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Physico-chemical properties of FeAlBEA and FeSiBEA zeolites and their catalytic activity in the SCR of NO with ethanol or methane

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ABSTRACT

FeAlBEA and FeSiBEA zeolites are prepared by a conventional ion exchange and a two-step postsynthesis method, respectively. Their physico-chemical properties are investigated by XRD, FTIR, and diffuse reflectance UV–vis. For FeAlBEA zeolite, framework tetrahedral Fe(III), extra-framework octahedral Fe(III) and FeO_x oligomers are observed by diffuse reflectance UV–vis. In contrast, for FeSiBEA mainly framework tetrahedral Fe(III) appears as a result of incorporation of Fe ions in vacant T-atom sites of SiBEA. The catalytic activity of FeAlBEA and FeSiBEA zeolites in the selective catalytic reduction of NO with ethanol or methane depends on the nature of iron and the presence of Al and Fe ions in the zeolite framework, respectively. The framework tetrahedral Al(III) and Fe(III) species, are origin of strong Brønsted and Lewis acidic centres which may influence the catalytic properties of FeAlBEA and FeSiBEA zeolite. FeAlBEA catalyst with higher strength and amount of these centres than FeSiBEA ones is more active and much more selective toward N_2 in SCR of NO with methane.

1. Introduction

Recently published works [1–4] show that iron zeolites are active in several reactions including selective catalytic reduction (SCR) of NO_x and N_2O [1,2] and N_2O decomposition [3,4]. We have earlier observed [5–7] that for dealuminated BEA zeolite containing Co, Cu or Fe species, NO conversion, both in SCR of NO with ethanol and during the NO oxidation reaction increases with the increase of the metal content. In all cases the NO conversion in SCR process is higher than in NO oxidation reaction. It suggests that metal species are responsible for the catalytic activity in both cases and points out that both processes are activated on the same centre but the NO_2 formation not precedes the surface NO_x complex formation.

Due to the dealumination procedure, BEA zeolite lost Brønsted acidic sites and the possibility of creating metal centres in exchange positions. Instead, well defined isolated framework tetrahedral metal centres are formed [5–7]. Along with the increase of metal content some other metal species such as extra-framework octahedral metal species, MeO_x oligomers and metal oxide phase are formed. However their formation is connected with the decrease of SCR activity and formation of NO_2 as the NO oxidation product.

We have shown that CoSiBEA, CuSiBEA and FeSiBEA with isolated framework metal species obtained by two-step postsynthesis method are good catalysts for the SCR of NO with ethanol. But they are less active in the SCR of NO with methane. As shown earlier [8,9], the metals containing BEA zeolites prepared by classical ion exchange or impregnation procedure (without earlier removal of Al atoms) are characterised by relatively high activity in SCR of NO with methane. So, in this work we compare catalytic activity of FeAlBEA and FeSiBEA prepared by conventional ion exchange and two-step postsynthesis method with similar Fe content. In addition, comparison of both catalysts in SCR of NO with ethanol has also been performed.

2. Experimental

2.1. Catalyst preparation

A tetraethylammonium BEA (TEABEA) zeolite was provided by RIPP (China). A first portion was calcined (15 h, 823 K) to obtain AlBEA (Si/Al = 11). FeAlBEA was prepared by conventional ion exchange by contacting AlBEA in air at 343 K with a

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1.0×10^{-2} mol L^{-1} aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ (pH 2.5). The exchange procedure was repeated twice. The solid was then filtered and washed with distilled water. The resulting solid, dried in air at 353 K for 24 h, containing 1.4 wt% Fe was labeled as FeAlBEA. A second portion of TEABEA was treated, as described earlier [10–12], by a 13 mol L^{-1} HNO_3 solution (4 h, 353 K) to obtain the dealuminated BEA zeolite. The resulting SiBEA zeolite (Si/Al = 1300) was recovered by centrifugation, washed with distilled water and dried overnight at 353 K. Then, in order to incorporate iron ions into vacant T sites of SiBEA zeolite, this sample was impregnated in air by a 0.6×10^{-2} mol L^{-1} aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ (pH 2.6). First, 2 g of SiBEA was stirred for 24 h at 298 K in excess solvent using 200 mL of the iron nitrate solution and the suspension (pH 2.6) was stirred for 2 h in air at 353 K until evaporation of water. The resulting solid, dried in air at 353 K for 24 h, containing 1.3 wt% Fe was labeled as FeSiBEA.

2.2. Catalyst characterization

Powder X-ray diffractograms (XRD) of samples as prepared were recorded at ambient atmosphere on a Siemens D5000 using the Cu Kα radiation (λ = 154.05 pm). Transmission FT-IR spectra of self-supported wafers (20 mg) are recorded at 298 K on a Bruker IFS 66 V spectrometer, with a resolution of 2 cm^{-1}. Before measurements, the wafers are dehydrated in flowing oxygen (120 mL/min) to 773 K (heating rate of 100 K/h), kept at this temperature for 8 h and finally outgassed for 6 h at 573 K (10^{-3} Pa) in the IR cell. DR UV–vis spectra were recorded at ambient atmosphere on a Cary 5000 Varian spectrometer equipped with a double integrator with polytetrafluoroethylene as reference.

2.3. Catalyst activity measurements

The activity of catalysts in the SCR of NO with ethanol or methane was investigated in a conventional flow reactor coupled to an analytical system. A gas chromatograph (CHROM-5) provided with TCD and FID detectors was used for the analysis of gas-phase components. The composition of the feed was: 1000 ppm NO, 1000 ppm ethanol or 2000 ppm CH_4, 2 vol.% O_2 with a catalyst volume 1 mL and GHSV (gas hour space velocity) 10,000 h^{-1}. Before catalytic tests, the samples were heated up to 523 K in oxygen/helium mixture and then NO and ethanol vapour or methane streams were switched on. The standard conditions were: 2 h catalytic runs at 523–623 K and 1 h runs at higher reaction temperatures (NO_x and CO_x concentrations at the reactor outlet were continuously monitored for checking if pseudo steady-state conditions were established). The reaction temperature was increased every 50 K intervals up to 773 K and then lowered in the same manner to 523 K for checking the reaction hysteresis loop.

Besides the SCR of NO experiments, the NO oxidation reaction in the absence of organic reducers was investigated: in that case, heating of the catalysts in 2 vol.% oxygen mixture over 723 K for 1 h was necessary in order to obtain a reproducible activity. All conversion and selectivity values quoted were defined and calculated in standard manner and presented in mol.%.

3. Results and discussion

3.1. Macroscopic and microscopic characteristics of the AlBEA and SiBEA support

The dealumination of TEABEA zeolite does not introduce significant changes in the BEA structure, as shown by similar XRD patterns of AlBEA and SiBEA zeolites (Fig. 1) and by the absence of any mesoporosity in the both samples evidenced by type 1 nitrogen adsorption/desorption isotherm and similar BEA surface (not shown). Neither calcination (at 853 K for 15 h in air) nor its dealumination by nitric acid affects the zeolite crystallinity. The decrease of the d_{302} spacing related to the narrow main diffraction peak near 22.6° from 3.942 (AlBEA) (with 2θ of 22.54°) to 3.915 Å (SiBEA) (with 2θ of 22.70) upon dealumination indicates contraction of the matrix as a result of removal of Al atoms, in line with earlier work [10,11,13].

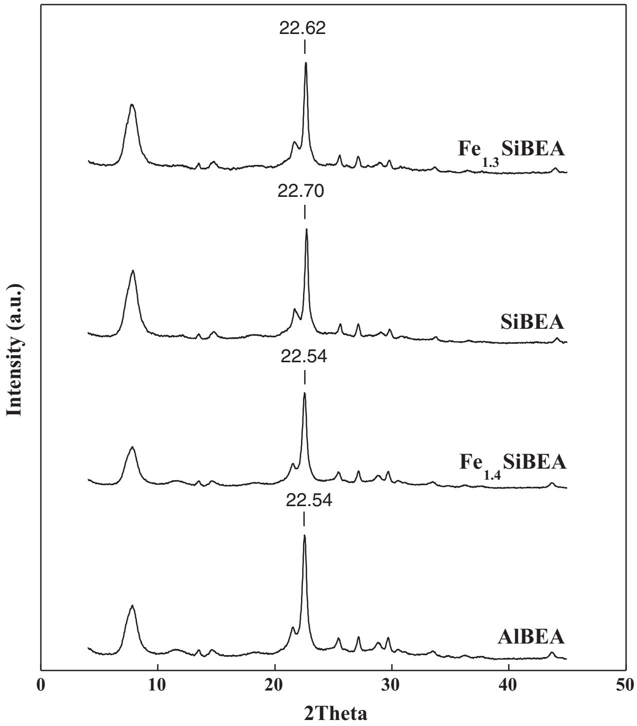

Fig. 1. X-ray diffractograms recorded at room temperature of as prepared AlBEA, $Fe_{1.4}$AlBEA, SiBEA and $Fe_{1.3}$SiBEA.

Moreover, the dealumination does not induce a change in the frequency or intensity of the IR bands due to overtones and combinations of the skeletal modes at 1994, 1876, 1714 and 1659 cm^{-1} (Fig. 2), confirming that this process does not affect zeolite crystallinity.

To see the modifications at the microscopic level, the AlBEA and SiBEA zeolites have been investigated by FT-IR spectroscopy in the range of vibration of OH groups (Fig. 2). As shown earlier [10,11], the FT-IR spectrum of TEABEA zeolite calcined at 550 °C for 15 h exhibits four main IR bands due to the OH stretching modes of AlO–H groups at 3665 cm^{-1}, Si–O(H)–Al groups at 3609 cm^{-1}, isolated SiO–H groups at 3741 cm^{-1} and H-bonded SiO–H groups at 3520 cm^{-1}. The last broad band reveals the presence in AlBEA zeolite of vacant T-atom sites with silanol groups. The treatment of TEABEA zeolite by aqueous acid nitric solution leads to the elimination of framework Al atoms, as evidenced by the disappearance of bands at 3665 (AlO–H groups) and 3609 cm^{-1} (Si–O(H)–Al groups). The appearance in as obtained SiBEA of narrow bands at 3736 and 3710 cm^{-1} related to isolated internal and terminal silanol groups and of an intense broad band at 3520 cm^{-1} due to H-bonded SiOH groups evidence creation of considerable amounts of vacant T-atom sites associated with silanol groups.

3.2. Macroscopic and microscopic characteristics of the FeAlBEA and FeSiBEA catalysts

The introduction of iron ions in AlBEA and SiBEA, respectively, by the conventional ion exchange and the two-step postsynthesis

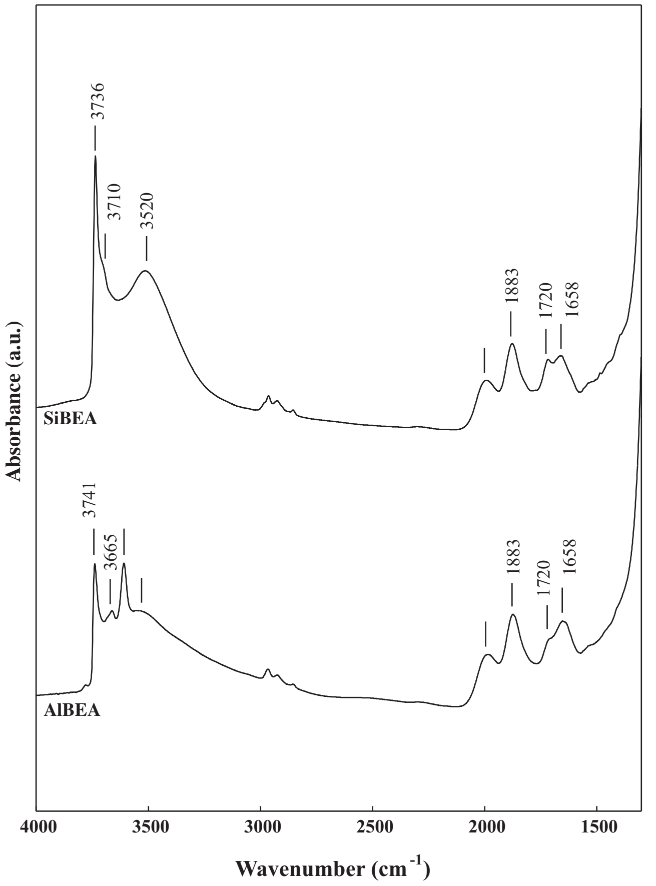

Fig. 2. FT-IR spectra of AlBEA and SiBEA (outgassed at 573 K for 6 h) recorded at room temperature in the vibrational range of OH groups (4000–3200 cm^{-1}) and overtones and combinations vibrational range (1800–1500 cm^{-1}).

method does not induce changes in BEA matrix, as shown by similar patterns of AlBEA, $Fe_{1.4}$AlBEA, SiBEA and $Fe_{1.3}$SiBEA, typical of BEA structure (Fig. 1). The significant increase of the d_{302} spacing from 3.915 Å (with 2θ of 22.70°) (SiBEA) to 3.941 Å (with 2θ of 22.62°) ($Fe_{1.3}$SiBEA) upon introduction of 1.3 wt% Fe into SiBEA indicates expansion of the matrix as a result of reaction of iron ions with OH groups of vacant T-atom sites and their incorporation in framework position of BEA zeolite, as reported earlier for VSiBEA [10,11,14] and FeSiBEA [15,16]. In spite of this expansion, $Fe_{1.3}$SiBEA exhibits similar intensity of diffraction lines as that observed for SiBEA suggesting that incorporation of Fe ions in this zeolite framework does not affect its crystallinity. The introduction of iron ions in AlBEA zeolite by conventional ion exchange does not lead to the increase of the d_{302} spacing (3.942 Å, with 2θ of 22.54°) suggesting that probably not high amount of Fe ions is incorporated in the zeolite framework.

This is confirmed by the DR UV–vis spectra of $Fe_{1.4}$AlBEA and $Fe_{1.3}$SiBEA catalysts (Fig. 3). $Fe_{1.4}$AlBEA exhibits several DR UV–vis bands in the range 260–550 nm. The band at 275 nm can be assigned to oxygen-to-metal charge transfer (CT) transitions involving framework tetrahedral Fe(III) species, in line with earlier results [17,18]. However, the broad band at 360 nm can be assigned to oxygen-to-metal CT transitions involving extra-framework octahedral Fe(III) and the broad bands near 400–550 nm to extra-framework FeO_x oligomers and/or iron oxide, in line with earlier studies [16,19,20].

In contrast, for $Fe_{1.3}$SiBEA the intense DR UV–vis band at 275 nm appears assigned to oxygen–to–metal charge transfer (CT) transitions involving framework tetrahedral Fe(III) species. It suggests that upon preparation of this sample by two-step postsynthesis method almost all Fe ions are incorporated in the zeolite framework as $\equiv Fe^{3+}–O(H)–Si\equiv$ acidic sites characterized by an IR band at around 3630 cm^{-1} as reported earlier [15,16].

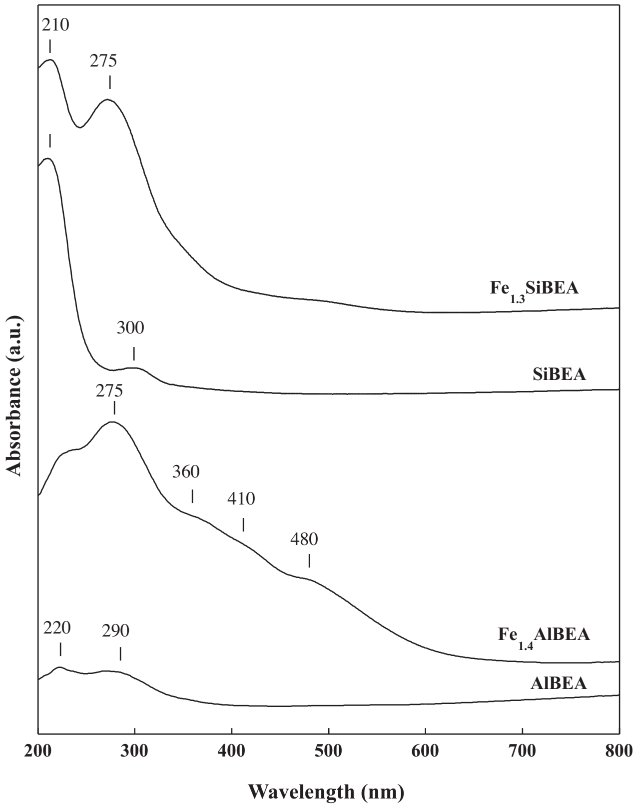

Fig. 3. DR UV–vis spectra recorded at room temperature and ambient atmosphere of AlBEA, $Fe_{1.4}$AlBEA, SiBEA and $Fe_{1.3}$SiBEA.

3.3. *Effect of the nature of the Fe species and acidity on catalyst activity*

Figs. 4 and 5 show the conversions of NO in SCR reaction with ethanol (NO_{SCR}) and oxidation reaction of NO measured in the absence of organic reducers in the gas phase (NO_{OX}) as well as ethanol conversion (Figs. 4A and 5A) and selectivities toward N_2, C_2H_4, NO_2, CO_2, CO and other organic products (Figs. 4B and 5B) on $Fe_{1.3}$SiBEA and $Fe_{1.4}$AlBEA zeolites, respectively.

$Fe_{1.3}$SiBEA with framework tetrahedral Fe(III) species is much more active in SCR of NO with ethanol than SiBEA, with maximum NO conversion of 40% at 623 and selectivity toward N_2 higher than 80% in the whole temperature range. In the same reaction condition, NO conversion on SiBEA is lower than 10%, as shown in our earlier work [21]. Moreover, the ethanol conversion for $Fe_{1.3}$SiBEA is close to the 100% at the reaction temperature range between 623 and 773 K. At low reaction temperature, the main ethanol conversion product is ethylene and total oxidation product, CO_2, dominating above 600 K. The increase of formation of NO_2 with the increase of reaction temperature is accompanied by the decrease of formation of organic products and CO. For this catalyst, NO_2 formation is already observed at 525 K.

$Fe_{1.4}$AlBEA with framework tetrahedral and extra-framework octahedral Fe(III) species is slightly more active than $Fe_{1.3}$SiBEA in SCR of NO with ethanol reaching the NO maximum conversion about 53% at 673 K (Fig. 5A). The $Fe_{1.4}$AlBEA is more selective toward N_2 than $Fe_{1.3}$SiBEA. Its selectivity toward N_2 is practically independent on the reaction temperatures between 573 and 773 K

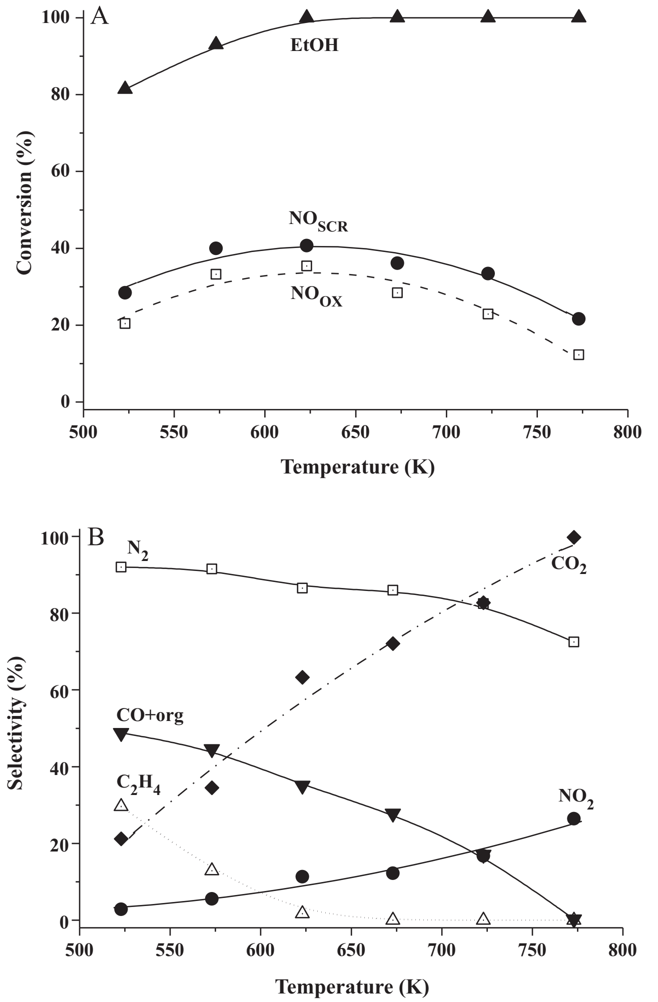

Fig. 4. Temperature-dependence of (A) ethanol and NO conversions and (B) product selectivities in SCR of NO with ethanol of $Fe_{1.3}SiBEA$.

(Fig. 5B) and reaches the values close to 95%. For $Fe_{1.4}AlBEA$, the increase of formation of NO_2 with the increase of reaction temperature is accompanied by the depletion of organic products such as acetaldehyde, acetic acid, acetonitrile and CO.

For both $Fe_{1.3}SiBEA$ and $Fe_{1.4}AlBEA$, N_2 is the main product of the SCR of NO and ethanol oxidation reaction leads to the products of partial oxidation (CO and organic intermediates, as aldehydes) besides CO_2. The differences in the organic product distribution for both catalysts may be due to the different oxidation power of their active sites related probably to the presence ($Fe_{1.4}AlBEA$) or absence ($Fe_{1.3}SiBEA$) of Al atoms in the environment of Fe species. It seems that in the presence of active sites with lower oxidation power, the higher activity in SCR of NO would be observed.

We have earlier observed [5,21], that in the case of CoSiBEA and FeSiBEA zeolites, NO conversion, both in SCR process and during the NO oxidation reaction (in the absence of reducing agent) increases with the increase of metal content. In all cases the NO conversion in SCR process is higher than in NO oxidation reaction. It suggests that metal species are responsible for the catalytic activity in both cases and points out that both processes may be activated on the same active centre but the NO_2 formation does not precede the surface NO_x complex formation.

The active centre in the case of $Fe_{1.3}SiBEA$ is related to the presence of framework tetrahedral $\equiv Fe^{3+}–O(H)–Si\equiv$ sites. These Fe(III) sites, are origin of strong Brønsted and Lewis acidic centres

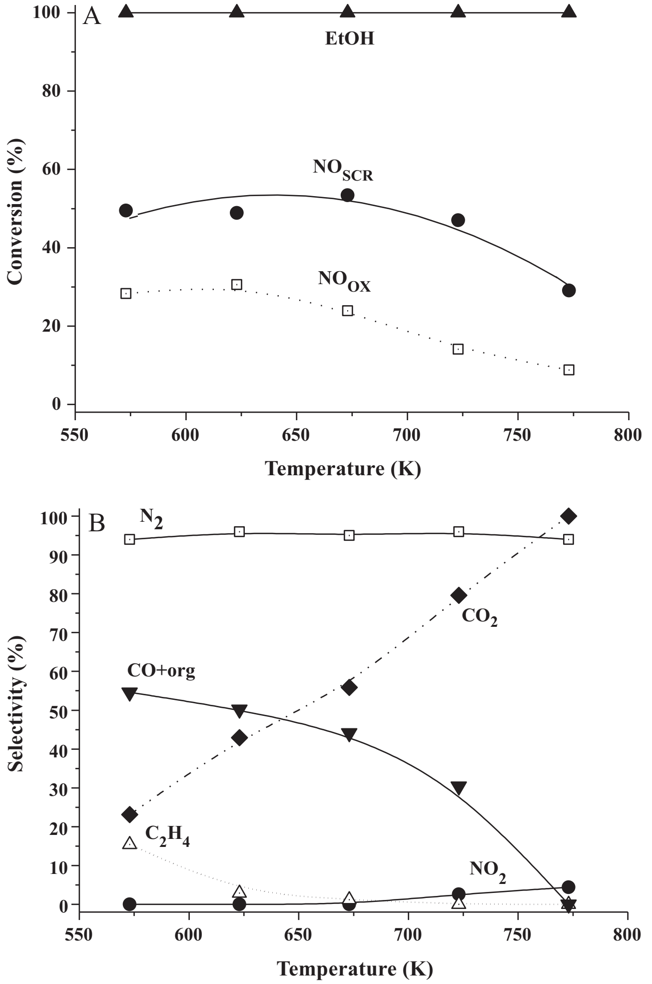

Fig. 5. Temperature-dependence of (A) ethanol and NO conversions and (B) product selectivities in SCR of NO with ethanol of $Fe_{1.4}AlBEA$.

which may play important role in the catalytic activity of $Fe_{1.3}SiBEA$ zeolite. As evidenced in our earlier work by low-temperature CO adsorption [16], these centres are only slightly less acidic than the corresponding $\equiv Al^{3+}–O(H)–Si\equiv$ analogues.

In the case of $Fe_{1.4}AlBEA$, the concentration of metal species in the zeolite is practically the same, but the distribution of Fe(III) ions is altered. Apart from tetrahedral Fe(III) species in framework positions, the high amount of octahedral Fe(III) species in extra-framework position appears. Moreover, the presence of Al ions and connected with this fact emerging of Brønsted and Lewis acidity can influence the catalytic behavior of this sample. Indeed, the $Fe_{1.4}AlBEA$ seems to be slightly more active in SCR of NO with ethanol and more selective toward N_2 (Figs. 4 and 5). It is connected with less pronounced activity of this catalyst to the total oxidation of the organic agent.

Thus, the difference in catalytic activity of $Fe_{1.4}AlBEA$ and $Fe_{1.3}SiBEA$ in SCR of NO with ethanol seems to be related to the presence of different nature of iron species and the presence of Al and Fe ions in the zeolite framework, respectively. The framework tetrahedral Al(III) and Fe(III) species, are origin of strong Brønsted and Lewis acidic centres which may have influence on catalytic properties of $Fe_{1.4}AlBEA$ and $Fe_{1.3}SiBEA$ zeolites.

The difference in catalytic behavior of $Fe_{1.3}SiBEA$ and $Fe_{1.4}AlBEA$ is much more pronounced in SCR of NO with methane. As it was shown earlier [8,9], the Me-BEA catalysts prepared by the conventional ion exchange or impregnation method are less active than Me–ZMS-5 or Me–ferrierite catalyst in this process [8,9]. On the

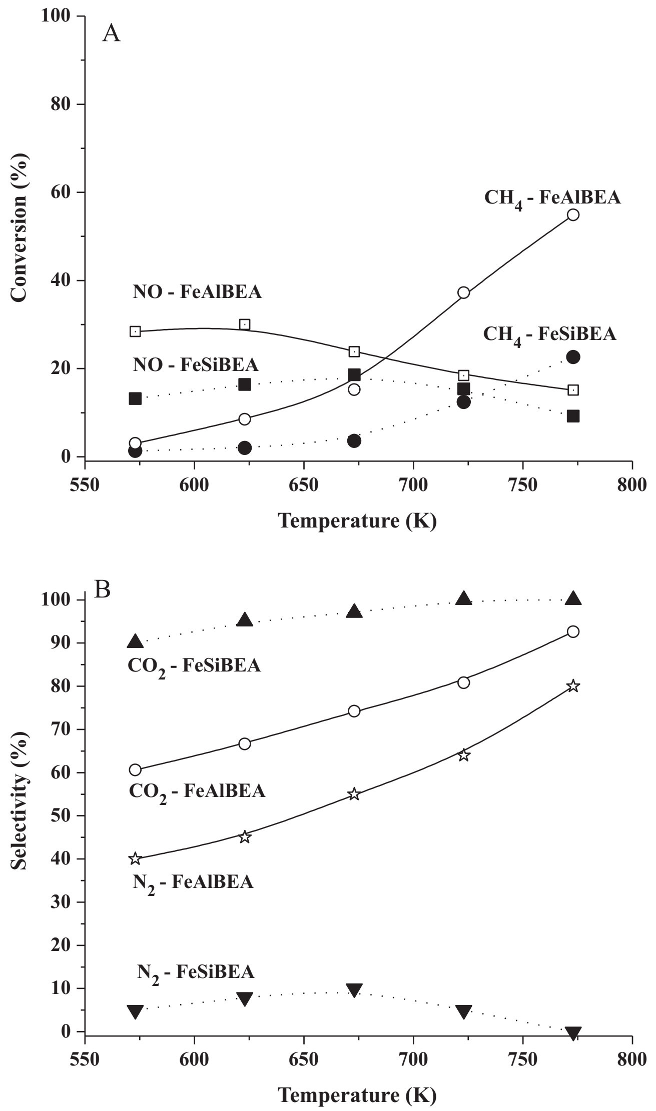

Fig. 6. Comparison of the temperature-dependence of (A) methane and NO conversions and (B) product selectivities in SCR of NO with methane on $Fe_{1.3}$SiBEA (filled figures) and $Fe_{1.4}$AlBEA (open figures).

other hand, our experimental data show that the $Fe_{1.3}$SiBEA is much less active in SCR of NO with methane than $Fe_{1.4}$AlBEA. In Fig. 6 the comparison of catalytic behavior of $Fe_{1.3}$SiBEA and $Fe_{1.4}$AlBEA catalysts is presented.

It is seen that the $Fe_{1.4}$AlBEA catalyst gives higher NO and CH_4 conversion almost in the whole temperature range from 575 to 775 K and is much more selective in SCR of NO with methane toward N_2 than $Fe_{1.3}$SiBEA ones what clearly indicates that the active centres involved in both cases are not the same. The higher strength and amount of Brønsted and Lewis acidic centres in $Fe_{1.4}$AlBEA than in $Fe_{1.3}$SiBEA catalyst seem to be responsible for its higher activity in the SCR of NO with methane and much higher selectivity toward N_2.

4. Conclusions

The calcination and dealumination of BEA zeolite do not induce the modification of its crystallinity as evidenced by XRD and FT-IR. Introduction of iron ion in AlBEA and SiBEA by conventional ion exchange and two-step postsynthesis method, respectively, leads to FeAlBEA and FeSiBEA catalysts also without modification of their crystallinity.

In the FeAlBEA catalyst, framework tetrahedral Fe(III), extra-framework octahedral Fe(III) and FeO_x oligomers are observed by DR UV–vis. In contrast, in the FeSiBEA catalyst mainly framework tetrahedral Fe(III) appears as a result of incorporation of Fe ions in vacant T-atom sites of SiBEA.

The catalytic activity of FeAlBEA and FeSiBEA catalysts in SCR of NO with ethanol or methane depends on the nature of Fe species and the presence of Al and Fe ions in the zeolite framework as $\equiv Al^{3+}–O(H)–Si\equiv$ and $\equiv Fe^{3+}–O(H)–Si\equiv$ sites, respectively.

These framework tetrahedral Al(III) and Fe(III) sites can act simultaneously as Brønsted and Lewis acidic centres and have influence on catalytic properties of $Fe_{1.4}$AlBEA and $Fe_{1.3}$SiBEA zeolites. The higher strength and amount of Brønsted and Lewis acidic centres in $Fe_{1.4}$AlBEA than in $Fe_{1.3}$SiBEA catalyst seem to be responsible for its higher activity in the SCR of NO with methane and much higher selectivity toward N_2.

Further investigations are underway on FeAlBEA and FeSiBEA zeolites to check the last hypothesis.

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References

[1] H.Y. Chen, W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[2] M. Kogel, R. Monnig, W. Schwieger, A. Tissler, T. Turek, J. Catal. 182 (1999) 470.
[3] G.D. Pirngruber, P.K. Roy, Catal. Lett. 93 (2004) 75.
[4] G.D. Pirngruber, P.K. Roy, Catal. Today 110 (2005) 199.
[5] S. Dzwigaj, J. Janas, T. Machej, M. Che, Catal. Today 119 (2007) 133.
[6] S. Dzwigaj, J. Janas, J. Mizera, J. Gurgul, R.P. Socha, M. Che, Catal. Lett. 126 (2008) 36.
[7] S. Dzwigaj, J. Janas, J. Gurgul, R.P. Socha, T. Shishido, M. Che, Appl. Catal. B 85 (2009) 131.
[8] H-Y. Chen, X. Wang, W.M.H. Sachtler, Appl. Catal. A 194 (2000) 159.
[9] B. Wichterlova, Top. Catal. 28 (2004) 131.
[10] S. Dzwigaj, M.J. Peltre, P. Massiani, A. Davidson, M. Che, T. Sen, S. Sivasanker, Chem. Commun. (1998) 87.
[11] S. Dzwigaj, P. Massiani, A. Davidson, M. Che, J. Mol. Catal. 155 (2000) 169.
[12] E. Bourgeat-Lami, F. Fajula, D. Anglerot, T. Des Courieres, Micropor. Mater. 1 (1993) 237.
[13] M.A. Camblor, A. Corma, J. Pérez-Pariente, Zeolites 13 (1993) 82.
[14] S. Dzwigaj, M. Matsuoka, M. Anpo, M. Che, J. Phys. Chem. B 104 (2000) 6012.
[15] J. Janas, J. Gurgul, R.P. Socha, T. Shishido, M. Che, S. Dzwigaj, Appl. Catal. B 91 (2009) 113.
[16] K. Hadjiivanov, E. Ivanova, R. Kefirov, J. Janas, A. Plesniar, S. Dzwigaj, M. Che, Micropor. Mesopor. Mater. 131 (2010) 1.
[17] S. Dzwigaj, L. Stievano, F.E. Wagner, M. Che, J. Phys. Chem. Solids 68 (2007) 1885.
[18] P. Wu, T. Komatsu, T. Yashima, Micropor. Mesopor. Mater. 20 (1998) 139.
[19] L. Capek, V. Kreibich, J. Dedecek, T. Grygar, B. Wichterlova, Z. Sobalik, J.A. Martens, R. Brosius, V. Tokarova, Micropor. Mesopor. Mater. 80 (2005) 279.
[20] M. Santhosh Kumar, M. Schwidder, W. Grunert, U. Bentrup, A. Bruckner, J. Catal. 239 (2006) 173.
[21] J. Janas, T. Machej, J. Gurgul, L.P. Socha, M. Che, S. Dzwigaj, Appl. Catal. B 75 (2007) 239.