

FTIRS study of the nature and reactivity of the products of nitromethane transformation on the surface of copper- and cobalt-exchanged ZSM-5 zeolites as related to the mechanism of NO_x CH_4 -SCR

S.A. Beloshapkin^{a,*}, E.A. Paukshtis^b, V.A. Sadykov^b

^a Novosibirsk State University, Boreskov Institute of Catalysis, Pirogova 2, Novosibirsk, 630090, Russia

^b Boreskov Institute of Catalysis SB RAS, pr. Laurentieva, 5, Novosibirsk, 630090, Russia

Abstract

For Cu- and Co-ZSM-5, at temperatures around 300°C, the adsorption of nitromethane followed by its acid-catalyzed transformation into isocyanates and melamine as well as the reactivity of these species with respect to oxygen and NO were studied by FTIRS. Both species easily interact with molecular oxygen, while no reaction with NO was observed. In the course of melamine oxidation, partial oxidation products including isocyanates appear to be produced. The reactivity of melamine and isocyanate depends upon the temperature and nature of transition metal cation, being reasonably high to suggest their role as intermediates in the NO_x CH_4 -SCR. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lately, NO_x selective reduction by hydrocarbons in excess of oxygen has attracted great attention due to its possible application for the clean-up of oxygen-rich exhausts. A lot of reaction mechanisms, claiming various species as intermediates, were suggested. For Cu- and Co-ZSM-5, FTIRS in situ, combined with pulse titration experiments, proved the reductive transformation of strongly bound nitrite–nitrate species under the effect of hydrocarbons to be the rate-determining stage [1,2]. Organic nitrocompounds (nitromethane, in the case of

methane, was used as reductant) are formed as the primary products of this reaction [1–3]. To get a deeper insight into the reaction scheme, the routes of these nitrocompounds subsequent transformations yielding at last N_2 , H_2O and CO_2 are to be studied. Our preliminary results for ZSM-5-based catalysts [4] revealed the nitromethane rapid transformation into other intermediates even at room temperature, those species being retained at the surface at temperatures above 200°C when nitromethane is already desorbed. FTIRS experiments for Cu-ZSM-5 in the flow cell demonstrated that nitromethane was transformed into N_2 , NO, CO, CO_2 and water, although the rates of the surface reactions were not estimated [5]. Meanwhile, to clarify

* Corresponding author.

the role of such intermediates in the NO_x CH_4 -SCR, the rates of their transformation at temperatures close to the operation temperatures of steady-state catalytic reaction are to be estimated and compared with the rates of surface nitrates transformation. That was the aim of this paper.

2. Experimental

The synthesis and some properties of Cu-ZSM-5 (Si/Al = 25; 2.6 wt.% Cu) and Co-ZSM-5 (Si/Al = 15; 2.25 wt.% Co) samples used in this work are presented elsewhere [1,2]. Experiments were carried out in a static IR cell of a 0.5 L volume, which allowed heating up to 600°C in controlled atmospheres. The samples were pressed into self-supported wafers with densities ~ 10 – 12 mg/cm^2 . The sample temperature was controlled by a thermocouple situated near its surface. Before the experiments were conducted, samples were pretreated in vacuum (10^{-3} Torr) at 500°C for 1 h, then kept for 1 h under 20 Torr of oxygen at the same temperature, cooled in O_2 to 280°C, and then evacuated. Nitromethane (1 μl) was inserted through the rubber diaphragm using a micro syringe. After 10 min of nitromethane contact with the catalyst, the gas phase was evacuated. Two sets of experiments were then carried out. In the first one, 7.6 Torr of O_2 were added. In the second set, NO was first dosed up to the residual pressure ~ 0.1 Torr, kept for 6 min followed by cell evacuation, and only after that was oxygen (7.6 Torr) introduced. The spectra were obtained by an accumulation of 32 scans at 4 cm^{-1} resolution using an IFS-113V Bruker spectrometer.

3. Results and discussions

3.1. Cu-ZSM-5

Fig. 1 shows the spectra recorded in the course of nitromethane adsorption. Several ab-

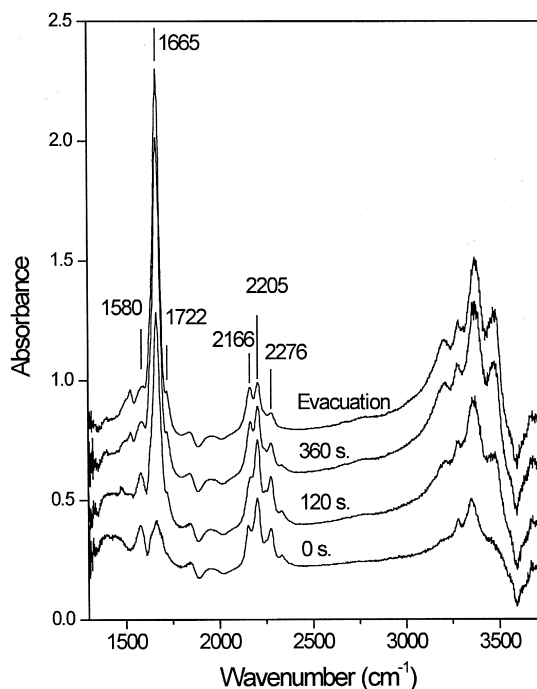
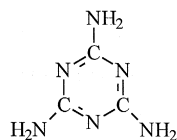


Fig. 1. Typical spectra for nitromethane adsorption on Cu-ZSM-5 at 280°C.

sorption bands arise, with their intensities varying in different ways.

In the 1500 – 1700 cm^{-1} region, a group of bands (1530 , 1580 , 1665 , 1722 cm^{-1}) is observed. The band at 1580 cm^{-1} corresponds to molecularly adsorbed nitromethane [6]. The small intensity of this band, in agreement with previous results [4], proves the rapid transformation of nitromethane at this temperature into another more stable species. The band at 1665 cm^{-1} , according to Ref. [5], corresponds to the heterocyclic *s*-triazine compound, melamine (Scheme 1) and/or its derivatives. On Co-ZSM-5 at 280°C, this species was shown to be quite inert, its accumulation within the zeolite channels leading to their blockage [5]. The low intensity band at 1722 cm^{-1} can be assigned to cyanuric acid, the cyclic trimer of HNCO (Scheme 2).

In the region of 2100 – 2300 cm^{-1} , a set of bands at 2166 , 2205 , 2247 , 2276 cm^{-1} and a weak band at 2333 cm^{-1} (disappearing upon

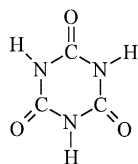


Scheme 1.

evacuation) are observed. This region is typical of the stretching of -NCO or -CN groups. By analogy with the results of Solymosi and Bansagi [7] for HNCN adsorption on Cu-ZSM-5, bands at 2205 and 2166 cm^{-1} can be assigned to the asymmetric stretching of $\text{Cu}^+\text{-NCO}$ and $\text{Cu}^{2+}\text{-NCO}$ species, respectively. The band at 2276 cm^{-1} was assigned earlier to isocyanate species bound to the zeolite matrix [2]. The band at 2247 cm^{-1} can be tentatively assigned to vibrations of the protonated NH_2 groups of melamine [5]. Such a protonation is suggested by the emergence in the difference spectrum of a negative peak around 3600 cm^{-1} due to the consumption of zeolite acidic Si-OH-Al groups. The nature of the band at 2333 cm^{-1} is not clear.

In the region above 3200 cm^{-1} , new bands are observed despite a high noise level. As judged by their position, these bands correspond to asymmetric and symmetric stretching of -NH_2 groups in the protonated melamine molecule, thus explaining a large number of such bands.

Fig. 2 illustrates the spectra variation following the oxygen admission. The intensity of the 1668 cm^{-1} band declines (see inset in Fig. 2), though some induction period is observed, probably due to oxygen diffusion limitations within zeolite channels filled by melamine molecules. The intensity of the 2205 cm^{-1} band goes



Scheme 2.

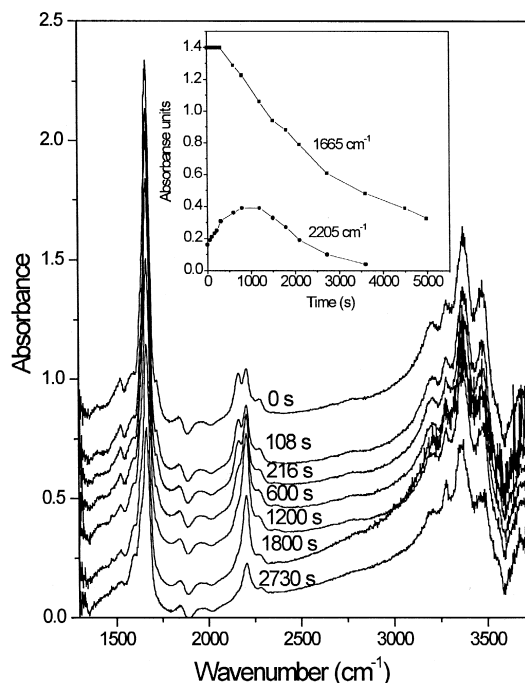


Fig. 2. The effect of oxygen on the spectra of surface adspecies on Cu-ZSM-5 at 280°C. Inset: dynamics of the 2205 and 1665 cm^{-1} absorption bands.

through the maximum as typical for reaction intermediates. It implies that the $\text{Cu}^+\text{-NCO}$ complex can be formed as a result of the melamine oxidative destruction. However, another possible reason for the specificity of the 2205 cm^{-1} band dynamics can be inferred from the intensity decline of the 2166 cm^{-1} band assigned to $\text{Cu}^{2+}\text{-NCO}$ species, while the band at 2276 cm^{-1} , which corresponds to NCO species stabilized on the zeolite matrix, remains unchanged. The last fact suggests a very slow exchange of NCO species between various adsorption sites. Hence, the increase of the $\text{Cu}^+\text{-NCO}$ species concentration can also be explained by a reduction of Cu^{2+} by the products of melamine partial oxidation due to limited oxygen access into the channels blocked by melamine.

After the induction period, the variation of the 1668 cm^{-1} band intensity is well described by a first-order rate equation, which allows the

estimation of the rate constant as being equal to $3 \times 10^{-4} \text{ s}^{-1}$. Taking into account the value of the rate constant of surface nitrates consumption at the same temperature under methane action ($2 \times 10^{-3} \text{ s}^{-1}$ [2]), and the fact that three N_2 molecules are formed from one melamine molecule, while only one N_2 molecule is derived from two nitrate species, melamine appears to be sufficiently reactive to be one of intermediates in the NO_x selective reduction by methane in the presence of excess oxygen, at least, under nonsteady-state conditions. Indeed, for Cu-ZSM-5, during the titration of adsorbed nitrates by methane and oxygen pulses [2] as well as in the oxidation of nitromethane by oxygen [8], N_2 selectivity was much higher than in the steady-state reduction of NO_x by methane in the presence of excess oxygen. Since the dynamics of the $\text{Cu}^+ \text{-NCO}$ species consumption reveals a reactivity comparable with that of melamine (see inset in Fig. 2), isocyanates can also be considered as probable intermediates.

In the set of experiments where oxygen admission was preceded by NO adsorption, neither new bands emerge nor existing bands noticeably change their intensity. In part, this is explained by the rapid transformation of NO into nitrite–nitrate species whose absorption bands situated at 1630 cm^{-1} [2] are masked by the melamine intense band.

3.2. Co-ZSM-5

As follows from the spectra presented in Fig. 3, the nitromethane adsorption is accompanied by the appearance of bands situated at 1585, 1665, 1720, 1801, 2196, 2265 cm^{-1} , along with a group of poorly resolved bands in the 3400–3500 cm^{-1} region. The assignment of first three bands as well as those situated at high frequencies is the same as in the case of Cu-ZSM-5 (vide supra). The absorption band at 1801 cm^{-1} corresponds to nitrosyl complexes with Co cations [9] as confirmed by the emergence of the same band after NO adsorption on Co-ZSM-5 with preadsorbed nitromethane (vide infra).

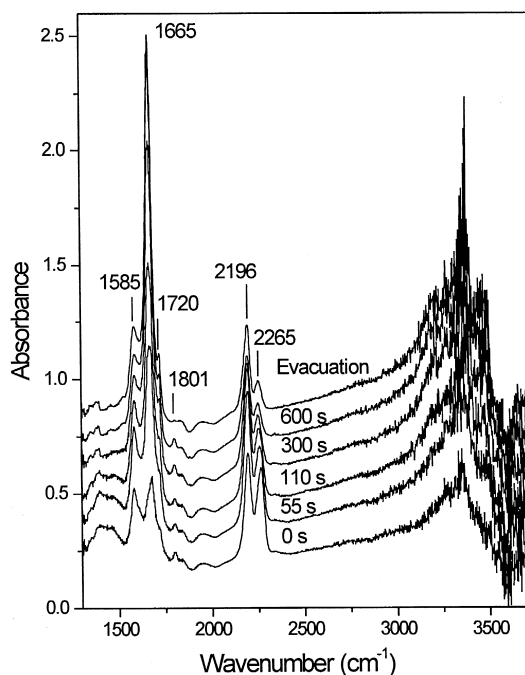


Fig. 3. Typical spectra for nitromethane adsorption on Co-ZSM-5 at 280°C .

Bands at 2196 and 2265 cm^{-1} are assigned to the asymmetric stretching of NCO species located on Co^{2+} cations and the zeolite matrix, respectively. For the latter band, some shift in position as compared with that on Cu-ZSM-5 can be tentatively explained by the difference in zeolite Si/Al ratio. For Co-ZSM-5, a smaller number of bands is observed in the 2100–2200 cm^{-1} region as compared with those found for Cu-ZSM-5, suggesting a higher uniformity of the coordination and oxidation states of Co cations.

At 280°C , in agreement with earlier results [5], the reactivity of the adspecies was too low to be detected. From the molecular point of view, such low reactivity can be explained by the stronger bonding of these intermediates with tetrahedrally coordinated Co cations as compared to the relatively weak axial bonding with square-planar coordinated Cu cations.

At 350°C , adspecies on Co-ZSM-5 become quite reactive, and the results are illustrated in Fig. 4. For the band at 1665 cm^{-1} , the first-order

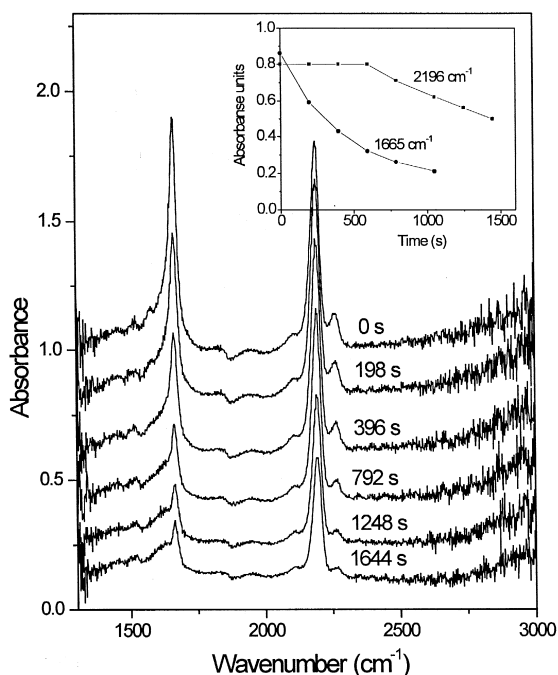


Fig. 4. The effect of oxygen on the spectra of surface adspecies on Co-ZSM-5 at 350°C. Inset: dynamics of the 2196 and 1665 cm^{-1} absorption bands.

reaction rate constant was estimated to be $\sim 1.4 \times 10^{-3} \text{ s}^{-1}$. Taking into account the rate constant of the surface nitrates transformation under methane action at the same temperature ($\sim 2 \times 10^{-2} \text{ s}^{-1}$) and the number of N_2 molecules produced from one melamine molecule, the last species can be considered as one of the intermediates in the reaction of NO_x with CH_4 in SCR conditions. The same conclusion is apparently valid for Co-NCO species of comparable reactivity (see inset in Fig. 4).

NO admission, after nitromethane adsorption, was accompanied by the emergence of new bands at 1800 and 1883 cm^{-1} corresponding to Co^{2+} and Co^{3+} nitrosyls. As for the case of Cu-ZSM-5, NO adsorption did not affect the intensities of other absorption bands for the reasons mentioned above.

The higher reactivity of species formed from nitromethane on Cu-ZSM-5 implies their lower surface concentration at NO_x CH_4 -SCR operation temperatures ($\sim 400^\circ\text{C}$) in steady-state

conditions. It explains the reason for the poor selectivity of Cu-ZSM-5 in this reaction [10].

4. Conclusions

For Cu- and Co-ZSM-5, at temperatures around 300°C , adsorbed nitromethane is shown to be easily converted into isocyanates and then melamine via polymerization of the former species. Molecular oxygen interacts with both species, and their reactivity depends upon the temperature and the nature of the transition metal cation. It is sufficiently high to suggest their role as possible intermediates in the NO_x CH_4 -SCR reaction.

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References

- [1] V.A. Sadykov, E.A. Paukshtis, S.A. Beloshapkin, G.M. Alikina, S.A. Veniaminov, R.V. Bunina, E.V. Lunina, A.N. Kharlanov, V.V. Lunin, V.A. Matyshak, Ya.A. Rozovskii, in: Proc. 8th Int. Symp. On Heterog. Catalysis, Vatra, 5–9 October, 1996, p. 347.
- [2] V.A. Sadykov, S.A. Beloshapkin, E.A. Paukshtis, G.M. Alikina, D.I. Kochubei, S.P. Degtyarev, N.N. Bulgakov, S.A. Veniaminov, E.V. Netyaga, R.V. Bunina, A.N. Kharlanov, E.V. Lunina, V.V. Lunin, V.A. Matyshak, Pol. J. Environ. Stud. 6 (1997) 21.
- [3] D.B. Lukyanov, E.A. Lombardo, G.A. Still, W.K. Hall, J. Catal. 163 (1996) 447.
- [4] S.A. Beloshapkin, V.A. Matyshak, E.A. Paukshtis, V.A. Sadykov, A.N. Ilyichev, A.A. Ukharskii, V.V. Lunin, React. Kinet. Catal. Lett. 66 (1999) 297.
- [5] A. Satsuma, A.D. Cowan, N.W. Cant, D.L. Trimm, J. Catal. 181 (1999) 165.
- [6] C.L. Levoquer, R.M. Nix, J. Chem. Soc., Faraday Trans. 1 93 (1997) 1813.
- [7] F. Solymosi, T. Bansagi, J. Catal. 156 (1995) 75.
- [8] E.A. Lombardo, G.A. Sill, J.L. d' Itri, W.K. Hall, J. Catal. 173 (1998) 440.
- [9] Y. Ukisu, S. Sato, G. Muramatsu, K. Yoshida, Catal. Lett. 26 (1995) 147.
- [10] J.N. Armor, Catal. Today 26 (1995) 147.