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Redox chemistry in excessively ion-exchanged Cu/Na-ZSM-5

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TPR/TPD and FTIR are used to characterize "excessively ion-exchanged" Cu/Na-ZSM-5. After calcination in O_2 at 773 K at least two copper–oxygen species are present in addition to Cu^{2+} ions; these have been identified as CuO and $[Cu–O–Cu]^{2+}$. Reduction in H_2 transforms all these into Cu^0 below 773 K. $[Cu–O–Cu]^{2+}$ is autoreduced to Cu^+ during outgassing. Reoxidation of Cu^0 by zeolite protons to Cu^+ is observed above 723 K in He or Ar; in the presence of CO this process is considerably enhanced and observed at much lower temperature, because CO is strongly adsorbed on Cu^+. At 293 K CO adsorption causes reversible changes in the FTIR spectra.

Keywords: H^+-induced reoxidation; Cu/Na-ZSM-5; CO; FTIR; TPR-TPD

1. Introduction

The class of copper containing zeolites of MFI structure type, conventionally described as Cu-ZSM-5, shows high promise for the catalytic abatement of NO_x emission even in O_2 containing gas [1]. Iwamoto showed that higher N_2 yields are obtained with "excessively exchanged" Cu-ZSM-5, i.e. samples with a Cu/Al ratio exceeding 0.5. The formation of $[Cu(OH)]^+$ ions was recently proposed in these catalysts [2,3] in accordance with the earlier suggestions for ion-exchanged Cu-Y [4,5]. Thermal decomposition of this complex results in the formation of $[Cu–O–Cu]^{2+}$, a proposed active species for NO decomposition [2]. This species has also been suggested for Cu-Y [4–8], Cu-X [9,10], as well as for systems containing Cu on amorphous supports, e.g., CuO/MgO [11] and Cu/SiO_2 [12]. In the case of Cu-Y, the concentration of $[Cu–O–Cu]^{2+}$ species increases with the Cu-loading, but it is also present at low ion-exchange levels [7].

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Zeolitic protons are a coproduct of the reduction of copper ions by H_2. It has been shown with other metal/zeolite systems that this reduction is, in part, reversible [13]; for instance, Cu atoms in Pd/Cu–NaHY are oxidized by zeolitic protons to Cu ions. The equilibrium of this reduction and reoxidation is affected by the presence of CO, because the relative bond strength of CO with the reduced and the oxidized metal will be different. In the present study TPR/TPD and FTIR are used to monitor the reduction of excessively ion-exchanged Cu/Na-ZSM-5 with H_2 and CO. Attention is focussed on characterizing the copper species present in the calcined sample and the reoxidation of Cu^0 by the combined action of zeolitic H^+ and CO.

2. Experimental

2.1. MATERIALS

Excessively ion-exchanged Cu/Na-ZSM-5 was prepared from a slurry of $NaNO_3$-washed MFI (UOP) and an aqueous solution of Cu-acetate (Aldrich) at pH = 7, following the method of Iwamoto et al. [2]. According to the nomenclature of Iwamoto et al., the degree of excess Cu loading is calculated under the assumption that one Cu^{2+} is exchanged for two Na^+ ions. The chemical compositions and contaminations of the samples (table 1) were determined by inductively coupled plasma (ICP) (Atomscan 25 spectrometer, Thermo Jarrel Ash Corp.). Iron was the largest impurity, ≈ 2 at% of the total Cu content (Cu/Fe = 52 and Fe/Al = 1.44×10^{-2}). The concentrations of other impurities were more than two orders of magnitude less.

Gases (He, Ar, O_2 and H_2 (Linde) and the 0.9790 vol% CO in He (Matheson)) were ultra high purity grade, and further purified as described in refs. [14,15]. The CuO used for the TPR/TPD calibrations was a product of Matheson Coleman & Bell.

Table 1
(A) Chemical composition of ZSM-5 zeolites. (B) Impurity analysis data of H-ZSM-5 as-received

(A)

Sample	Cu (wt%)	Si/Al	Cu/Al	Na/Al	Cu/Fe
H-ZSM-5					
as-received		20		0.07	
$NaNO_3$-washed		20		0.50	
Cu/Na-ZSM-5	3.1	20	0.75	0.09	52

(B)

Fe/Al	Cr/Al	Mn/Al	Co/Al	Cu/Al
1.44×10^{-2}	9.97×10^{-4}	2.22×10^{-4}	7.76×10^{-5}	7.20×10^{-5}

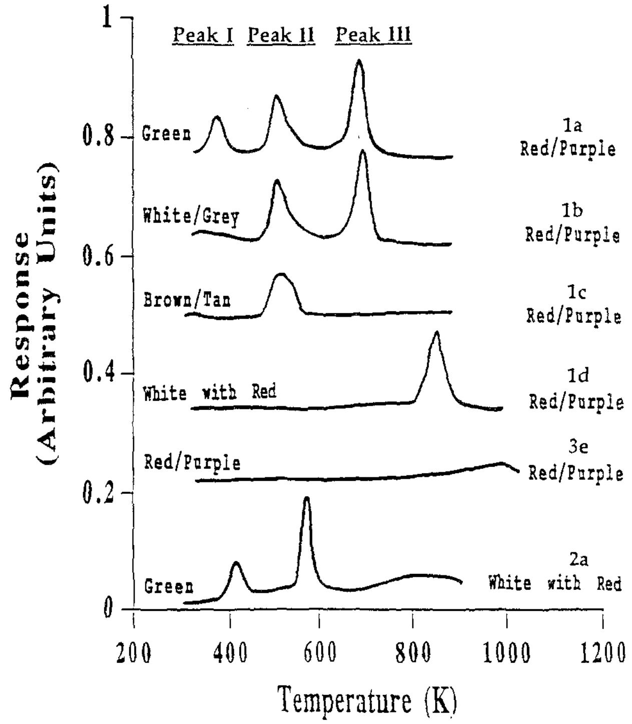

Fig. 1. H_2-TPR (1), CO-TPR/MS (2) and H_2-TPD (3) patterns of Cu/Na-ZSM-5: after (a) calcination, (b) calcination followed by a 20 min degassing at 773 K in Ar; (c) reoxidation (O_2, 473 K, 1 h), (d) prereduction in CO, and (e) H_2-TPR. (Positive signal means H_2 consumption for H_2-TPR, H_2 formation for H_2-TPD and CO_2 formation for CO-TPR.)

2.2. APPARATUS AND PROCEDURE

The TPR(MS)/TPD equipments, the FTIR instrument, the IR cell, and the procedure were described earlier [14,15]. The catalyst was calcined in flowing O_2 (180 ml/min) from 293 to 773 K at 0.66 K/min, held at 773 K for 2 h, then cooled to 293 K in O_2. For FTIR the temperature was increased (8 K/min) after a purge with He in H_2 (40 ml/min) to 723 K, held for 20 min followed by a 20 min purge with He (40 ml/min) and cooling to 293 K.

3. Results and discussion

3.1. TPR/TPD (FIG. 1)

Fig. 1/1a shows for calcined Cu/Na-ZSM-5 three H_2-TPR peaks. The total H_2 consumption obtained from peak integration corresponds to complete reduction of Cu^{II} to Cu^0. The color change from light green to red-purple and the

FTIR results below support this total reduction to Cu^0. Outgassing of the calcined sample in Ar at 773 K for 2 h prior to a H_2-TPR run eliminates peak I almost totally, leaving peaks II and III essentially intact (fig. 1/1b). Heating the reduced sample in O_2 to *473 K* (temperature ramp 1.5 K/min) and holding for 1 h regenerates only peak II (fig. 1/1c), which becomes wider; its area increases by 38%. In order to distinguish copper ions from oxygen containing Cu moieties, a calcined sample was reduced with CO. The H_2-TPR profile subsequent to this CO treatment is shown in fig. 1/1d. The elimination of peaks I and II suggests that these are due to the reduction of oxygen containing Cu species, whereas peak III is attributed to copper ions.

On the basis of these data and the concomitant color changes, the following assignments are made: I: $[Cu\text{-}O\text{-}Cu]^{2+}$; II: CuO; III: Cu^+ ions. A separate peak attributed to the reduction of Cu^{2+} ions to Cu^+ is not observed, suggesting formally that any Cu^{2+} species are reduced at the same temperature as Cu^+ or in a step leading to peak broadening between peaks II and III. The water formed during the reduction of the O-containing species may influence the transformation of Cu^{2+} to Cu^+. The presence of CuO in a calcined sample suggests that along with the exchange of Cu^{2+} and $[Cu(OH)]^+$ at pH = 7, some $Cu(OH)_2$ may also form and/or some Cu-acetate may remain in the ZSM-5 zeolite after rinsing. Subsequent calcination leads to the formation of small CuO particles. Similarly, for Cu-Y prepared from Cu-nitrate, "excess exchange" was observed and attributed to the precipitation of a hydroxide species followed by dehydration to the oxide [16].

With H_2 the following reduction processes are thus discerned:

$$[Cu\text{-}O\text{-}Cu]^{2+} + H_2 = 2Cu^+ + H_2O \quad (293\ K); \tag{1}$$

$$CuO + H_2 = Cu^0 + H_2O \quad (443\ K); \tag{2}$$

$$Cu^{2+} + \tfrac{1}{2}H_2 = Cu^+ + H^+ \quad (> 443\ K); \tag{3}$$

$$Cu^+ + \tfrac{1}{2}H_2 = Cu^0 + H^+ \quad (608\ K). \tag{4}$$

By assigning peak I in fig. 1/a to process (1), peak II to (2) and (3), and peak III to (4), we arrive at the following rough estimation for the distribution of the three Cu-species prior to reduction: $[Cu\text{-}O\text{-}Cu]^{2+} = 35\%$, $CuO = 25\%$, and $Cu^{2+} = 40\%$.

With CO the following reduction processes are proposed:

$$[Cu\text{-}O\text{-}Cu]^{2+} + CO = 2Cu^+ + CO_2 \quad (343\ K); \tag{5}$$

$$CuO + CO = Cu^0 + CO_2 \quad (508\ K). \tag{6}$$

In Ar, thermal decomposition of $[Cu\text{-}O\text{-}Cu]^{2+}$ also takes place:

$$[Cu\text{-}O\text{-}Cu]^{2+} = 2Cu^+ + \tfrac{1}{2}O_2 \quad (773\ K). \tag{7}$$

O_2 formation is detected by MS when heating the calcined sample in Ar; the FTIR data confirm the formation of Cu^+ by the characteristic band for $CO-Cu^+$ which is obtained after CO exposure at 293 K of an outgassed sample. Eq. (2) is also in good agreement with the earlier findings [2,17,18]. An FTIR band at 2295 cm^{-1} was identified and may be attributed to a superoxide in analogy to findings on Ce-oxide [19]. We refrain from speculating on how formation and decomposition of Cu-superoxide might take part in the selective reduction of NO. MS analysis of the gas formed during CO-TPR (fig. 1/2a) also shows a wide CO_2 peak centered at 763 K, which might indicate formation and decomposition of a carbonate.

Wendlandt et al. [20] recently found that after thermal treatment to 773 K only 73% of the Cu in ion-exchanged Cu/Na-ZSM-5 was reduced during H_2-TPR, but after heating the sample in O_2 to 523 K for 2 h, the extent of reduction calculated from H_2 consumption was 100%. Although their samples contained only 0.5 wt% Cu and the Si/Al ratio of the zeolite was 47, these results agree with ours.

H_2-TPD in Ar (fig. 1/3e) reveals H_2 evolution above 723 K suggesting reoxidation of Cu^0 by zeolite protons to Cu^+ (see also below). The extent of reoxidation is kinetically limited, viz., a higher maximum TPD temperature results in a greater degree of reoxidation.

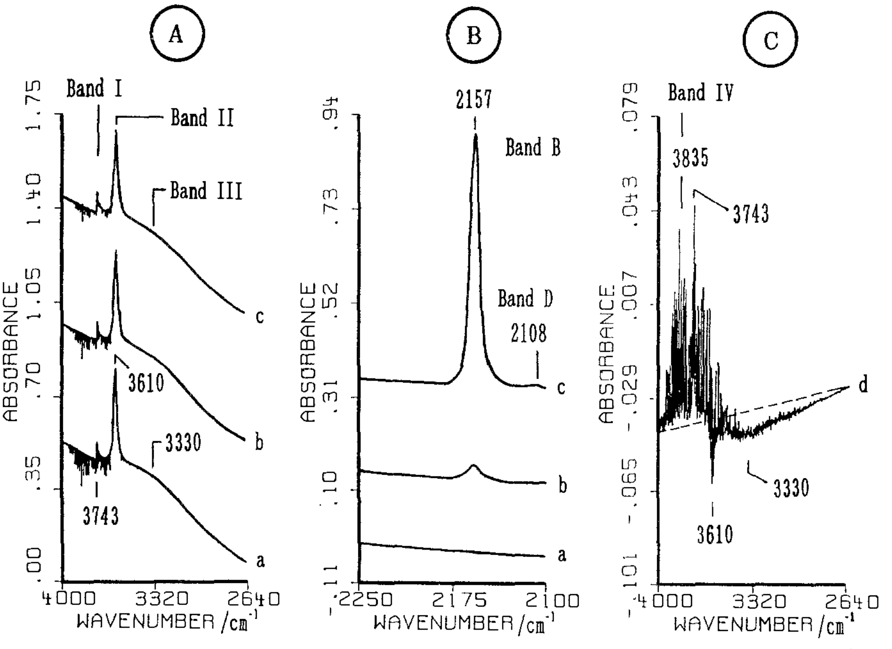

Fig. 2. FTIR spectra of Cu/Na-ZSM-5 *in He* in the regions of (A) 4000–2640 cm^{-1} and (B) 2250–2100 cm^{-1}: after (a) H_2-reduction; (b) a 20 min CO exposure at 293 K; (c) CO admission at 723 K for 20 min. Difference spectra (C) between A/c and A/a.

3.2. FTIR (FIGS. 2 AND 3)

3.2.1. *Reoxidation of Cu^0 to Cu^+ (Fig. 2)*

After H_2-reduction to 723 K, three OH bands are found in the FTIR spectrum (fig. 2A/a) assigned to: silanol (band I; 3743 cm^{-1}), protonic (bridged, Si(OH)Al) (band II; 3610 cm^{-1}; absorbance, $A_{OH} = 0.3529$) (fig. 2A/a), and H-bonded (band III; ≈ 3330 cm^{-1}) OH groups [21–25]. Following exposure to CO at 293 K a very small CO band ($A_{CO} = 0.0337$; half-width, $\Delta\nu_{1/2} = 11.4$ cm^{-1}) is detected at 2157 cm^{-1} (fig. 2B/b) due to Cu^+–CO species [25]. Upon cooling the reduced sample from 723 to 293 K in H_2, this band becomes even smaller ($A_{CO} = 0.0009$); it is not observed for a Cu-free sample. In good agreement with temperature programmed studies, this shows that the Cu^{II} in Cu/Na-ZSM-5 is totally reduced in H_2 at 723 K, whereas the extent of reoxidation of Cu^0 by protons to Cu^+ *in He* is very small at 723 K and slightly larger at 773 K.

However, we observed a significant increase of the band Cu^+–CO ($A_{CO} = 0.5611$; $\Delta\nu_{1/2} = 8.3$ cm^{-1}) at 723 K *in CO/He* (fig. 2B/c) accompanied by a decrease of 6.7% in A_{OH}(II) (figs. 2A/a,c and 2C/d). This is clear evidence for a combined effect of zeolite protons and CO in the reoxidation of Cu^0 to Cu^+. The strong chemisorption of CO on Cu^+ [26] provides a thermodynamic driving

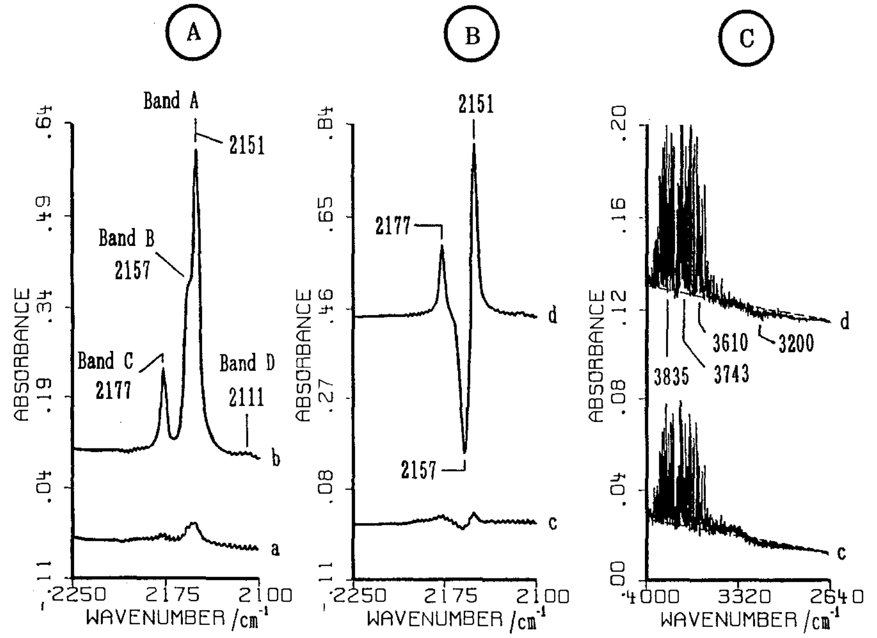

Fig. 3. FTIR spectra of Cu/Na-ZSM-5 *in 7.5 Torr CO/He* (A) in the region of 2250–2100 cm^{-1}: after (a) a 20 min CO exposure at 293 K; and (b) CO-treatment at 723 K for 20 min (see figs. 2/b and 2/c). (B) and (C) difference spectra between those obtained in the presence of 7.5 Torr CO/He and only in He: (c) after (a) (i.e. fig. 3/a – fig. 2/b) and (d) after (b) (i.e. fig. 3/b – fig. 2/c) in the regions of (B) 2250–2100 cm^{-1} and (C) 4000–2640 cm^{-1}.

force for this process. Similar results were obtained with Rh/Na-Y [13]. The reoxidation of Cu^0 by zeolitic protons is also really observed at lower temperature, e.g., at 570 K. At 723 K it is accompanied by a decrease in A_{OH}(III) and a small increase in A_{OH}(I) (fig. 2C). As these OH bands are complex, it is not clear what fraction of band III is due to acidic protons, and how much to bridged [24], internal silanol [23] OH groups, or non-framework Al–OH groups. The small band at around 3835 cm^{-1} (band IV, $A_{CO} = 0.005$) in the difference spectrum in fig. 2C may be due to OH groups related to extra framework aluminum [27].

A very weak CO band (band D, $A_{CO} = 0.0056$) is present at 2108 cm^{-1} in fig. 2B/c. Bands in this frequency region have been attributed to Cu^0–CO [28,29]. However, we find it only for *partially* reoxidized or reduced samples, but never in totally reduced Cu/Na-ZSM-5. Moreover, this band shows a high thermal stability, viz., it is still present after heating the sample in flowing He at 473 K for 10 min.

3.2.2. *Effect of gaseous CO on the IR spectra (Fig. 3)*

In CO/He at 293 K new CO bands appear at 2177 (band C, $A_{CO}(C) = 0.1433$) and 2151 cm^{-1} (band A, $A_{CO}(A) = 0.5016$), whereas the band at 2157 cm^{-1} (band B, $A_{CO}(B) = 0.2917$) decreases in intensity (see figs. 3/A and 3/B). Simultaneously, a small decrease in A_{OH} at 3300–3200 cm^{-1} is accompanied by small increases of bands at 3610, 3743 and 3835 cm^{-1} (fig. 3C), suggesting some destruction of the H-bonds at 3300–3200 cm^{-1}. This effect seems to be somewhat larger for the reoxidized sample having more Cu^+–CO, but less zeolitic protons (fig. 3C/d). However, these changes alone do not provide sufficient explanation to the very high sensitivity of the interconversion $B \rightleftharpoons A + C$ to temperature and CO pressure. This interconversion presumably implies a migration of Cu^+–CO induced by a weak CO adsorption, increasing the coordination number of Cu^+, while also changing its charge and the extent of backdonation to the $2\pi^*$-CO. It is worth noting that the three-band CO-structure is also observed with support-free Cu-oxide [30,31].

In CO/He at 293 K band D also shifts from 2108 (fig. 2B/c) to 2111 cm^{-1} (fig. 3A/b), while the CO band of Cu^+–CO shifts from 2157 to 2151 cm^{-1}. This might support some kind of electronic interaction between the two species, which seems to be larger in the presence of gaseous CO. Consequently, more charge would be donated from Cu^0 to Cu^+ which might increase the direct donation of CO to Cu^0 and the backdonation from Cu^+ to the $2\pi^*$-CO contributing to the opposite shifts of the two CO bands.

4. Conclusions

"Excessively ion-exchanged" Cu/Na-ZSM-5 contains copper oxide in addition to copper ions. In a calcined sample, the excess Cu is primarily present as

Cuo and $[Cu-O-Cu]^{2+}$. The latter species is transformed to Cu^+ during outgassing in He or Ar. Further work is necessary to establish which of the copper species identified in this work is involved in the catalysis of NO abatement. Reoxidation of Cu^0 to Cu^+ by zeolitic protons is enhanced by CO adsorption.

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References

[1] M. Iwamoto, in: *Future Opportunities in Catalytic and Separation Technology*, Studies in Surface Science and Catalysis, Vol. 54, eds. M. Misono, Y. Moro-oka and S. Kimura (Elsevier, Amsterdam, 1990) ch.II.3, p. 121.

[2] M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno and Y. Mine, J. Phys. Chem. 95 (1991) 3727.

[3] A.V. Kucherov, A.A. Slinkin, D.A. Kondrat'ev, T.N. Bondarenko, A.M. Rubinstein and Kh.M. Minachev, Kinet. Catal. 26 (1985) 353; Zeolites 5 (1985) 320.

[4] C.M. Naccache and Y.B. Taarit, J. Catal. 22 (1971) 171.

[5] P.A. Jacobs, W. Wilde, R.A. Schoonheydt, J.B. Uytterhoeven and H. Beyer, J. Chem. Soc. Faraday Trans. I 72 (1976) 1221.

[6] C.C. Chao and J.H. Lunsford, J. Chem. Phys. 57 (1972) 2890.

[7] J.C. Conesa and J. Soria, J. Chem. Soc. Faraday Trans. I 75 (1979) 406.

[8] M. Iwamoto, M. Nakamura, H. Nagano and S. Kagawa, J. Phys. Chem. 86 (1982) 153.

[9] F.R. Benn, J. Dwyer, A. Esfahani, N.P. Evmerides and A.K. Szczepura, J. Catal. 48 (1977) 60.

[10] F. Mahoney, R. Rudham and J.V. Summers, J. Chem. Soc. Faraday Trans. I 75 (1979) 314.

[11] A.A. Davydov, N.A. Rubene and A.A. Budneva, Kinet. Catal. 19 (1978) 776.

[12] M. Amara, M. Bettahar, L. Gengembre and D. Olivier, Appl. Catal. 35 (1987) 153.

[13] T.T. Wong, A.Yu. Stakheev and W.M.H. Sachtler, J. Phys. Chem., to be published.

[14] S.T. Homeyer and W.M.H. Sachtler, J. Catal. 117 (1989) 91.

[15] L.M. Kustov, D. Ostgard and W.M.H. Sachtler, Catal. Lett. 9 (1991) 121, and references therein.

[16] R.A. Schoonheydt, L.J. Vandamme, P.A. Jacobs and J.B. Uytterhoeven, J. Catal. 43 (1976) 292.

[17] M. Iwamoto, K. Maruyama, N. Yamazoe and T. Selyama, J. Phys. Chem. 81 (1977) 622.

[18] P.A. Jacobs and H.K. Beyer, J. Phys. Chem. 83 (1979) 1174.

[19] C. Li, K. Domen, K.-I. Maruya and T. Onishi, J. Am. Chem. Soc. 111 (1989) 7683.

[20] K.-P. Wendlandt, F. Vogt, W. Mörke and I. Achkar, *Zeolite Chemistry and Catalysis*, eds. P.A. Jacobs, N.I. Jaeger, L. Kubelková and B. Wichterlová (Elsevier, Amsterdam, 1991) p. 223.

[21] P.A Jacobs and R. von Ballmoos, J. Phys. Chem. 86 (1982) 3050.

[22] J. Datka and E. Tuznik, Zeolites 5 (1985) 230.

[23] G.L. Woolery, L.B. Alemany, R.M. Dessau and A.W. Chester, Zeolites 6 (1986) 14.

[24] V.L. Zholobenko, L.M. Kustov, V.Yu. Borovkov and V.B. Kazansky, Zeolites 8 (1988) 175.

[25] T. Romotowski, J. Komorek, Ye.A. Paukshtis and E.N. Yurchenko, Zeolites 11 (1991) 497.

[26] Y.Y. Huang, J. Catal. 30 (1973) 187; J. Am. Chem. Soc. 95 (1973) 6636.

[27] E. Loeffer, U. Lohse, Ch. Peuker, G. Oehlmann, L.M. Kustov, V.L. Zholobenko and V.B. Kazansky, Zeolites 10 (1990) 266.
[28] F. Vogt, I. Achkar, K.-P. Wendlandt, H. Hobert and M. Meier, Z. Chem. (Leipzig) 30 (1990) 112.
[29] A.A. Davydov, Kinet. Catal. 26 (1985) 135.
[30] G. Busca, J. Mol. Catal. 43 (1987) 225.
[31] A.A. Davydov and A.A. Budneva, React. Kinet. Catal. Lett. 25 (1984) 121.