ELSEVIER

Catalysis Today 35 (1997) 121–127

CATALYSIS TODAY

The direct decomposition of nitrogen monoxide

T. Curtin *, P. Grange, B. Delmon

Catalyse et Chimie des Matériaux Divisés, U.C.L., Place Croix du Sud 2 / 17, 1348 Louvain-la-Neuve, Belgium

Abstract

A series of copper-exchanged ZSM-5 samples of various copper contents were prepared. In freshly prepared Cu/ZSM-5, there is surface enrichment in copper, especially for the over-exchanged samples. This enrichment diminishes after heat treatments such as calcination or treatment in an inert gas. The oxidation state of copper can be easily altered. The introduction of nickel into over-exchanged Cu/ZSM-5 did not improve the activity. However, the activity of under-exchanged Cu/ZSM-5 slightly improved in the presence of the second metal.

Keywords: Zeolites; Over-exchanged samples; Oxidation state; Heat treatment; Copper

1. Introduction

In the field of environmental catalysis, the issue concerning the abatement of NO_x is of extreme importance. The unique ability of copper-exchanged ZSM-5 to decompose NO directly into N_2 and O_2 without the help of reducing agents have initiated a multitude of studies in this area [1–4]. These include investigations into the mechanism of the decomposition reaction and the identification of the active site.

Many mechanisms have been presented, the best documented being the redox mechanism [3,5]. In this scheme, two copper ions are required for the decomposition of the dinitrosyl species, leaving behind oxygen which oxidises Cu^+ to Cu^{2+}. Desorption of oxygen above 300°C regenerates the active sites, thus making it possible for the reaction to continue. However, questions remain unanswered. How can two copper species be situated so close in a zeolite of high Si/Al ratio thus allowing such a reaction? In addition, how does the subsequent recombination of two oxygens located so far apart in the zeolite network proceed?

Vaylon and Hall [6,7] proposed that the reaction intermediate is a copper *cis*-nitrosyl-nitro complex. The reactive species in this case are thought to be extralattice oxygens which are thought to be introduced into the zeolite during catalyst preparation [8]. Shelef proposed that the sites responsible for the decomposition are the coordinatively unsaturated Cu^{2+} sites in a square planar configuration [9]. This square planar Cu^{2+} species allows the adsorption of two molecules of NO in a gem-nitrosyl form which simply desorb at high temperature as nitrogen and oxygen. In a Cu^+ luminescence study [10,11], Cu^{2+} was reported to exchange at two sites with different coordination. In a ZSM-5 of high Al content and low level of exchange, copper is thought to be in close proximity to

* Corresponding author.

PII S0920-5861(96)00138-1

two Al framework atoms. In silica-rich zeolites with a high copper content, copper species are found adjacent to one Al atom.

This paper deals with a series of copper-exchanged ZSM-5 zeolites containing various copper contents. A detailed characterization study was carried out in an effort to contribute to the identification of the active sites responsible for the decomposition of nitrogen monoxide. Particular emphasis was given to the copper contents of the zeolite and to the preparation method. The effect of adding a second metal to the zeolite was also examined.

2. Experimental

A series of copper-exchanged zeolites were prepared following a procedure documented in the literature [12]. In brief, 11 mmoles of copper acetate monohydrate (Aldrich) was dissolved in 1 l distilled water. Then 15 g of ZSM-5 zeolite (Si/Al ratio = 25, ammonium form) supplied by P.Q. Zeolites B.V., was added to the prepared solution and this mixture was stirred for 24 h. Subsequently, a dilute solution of ammonia (Merck) was added dropwise until the desired pH was reached. The solution was stirred for an hour before centrifuging, washing and drying.

The two component CuNi/ZSM-5 was synthesised by initially preparing a nickel-modified H/ZSM-5 catalyst (0.35 wt% Ni) following a procedure reported by Hoang et al. [13]. H/ZSM-5 was impregnated with a 3 mmolar solution of nickel nitrate at pH 3.9 and excess water was removed using a vacuum rotary evaporator. The samples were dried overnight in air, then calcined for 2 h at 300°C before finally calcining at 500°C for 2 h. The second step involved exchanging the pre-prepared 0.35 wt% Ni/ZSM-5 with a copper acetate solution as described above. Both under-exchanged (no pH adjustment) and over-exchanged samples (pH adjusted to 7.5) were prepared. After the exchange procedure, all samples were thoroughly washed, centrifuged and dried at room temperature. They were then calcined at 500°C for 2 h. For comparison, an under-exchanged (no pH adjustment) and over-exchanged (pH 7.5) Cu/ZSM-5 were prepared.

The XRD patterns of the prepared solids were obtained using a Siemens Diffractometer D500 system (CuK_α radiation) set to scan at a rate of 0.5° per minute.

Elemental analyses of copper, aluminium, nickel and silicon were determined by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES).

In preparation for X-Ray Photoelectron Spectroscopy (XPS) analysis, samples were pressed with a polyacetate cylinder onto stainless steel sample holders 4mm in diameter. Following outgassing overnight at 7×10^{-5} Pa, the samples were directly introduced into the analysis chamber. XPS analyses were performed at room temperature with an SSX-100 model 206 Surface Science Instrument (SSI) photoelectron spectrometer, interfaced to a Hewlett Packard 9000/310 computer. The residual pressure in the spectrometer was in the range of $1.3–6.5 \times 10^{-7}$ Pa. A monochromated Al anode powered at 10 kV and 15 mA was used for X-ray production. The positive charge, developed on the samples due to the photoejection process, was compensated by a charge neutraliser (flood gun) whose energy was adjusted to 6 eV. The binding energies were calculated with respect to the C1s peak set at 284.8 eV.

Infrared spectra of catalysts with adsorbed NO were recorded at ambient temperature in the range of 2300–1400 cm^{-1} by a Bruker IFS 88 Fourier Transform Infra-Red (FTIR) spectrophotometer and an infrared data station to collect and treat the spectra. Each sample was compressed into self-supporting discs (10–20 mg cm^{-1}) and placed in an IR cell with CaF_2 windows. The samples were initially pretreated under vacuum overnight at 400°C, then allowed to cool to room temperature. NO (5066ppm in He, 30ml min^{-1}) was passed through the IR cell and the self-supported discs heated to the

desired temperature at a rate of 5° min^{-1}. After 2 h at this temperature, the flow was stopped and the samples cooled to room temperature (approx. 5 min) before recording the infrared spectra. The presented spectra are the result of subtracting the spectra of NO adsorbed on the indicated samples from the spectra of the corresponding samples after standard pretreatment.

The NO decomposition reaction was carried out using a continuous flow system operated at atmospheric pressure. The feed gas, a mixture of NO (5120 ppm) and He (balance), flowed at a rate of 30 ml min^{-1} over 1–0.5 g of catalyst. The reactor was a quartz glass U-tube. Before testing, the catalyst was pre-treated in a stream of helium (30 ml min^{-1}) overnight at 500°C. After this pretreatment, the samples were cooled to the desired temperature and the reaction started by initiating the flow of NO. The reaction temperature was increased stepwise in intervals of 50°C or 100°C and analysis was carried out at each temperature until steady state was reached, i.e. 1–2 h. The gases leaving the catalytic reactor were analysed using a Balzers Quadrupole QMG 311 mass spectrometer.

3. Results

Fig. 1 presents the final copper content (wt%) of the zeolite as a function of the preparation pH. As the pH was increased, the amount of copper in the final zeolite increased up to 4 wt% at pH 8. The horizontal dotted line represents the total amount of copper in the original ex-

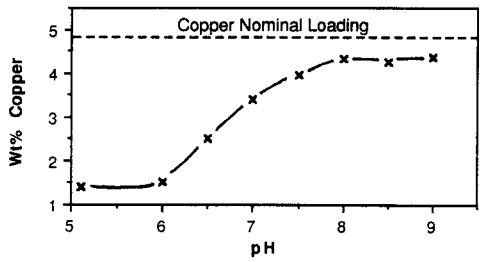

Fig. 1. Weight percentage copper of the prepared Cu/ZSM-5 catalysts as a function of preparation pH.

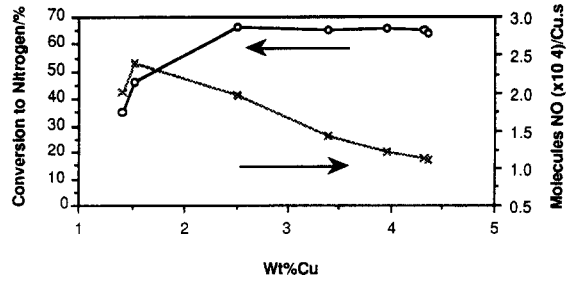

Fig. 2. NO decomposition with variation of copper in Cu/ZSM-5 prepared at different pHs. Temperature 450°C, 5120 ppm NO in He and W/F = 2 gs/ml

changing solution, which is conventionally called 'nominal loading'. The graph clearly demonstrates that the amount of copper introduced into a ZSM-5 zeolite can be easily controlled by adjusting the pH of the exchanging solution. A 100% exchange Cu/ZSM-5 corresponds to a copper content of 1.8 wt% where the percentage exchange is defined as (2 × no. moles Cu/no. moles Al) × 100.

The X-ray diffraction patterns of all prepared copper-exchanged zeolites were identical and showed no evidence of a crystalline phase containing copper.

Fig. 2 presents the decomposition of NO, as conversion to nitrogen, at 450°C for the series of prepared Cu/ZSM-5 catalysts. Also presented is the activity in terms of NO molecules converted per atom of copper per second. The activity, expressed as conversion to nitrogen, increases with copper content up to 2.5 wt%. Increasing the copper content above this level does not result in any further improvement in activity. In the reaction conditions used, nitrogen oxide conversion to nitrogen does not exceed 65%, no matter what the loading of copper. On the other hand, NO conversion per atom of copper exhibits a different trend. Increasing the copper initially resulted in an increase in the turnover, but this continually decreased with an increase in copper content above ca. 2 wt%.

Introduction of nickel does not improve the activity of over-exchanged copper zeolites and in fact a slight decrease is observed compared to the over-exchanged ZSM-5 containing copper

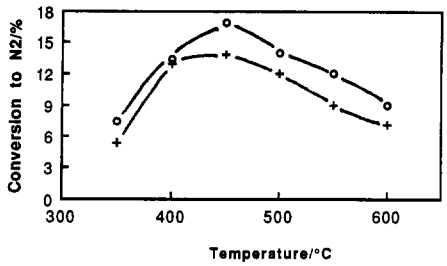

Fig. 3. NO conversion to N_2 using (circles) CuNi/ZSM-5 (0.35 wt% Ni, 1.0 wt% Cu) and (plus signs) 1.3 wt% Cu-ZSM-5. 5120 ppm NO in He and W/F = 1 gs/ml.

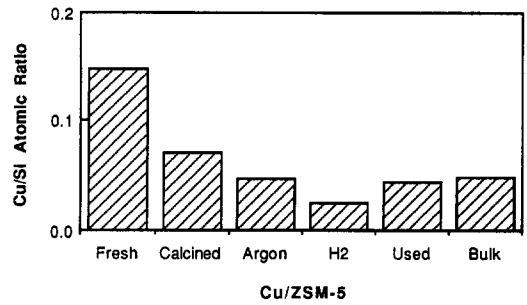

Fig. 5. XPS surface Cu/Si atomic ratios of 4 wt% Cu/ZSM-5 subjected to the indicated treatments.

only. On the other hand, the activity of the under-exchanged copper sample exhibited a slight improvement in activity with the introduction of nickel (Fig. 3).

Fig. 4 presents the Cu/Si atomic ratios obtained from surface analysis of fresh, non-calcined copper-exchanged ZSM-5 zeolites and the samples after catalytic testing. The Cu/Si atomic ratio, assuming a uniform distribution, as deduced from the ICP–AES data, is also presented ('bulk'). A surface copper enrichment is observed for all fresh catalysts except for the lowest copper content. A large decrease in this surface copper was observed after catalytic testing, this being especially true for the higher copper contents. This high surface copper content decreased after testing to a level matching the bulk values.

From Fig. 4 it is clear there is a decrease in the total amount of copper detected at the surface of the prepared Cu/ZSM-5 zeolites after reaction. A series of tests were carried out to examine in greater detail this effect, with particular emphasis on the change of the surface copper content with different treatments (Fig. 5). This figure presents the total surface Cu/Si atomic ratio of a 4 wt% copper ZSM-5 sample as: fresh catalyst, fresh catalyst calcined in air at 500°C for 2 h, fresh catalyst treated in an argon flow at 500°C for 2 h, fresh catalyst after treatment 30 ml min^{-1} hydrogen for 2 h at 250°C and the catalyst after testing. For the treatment in hydrogen, the treated catalyst was directly introduced into iso-octane in an effort to avoid exposure to air. For comparison, the bulk Cu/Si ratio is also presented. It can be seen that each treatment results in an observed lowering of the

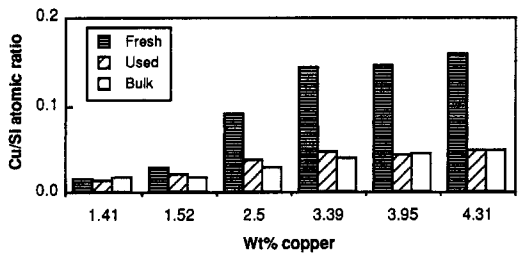

Fig. 4. Surface Cu/Si atomic ratios of fresh and used Cu/ZSM-5 as measured by XPS and bulk Cu/Si atomic ratios as measured by ICP–AES.

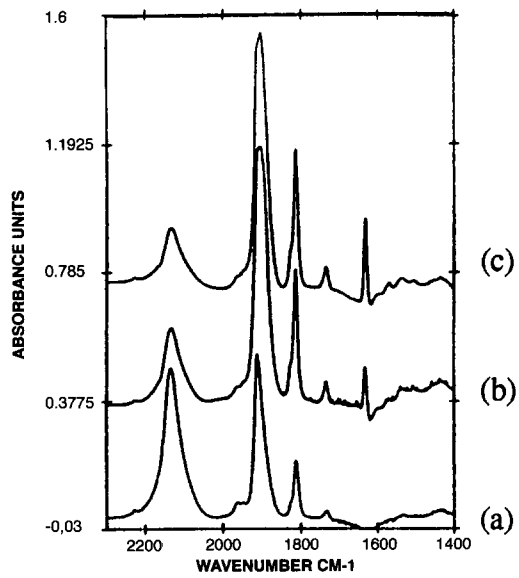

Fig. 6. FTIR spectra of NO adsorbed on (a) 1.3 wt% Cu/ZSM-5, (b) 3.0 wt% Cu/ZSM-5, and (c) 3.9 wt% Cu/ZSM-5 following NO/He flow at 450°C.

Cu/Si ratio compared to the fresh sample. For the catalyst treated in hydrogen this ratio is lower than the bulk value.

Fig. 6 shows the spectra of a 1.3 wt%, 3.0 wt% and 3.9 wt% Cu/ZSM-5 following treatment in a flow of NO (5066 ppm in He) at 450°C for 2 h. The formation of these peaks were due to copper, since no such peaks were observed for the ZSM-5 alone. Bands at 1733 and 1826 cm^{-1} have been assigned to an asymmetric and symmetric stretching vibration of dinitrosyl species, respectively, on Cu^{+} [5,14]. Mononitrosyl species adsorbed on Cu^{+} and Cu^{2+} are also present with their characteristic bands at 1812 cm^{-1} and ca. 1900 cm^{-1}, respectively. For the highest copper containing sample, the most intense band at 1900 cm^{-1} is that of the mononitrosyl adsorbed on Cu^{2+}. The bands of the mononitrosyl and the dinitrosyls adsorbed on Cu^{+} are present as very weak peaks, one of the dinitrosyl species being present as a shoulder on the 1813 cm^{-1} peak. Additional bands are observed at 1569 cm^{-1} and 2134 cm^{-1}. The band at 2134 cm^{-1}, characteristic of adsorbed NO_2, becomes very important at low copper contents. However, the band at 1630 cm^{-1}, assigned to an adsorbed oxidized NO species, increases with copper loading.

Increasing the reaction temperature results in a stronger adsorption band for the mononitrosyl on Cu^{+} at 1813 cm^{-1}. However, this band is unstable and disappears rapidly at room temperature.

A closer examination of the bands at 1900 cm^{-1}, corresponding to the mononitrosyl species adsorbed on Cu^{2+}, shows that with increasing copper contents there is a enlargement of the band towards lower wavenumbers. This trend was independent of reaction temperature.

4. Discussion

Increasing the pH of the exchanging solution resulted in an increase of the copper content in the final zeolite (Fig. 1). Early work involving cation exchange showed that the exchange may proceed in two different ways [15,16]. At pHs below the value required for hydrolysis of the salt, exchange of isolated cations result. At higher pH values, partial hydrolysis of the exchanging salt may occur with the formation of dimeric or polynuclear cations. Such an effect would lead to an over-exchange, which is observed in this work at pHs above 6.5. In a study of Vaylon and Hall at pH 4 and 6 [17] it was proposed that higher pH favours hydrolysis of the H_2O molecules in the hydration sphere of Cu^{2+} forming $(CuOH)^{+}$. It is this monovalent entity which acts as the exchange species, therefore, the exchange sites would be replaced with two monovalent entities rather than one divalent cation.

From Fig. 1 it can be seen that an over-exchange is obtained at pHs above 6.5 when the concentration of the exchanging solution was 11 mmole/l. Catalysts containing up to 5 wt% copper were prepared and from X-ray analyses there was no evidence of the existence of a crystalline phase containing copper This may suggest that the copper is well dispersed. This is probably due to the relatively narrow pores of the ZSM-5 and the absence of cages; this limits the formation of large copper particles.

Optimum activity for the decomposition of NO was observed for catalysts containing an amount of copper exceeding the level required for 100% exchange. However, it should be added that a catalyst containing an amount of copper less than this 100% exchange level also exhibited activity (Fig. 2). Increasing the copper content to high levels may result in the situation where some copper atoms no longer take part in the catalytic reaction because of inaccessibility or inactivity. Indeed an examination of the textural properties of the prepared catalysts shows that surface area and micropore volume continually decrease with increasing copper content. A relatively sharp decrease in micropore volume was observed when the copper content surpassed 3 wt%. The size of the zeolite microp-

ores also decreased with increasing copper content.

Binding energies for the $Cu2p_{3/2}$ observed in XPS are higher than those reported for bulk copper compounds, i.e. CuO has a binding energy of 933.8 eV and Cu_2O 932.3 eV [18]. These shifts in binding energy compared to bulk oxides are widely reported [19] and are considered to reflect the presence of isolated metal ions and small clusters of ions dispersed in the zeolite matrix. XPS analysis of the Cu/Si atomic ratio of the prepared samples indicated surface enrichment of copper. This was especially true for samples containing 2.5 wt% copper or more. This is not surprising since, as already discussed, 1.8 wt% copper is representative of an 'over-exchanged' zeolite. However, after reaction there is a marked decrease in this surface copper content, which falls to the level matching that expected if a homogeneous distribution of copper was assumed (Fig. 4). This decrease can be explained either by formation of copper aggregates on the surface of the zeolite or by migration of the surface copper species into the channels of the zeolite. An examination of the position of the $Cu2p_{3/2}$ peaks of the various prepared samples shows that there is no change before and after reaction, from sample to sample, for the main $Cu2p_{3/2}$ peak at about 933 eV. This would suggest that there is migration of copper into the zeolite during reaction.

Evidence of copper aggregate formation was noted when the Cu/ZSM-5 was subjected to stringent reducing conditions. Fig. 5 shows that the surface copper content fell to a level below that of the bulk when treated in hydrogen. The position of the main $Cu2p_{3/2}$ line was considerably lower than those of the oxygen and argon treated samples. This low value of binding energy indicates the presence of aggregates of copper metal, which is quoted to have a $Cu2p_{3/2}$ binding energy of 932.4 eV. Therefore, treatment in hydrogen at 250°C reduces the copper at the surface of a Cu/ZSM-5 to copper metal.

Many infrared studies of adsorbed NO have been carried out in the investigation of Cu/ZSM-5 for the decomposition of NO. In most studies, three distinct states of adsorbed NO have been detected: $NO–Cu^+$, $NO–Cu^{2+}$ and the dinitrosyl $Cu^+–(NO)_2$ and these are thought to be important species in the reaction conditions. In these infrared experiments, at all temperatures analysed, the under-exchanged Cu/ZSM-5 presented a strong band at ca. 2134 cm^{-1} which has been assigned to adsorbed NO_2 [7]. At 450°C (see Fig. 6) this peak is most important only for low levels of copper exchange.

The bands that increased with copper loading and reaction temperature were the mononitrosyl and dinitrosyls associated with reduced copper. This follows the performance of the copper catalysts in the decomposition of NO and may indicate the importance of these species in the reaction.

With increasing copper content, the band assigned to mononitrosyl adsorbed on Cu^{2+} changes. The peak broadens towards lower wavelength. This may be an indication of a second type of copper, different from that present in the under-exchanged sample. This correlates with the two types of copper reported by Wichterlová et al. [11] using Cu^+ luminescence. One copper type is located in the proximity of 2 Al atoms and is produced at low copper loadings and the second associated with one Al atom containing an extra lattice oxygen. This species is formed at high copper loadings.

The presence of nickel in the over-exchanged sample did not help in improving the activity of the Cu/ZSM-5 alone and in fact a slight decrease was observed. For the under-exchanged Cu/ZSM-5, the presence of nickel resulted in a slightly more active catalyst. The bi-component catalyst exhibited a slightly higher activity at all temperatures, despite the fact that it contained less copper than the simple copper exchanged zeolite, namely, 1.0 and 1.3 77 wt% copper, respectively. This may indicate that the presence of nickel forces the copper ions to occupy the active sites or may force the copper species to associate and form active sites. The results

dealing with the oxidation state of copper (i.e. XPS and IR) show, in agreement with several studies [20–22], that the oxidation state easily changes according to the experimental conditions. The copper zeolite seems very fragile in this respect. One may speculate that this may be a property that renders it an active catalyst for the decomposition reaction.

5. Conclusions

An over-exchanged Cu/ZSM-5 can be easily prepared in a single step by adjusting the pH of the exchanging solution. The decomposition activities exhibited by all over-exchange zeolites were similar. In freshly prepared copper zeolites, there is surface enrichment in copper especially for over-exchanged samples. After heat treatments, such as calcination or treatment in an inert gas, this copper enrichment diminishes; copper probably migrates into the zeolitic channels. The oxidation state of copper in ZSM-5 can be easily altered by modifying the atmosphere or temperature.

References

[1] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya and S. Kagawa, J. Chem. Soc., Chem. Commun., (1986) 1272.
[2] M. Iwamoto, S. Yokoo, K. Sakai and S. Kagawa, J. Chem. Soc. Faraday Trans., 1, 77(1981) 1629.
[3] M. Iwamoto, in M. Misono, Y. Moro-oka and S. Kimura (Eds.), Future Opportunities in Catalytic and Separation Technology, Stud. Surf. Sci. Catal., 54 (1990) 121.
[4] M. Iwamoto and H. Hamada, Catalysis Today, 10 (1991) 57.
[5] M. Iwamoto, H. Yahiro, N. Mizuno, W.X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem., 96 (1992) 9360.
[6] J. Vaylon and W.K. Hall, in L. Guczi et al. (Ed.), New Frontiers in Catalysis, Proc. 10th Int. Congr. Catal., Budapest, 1992, Elsevier, Amsterdam, 1993.
[7] J. Vaylon and W.K. Hall, J. Phys. Chem., 97 (1993) 1204.
[8] J.O. Petunchi, G. Marcelin and W.K. Hall, J. Phys. Chem., 96 (1992) 9967.
[9] M. Shelef, Catal. Lett., 15 (1992) 305.
[10] J. Dedecek and B. Wichterlová, J. Phys. Chem., 98 (1994) 5721.
[11] B. Wichterlová, J. Dedecek and Z. Tuaruzková, in J. Weitkamp, H.G. Karge, H. Pfeifer and W.H. Holderich (Eds.), Zeolites and Related Microporous Materials: State of the Art, Stud. Surf. Sci. Catal., 84, Elsevier, Amsterdam, 1994.
[12] M. Iwamoto, H. Yahiro, Y. Torikai, T. Yoshioka and N. Mizuno, Chem. Lett., (1990) 1967.
[13] D.L. Hoang, H. Berndt, H. Miessner, E. Schreier, J. Volter and H. Lieske, Appl. Catal. A: General, 114 (1994) 295.
[14] E.G. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, J. Catal., 136 (1992) 510.
[15] N.G. Maksimov, K.G. Ione, V.F. Anufrienko, P.N. Kuznetsov, N.N. Bobrov and K.G. Boreskov, Dokl. Akad. Nauk SSSR, 210 (1973) 388.
[16] K.G. Ione, N.N. Bobrov, K.G. Boreskov and L.A. Vostrikova, Dokl. Akad. Nauk SSSR, 217 (1974) 3135.
[17] J. Vaylon and W.K. Hall, Catal. Lett., 19 (1993) 109.
[18] K.M. Minachev and E.S. Shpiro, Catalyst Surface: Physical Methods of Studying, CCRC Press, Boca Raton, 1990.
[19] Y. Okamoto, M. Ogawa, A. Maezawa and T. Imanaka, J. Catal., 112 (1988) 427.
[20] E.S. Shpiro, W. Grunert, R.W. Joyner and G.N. Baeva, Catal. Lett., 24 (1994) 159.
[21] J. Sárkány, J.L. d'Itri and W.H. Sachtler, Catal. Lett., 16 (1992) 241.
[22] V. Parvulescu, P. Oelker, P. Grange and B. Delmon, unpublished results.