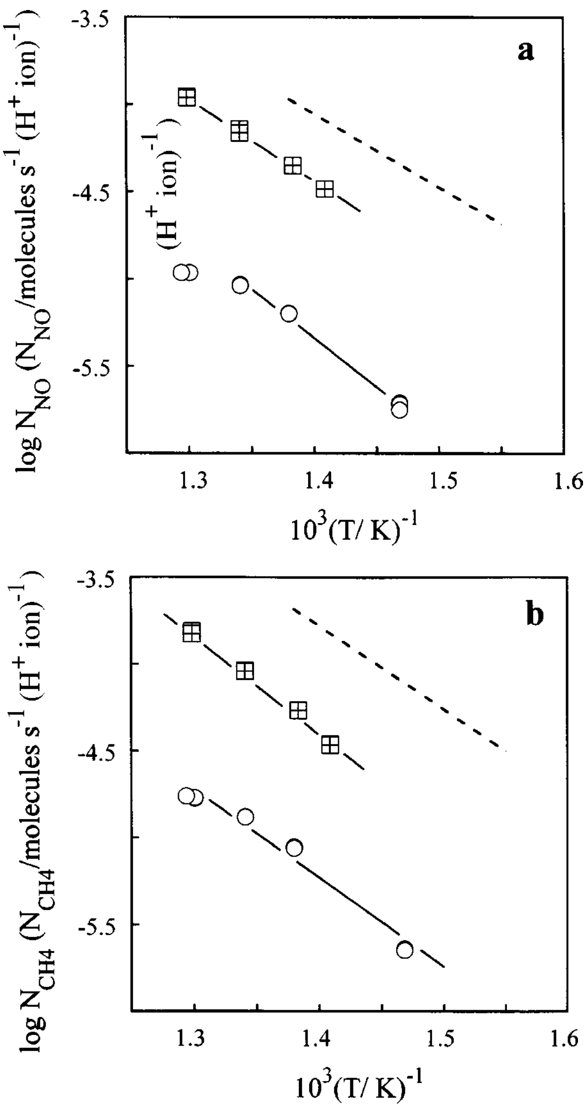

Figure 5. Turnover frequency values on H-ZSM5, H-MOR and H-Y: (a) log N_{NO} vs. $1/T$ and (b) log N_{CH_4} vs. $1/T$. Catalysts: (⊞) H-MOR and (○) H-Y. (- - -) reports the average log N_{NO} (a) and log N_{CH_4} values (b) of the various H-ZSM5 samples with Si/Al = 15–200.

The activity order of H-ZSM5, H-MOR, and H-Y was assessed by comparing the relevant turnover frequency numbers. These values were calculated as $N = R/C_{\mathrm{H}^+}$ (N in molecules per second per H^+ ion), where R are the specific velocities R_{NO} or $R_{\mathrm{CH_4}}$ (molecules $\mathrm{s}^{-1}\,\mathrm{g}^{-1}$) and C_{H^+} the proton content (ions g^{-1}). Because the calculation assumes that all protons are active sites, the N values should be regarded as a lower limit. The comparison shows that H-ZSM5 is slightly more active than H-MOR, and both H-ZSM5 and H-MOR are far more active than H-Y (figure 5), in agreement with the proton acid strength order of these materials [21,22] and with their reported activity order [8,12,13].

4. Conclusions

As previously shown for several hydrocarbon conversion reactions, the catalytic activity of acid zeolites for the abatement of NO with methane is dependent on proton concentration and acid strength. Our finding strongly suggests that all these reactions involve the formation of a similar hydrocarbon surface intermediate. That is, for all these reactions, the Brønsted acid sites of zeolites play a similar role in activating hydrocarbons.

At lower Si/Al ratios, replacing H-ZSM5 protons with sodium ions makes the remaining protons less active.

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References

[1] W.O. Haag, in: *Zeolites and Related Microporous Materials*, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 1375.
[2] F. Ramôa Ribeiro, F. Alvarez, C. Henriques, F. Lemos, J.M. Lopes and M.F. Ribeiro, J. Mol. Catal. A 96 (1995) 245.
[3] H. Vinek and J.A. Lercher, J. Mol. Catal. 64 (1991) 23.
[4] T. Baba, Y. Inoue and Y. Ono, J. Catal. 159 (1996) 230.
[5] S. Kotrel, M.P. Rosynek and J.H. Lunsford, J. Catal. 182 (1999) 278.
[6] B. Schoofs, J.A. Martens, P.A. Jacobs and R.A. Schoonheydt, J. Catal. 183 (1999) 355.
[7] B. Coq, J. Pardillos and F. Figueras, Appl. Catal. 62 (1990) 281.
[8] H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, Appl. Catal. 64 (1990) L1.
[9] M.C. Campa, S. De Rossi, G. Ferraris and V. Indovina, Appl. Catal. B 8 (1996) 315.
[10] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L31.
[11] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.
[12] K. Yogo, M. Umeno, H. Watanabe and E. Kikuchi, Catal. Lett. 19 (1993) 131.
[13] J.T. Miller, E. Glusker, R. Peddi, T. Zheng and J.R. Regalbuto, Catal. Lett. 51 (1998) 15.
[14] A. Satsuma, K. Yamada, T. Mori, M. Niwa, T. Hattori and Y. Murakami, Catal. Lett. 31 (1995) 367.
[15] T. Gerlach, U. Illgen, M. Bartoszek and M. Baerns, Appl. Catal. B 22 (1999) 269.
[16] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Petrini, G. Leofanti, M. Padovan and C. Otero Areàn, J. Chem. Soc. Faraday Trans. 88 (1992) 2959.
[17] S. Bordiga, E. Escalona Platero, C. Otero Areàn, C. Lamberti and A. Zecchina, J. Catal. 137 (1992) 179.
[18] M.C. Campa, V. Indovina, G. Minelli, G. Moretti, I. Pettiti, P. Porta and A. Riccio, Catal. Lett. 23 (1994) 141.
[19] M.C. Campa, D. Pietrogiacomi, S. Tuti, G. Ferraris and V. Indovina, Appl. Catal. B 18 (1998) 151.
[20] Y. Li and J.N. Armor, J. Catal. 150 (1994) 376.
[21] D. Barthomeuf, J. Phys. Chem. 97 (1993) 10780.
[22] D. Barthomeuf, Mater. Chem. Phys. 17 (1987) 49.