

Selective Catalytic Reduction of NO to N₂ with Copper and Cobalt Exchanged ZSM-5 Zeolites: The Effect of Calcium Addition

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Zeólitas ZSM-5 contendo cobre ou cobalto, ou simultaneamente cobre e cálcio, ou cobalto e cálcio foram preparadas por troca-iônica e testadas como catalisadores na redução de NO a N₂ na presença de metano ou propano. Nos catalisadores trocados com cobre, este se apresentou como Cu²⁺ e [Cu-O-Cu]²⁺ em sítios de compensação de carga. A quantidade do último cátion aumentou com o teor de cobre e na presença de Ca²⁺ e foi mais ativo na redução de NO; no entanto, em temperaturas superiores a 400 °C a sua atividade diminuiu acentuadamente. Para os catalisadores trocados com cobalto, este foi encontrado como Co²⁺ em sítios de compensação ou Co³⁺ fazendo parte de precipitados extra-estruturais, sendo que, a quantidade de Co³⁺ diminuiu na presença de Ca²⁺. Nestes catalisadores a presença de cálcio não provocou diferenças significativas na atividade específica para a redução de NO ou para a oxidação do metano.

ZSM-5 catalysts containing either Cu or Co cations individually or Cu/Ca or Co/Ca cation combinations were prepared by ion exchange. These materials were tested as catalysts for the reduction of NO to N₂ in the presence of propane or methane. Cu²⁺ and [Cu-O-Cu]²⁺ species were identified in ion exchangeable sites in the copper-containing catalysts. The amount of the latter cation increased with increasing copper content and in the presence of Ca²⁺ and was the most active in the reduction of NO. However, at temperatures higher than 400 °C its activity decreased markedly. For cobalt-exchanged zeolites, Co²⁺ in charge-compensation sites or Co³⁺ in extra-framework precipitates were present in the catalysts. It was verified that the amount of Co³⁺ diminished with the presence of Ca²⁺. For the catalysts prepared in this study no significant differences in specific activity for the reduction of NO or for methane oxidation were observed in the presence of calcium.

Keywords: NO reduction, exchanged ZSM-5 zeolites, copper, cobalt, calcium

Introduction

The improvement of catalysts used for the reduction of NO in exhaust gases is necessary in order to satisfy the increasing legal demands to reduce emission levels. Special attention has been given to the selective catalytic reduction of NO with hydrocarbons under oxidising conditions (SCR-HC), which might be able to remove NO_x from exhaust gases generated by diesel engines and other combustion processes,¹ such as incinerators, industrial boilers and power plants.

In spite of their high activity in the SCR-HC, the copper exchanged ZSM-5 catalysts deactivate quickly in the presence of water and/or sulphur dioxide, which prevents their use in commercial applications. On the other hand, replacement of copper by cobalt has resulted in catalysts

with improved stability under hydrothermal conditions.²

A further modification to improve the activity of transition metal exchanged ZSM-5 catalysts is the addition of a second cation (co-cation), which can influence the redox properties and the stability of the transition metal species located in charge compensation sites.³ Although many authors have observed the positive effect of such co-cations, their role in the reaction mechanism is still unclear.

Yokomichi *et al.*⁴ demonstrated that the addition of Ca²⁺ cations in ZSM-5 exchanged with copper cations reduced the deactivation caused by oxygen or water vapour and increased the range of temperatures in which these catalysts are active. For cobalt containing ZSM-5 catalysts, the addition of alkaline-earth metals suppressed the conversion of the hydrocarbon and increased NO conversion. The formation of NO₂ was also diminished.⁵

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In this context, the preparation of bicationic Cu/Ca and Co/Ca-ZSM-5 catalysts will be described. In addition, the catalytic activity for the reduction of NO to N₂, in the presence of hydrocarbons, will be compared to that observed for monocationic Cu and Co-ZSM-5 catalysts.

Experimental

Considering the IUPAC recommendations,⁶ the samples prepared in this study were identified in the simplified form as: [guest composition][host composition]-**IZA** where **IZA** refers to the zeolite structure code (*i.e.* **MFI** for the ZSM-5 zeolite). To aid brevity, only the guest cations introduced by ion exchange are considered and the oxygen atoms of the host structure are omitted, resulting in the typical code: [Cu_xCa_y] or [Co_xCa_y][Si₁₂Al]-**MFI**, where *x* or *y* represents the metal/Al molar ratio in the sample.

Catalyst preparation

[Cu_x] and [Co_x][Si₁₂Al]-**MFI** catalysts were prepared by ion exchange in an aqueous solution from an [Na][Si₁₂Al]-**MFI** zeolite, prepared as described elsewhere.⁷ A metal concentration of 0.015 mol L⁻¹ and a metal/Al ratio of 1.3 were employed. In order to obtain catalysts with different metal contents the temperature, the number and the duration of the exchange cycles were varied as is given in Table 1. Copper (II) acetate (Merck, 99%), cobalt (II) acetate (Aldrich, 99%) and calcium nitrate (Merck, 99%) were used as sources of the respective cations. The catalysts were activated for one hour at 520 °C (heating rate of 10 °C min⁻¹) under an airflow (100 mL min⁻¹ g⁻¹).

Catalyst characterisation

The X-ray diffraction (XRD) patterns of the parent zeolite and of the prepared catalysts were obtained using a Siemens D500 Diffractometer with monochromatic CuK_α radiation. The XRD data were collected from 3 to 40° (2θ) at a scanning rate of 2° (2θ) min⁻¹.

Nuclear Magnetic Resonance analysis (²⁷Al MAS NMR) was performed using a Varian Unity Plus 400 MHz spectrometer, which was operated at 104.2 MHz. During the analysis a pulse length of 0.4 μs (π/16) was used with a 2 s delay time.

Temperature Programmed Reduction with hydrogen (H₂-TPR) was carried out using a Micromeritics apparatus, Model 2705, coupled to a thermal conductivity detector in order to monitor the effluent gas. A hydrogen flow of 30 mL min⁻¹ (5% v/v in N₂), a dried sample of 150 mg and a heating rate of 10 °C min⁻¹ were employed. Prior the

measurements the fresh samples were thermally treated in dry air (30 mL min⁻¹) at 200 °C for 1 h.

Raman spectra of the Co-catalysts were obtained in air at room temperature using 633 nm radiation from an Ne ion laser equipped with a CCD detector. A spot size of 1 μm diameter and a potency varying from 70 to 175 μW were employed.

Diffuse Reflectance Spectra in the UV-Visible region (DRS-UV-VIS) were obtained at room temperature using a UV-VIS Varian Cary 5G Spectrometer equipped with a polytetrafluorethylene (PTFE) sample support, a quartz window and a PTFE pattern as reference. Before the analysis, the samples were dried at 110 °C for 12 h and the data obtained was treated using the F(R) Schuster-Kubelka-Munk function.

Electron Paramagnetic Resonance (EPR) spectra were recorded using a Bruker ESP 300 E Spectrometer at -196 °C and -267 °C for the copper-containing and cobalt-containing samples, respectively.

Catalytic tests

To perform the catalytic tests, a sample of 50 mg was mixed with 150 mg of quartz in order to avoid the formation of localised hot spots. The reactants were fed using a total gas flow of 70 mL min⁻¹ with a composition of 0.3% NO, 1.8% O₂, 0.3% hydrocarbon (C₃H₈ or CH₄) in He (v/v). Under these conditions, the resulting gas hourly space velocity (GHSV) was 42,000 h⁻¹. By increasing the catalyst mass to 100 mg, the cobalt containing catalyst was also studied at a GHSV of 21,000 h⁻¹. The reaction temperature was varied between 150 and 500 °C.

The reaction products were analysed by gas chromatography using a capillary column (alumina/KCl; 0.32 mm × 30 m) connected to an FID for the analysis of hydrocarbons. Two other packed columns (Hayesep D and 13 X) connected to a TCD were used for the analysis of NO, N₂O, N₂, O₂, CO, and CO₂. As NO and the possibly formed NO₂ cannot be separated under the GC conditions used, the apparent specific activity for NO reduction was expressed by the moles of nitrogen molecules formed per mole of transition metal per hour. Carbon dioxide was the only product obtained in the alkane oxidation and the transformation of the hydrocarbon was expressed by the moles of hydrocarbon consumed per mole of transition metal per hour. The amount of hydrocarbon effectively used for the reduction of NO, defined as the competitiveness factor (C_f), was calculated as: C_f(propane) = [2(N₂)_{produced} / (10 × (C₃H₈)_{consumed})] × 100% and C_f(methane) = [2(N₂)_{produced} / (4 × (CH₄)_{consumed})] × 100%.

Results and Discussion

Catalyst characterisation

The XRD patterns of the parent [Na][Si₁₂Al]-MFI, of the [Cu_{0.49}][Si₁₂Al]-MFI and [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI are shown in Figure 1a. As for the cobalt-exchanged zeolites (not shown) the XRD patterns reveal the presence of fully crystalline ZSM-5 before and after ion exchange. The diffractograms further show that the samples do not contain detectable amounts of copper or cobalt oxides. However, such oxides might be present as crystals that are smaller than 3 nm or well dispersed over the zeolite surface and therefore are not detected by XRD. Figure 1b shows the ²⁷Al MAS NMR spectrum of the parent [Na][Si₁₂Al]-MFI. It can be seen by the intense peak at around 55 ppm, that the aluminium is mainly tetrahedrally co-ordinated, indicating its incorporation into the ZSM-5 structure. However, a small peak can be observed at around 0 ppm, which indicates octahedrally co-ordinated aluminium, which is usually attributed to extra-framework aluminium species.

The metal content was determined by atomic absorption spectroscopy after ion exchange had been completed and the values are presented in Table 1. It can be seen that for [Cu_x] and [Cu_xCa_y][Si₁₂Al]-MFI catalysts,

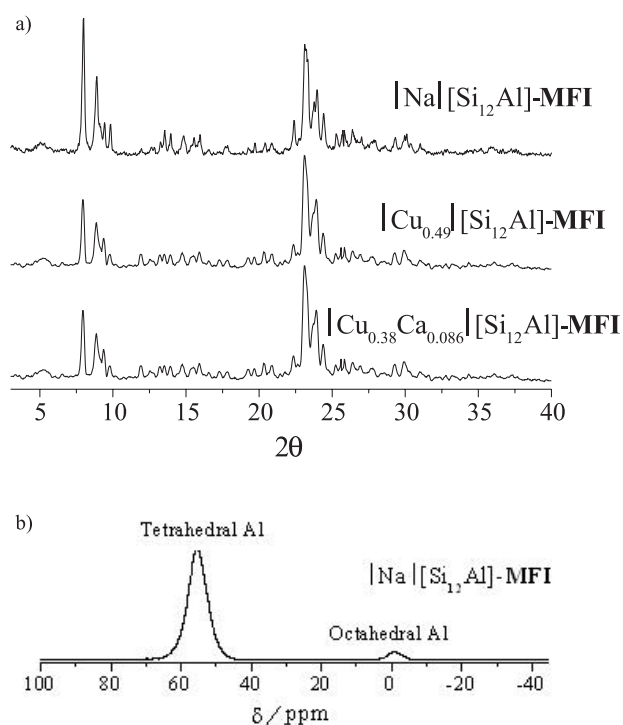


Figure 1. (a) X-ray Diffraction pattern of the parent [Na][Si₁₂Al]-MFI and of the samples exchanged with copper and/or calcium; (b) ²⁷Al MAS NMR spectrum of parent [Na][Si₁₂Al]-MFI.

the observed (Cu/Al)_{bulk} and ((Cu+Ca)/Al)_{bulk} ratios are below or near 0.5, a value that is expected for complete framework charge compensation by bivalent cations, compatible with the light blue colour of zeolites containing extra-framework hydrated Cu²⁺ ions. However, the aluminium content observed includes the extra-framework aluminium indicated by ²⁷Al MAS NMR, which does not contribute to the negative framework charge; on the other hand, the copper content might include neutral copper oxide or hydroxide species. Therefore, the calculated (Cu/Al)_{bulk} ratio below or near of 0.5 is not a sufficient proof of the exclusive presence of copper on ion exchange sites. No sodium cations were detected in the samples after ion exchange, which suggests their complete substitution by copper cations and/or protons generated in the ion exchange medium by the precipitation of cationic or neutral hydroxide species. This is true even in [Cu_{0.30}][Si₁₂Al]-MFI where the metal to Al ratio is below 0.5. As the formation of copper hydroxide species leads to the formation of protons, the decrease of the pH (see Table 1) observed during the preparation of [Cu_{0.49}] and [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI is a further indication of the formation of such species in these catalysts.

On the other hand for [Co_{0.58}] and [Co_{0.53}Ca_{0.055}][Si₁₂Al]-MFI catalysts, the (Co/Al)_{bulk} and ((Co+Ca)/Al)_{bulk} ratios were higher than the 0.5 or 0.3 expected for complete Co²⁺ or Co³⁺ ion exchange, respectively. The reduction of Co²⁺ to Co⁺, which would result in a Co/Al ratio higher than 0.5, is unlikely in these catalysts. Therefore, cobalt is probably present in all samples, at least partly as neutral precipitates or as cationic hydroxide species. This is also indicated by the colour of the catalyst, which changed from a light pink/red, typical for octahedrally co-ordinated Co²⁺ (e.g. [Co(H₂O)₆]²⁺) or Co(OH)₂ in the freshly exchanged samples to a greenish brown in the activated samples, which indicates the formation of CoO(OH).⁸ As already commented, the formation of precipitated hydroxide species is also indicated by the observed decrease of the pH value during the ion-exchange, shown in Table 1.

Figure 2 shows the H₂-TPR profiles of the catalysts and in Table 1 the ratios of hydrogen consumed per mol of transition metal (H₂/TM) are indicated. For [Cu_{0.30}][Si₁₂Al]-MFI two more intense reduction peaks of nearly equal area at around 240 and 450 °C are observed. These peaks are attributed to the reduction of Cu²⁺ to Cu⁺ and to the reduction of Cu⁺ to Cu⁰, respectively.⁹ The presence of metallic copper in the reduced catalysts is confirmed by the typical orange-reddish colour of zeolites after the reduction experiment. For the [Cu_{0.49}][Si₁₂Al]-MFI catalyst a small increase in the reduction temperature to 260 °C

Table 1. Exchange conditions, metal content in the catalysts and hydrogen consumption in the H₂-TPR analysis

Catalysts	Exchange conditions ^a	pH _{initial}	pH _{final}	TM ^c content ^d	Ca content ^d	H ₂ ^e /TM ^c
[Cu _{0.30}][Si ₁₂ Al]-MFI	50/(1 × 12)	5.3	5.2	2.41	-	0.98
[Cu _{0.49}][Si ₁₂ Al]-MFI	25/(4 × 12)	5.6	4.6	4.00	-	1.07
[Cu _{0.38} Ca _{0.086}][Si ₁₂ Al]-MFI	60/(1 × 48) ^b	7.4	5.0	3.09	0.43	1.11
[Co _{0.29}][Si ₁₂ Al]-MFI	80/(1 × 48)	6.2	4.6	2.17	-	1.15
[Co _{0.58}][Si ₁₂ Al]-MFI	80/(3 × 48)	5.6	4.8	4.80	-	1.32
[Co _{0.53} Ca _{0.055}][Si ₁₂ Al]-MFI	60/(1 × 48) ^b	8.4	6.1	4.40	0.31	1.19

^aExchange temperature [°C]/(number of exchanges × time [h]); ^b Corresponding to the ion exchange with calcium; ^cTM = Cu or Co; ^dweight percent; ^e consumed H₂ in the H₂-TPR measurements (see Figure 2).

and an increase of its broadness is observed for the peak attributed to the reduction of Cu²⁺ to Cu⁺. The second reduction peak also broadens and displays a strong shoulder at around 360 °C, which could already be observed as a low-intensity peak for [Cu_{0.30}][Si₁₂Al]-MFI. The observed peak broadening and the appearance of a shoulder around 360 °C in the Cu⁺ to Cu⁰ reduction peak would suggest the presence of different Cu-species in the catalyst. Mascarenhas *et al.*¹⁰ proposed that as well as isolated Cu²⁺ compensating two negative framework charges, another cationic copper species that bears an extra-lattice oxygen in the form of [Cu-O-Cu]²⁺, might be present in the zeolites. Such species could be formed by the

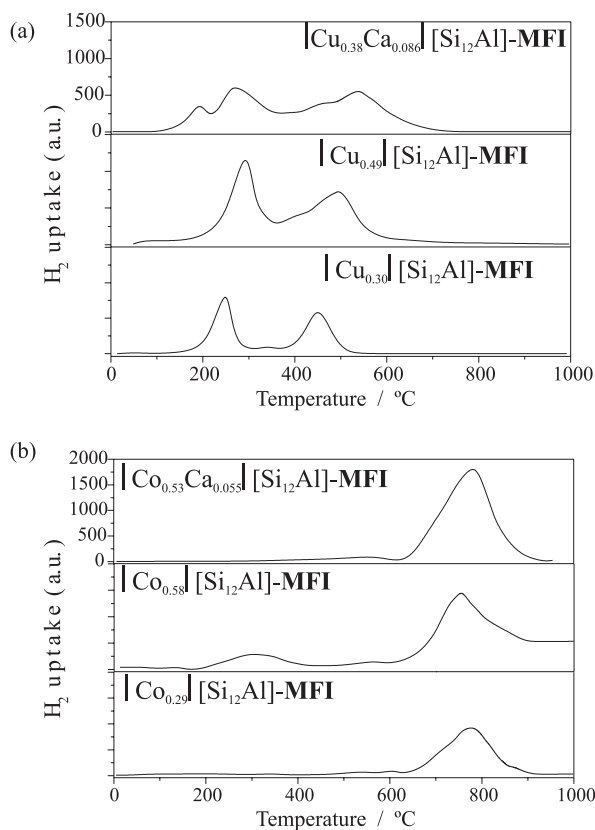
dehydration of neighbouring copper hydrates during the activation process. Due to the higher copper content in [Cu_{0.49}][Si₁₂Al]-MFI more [Cu-O-Cu]²⁺ is formed in this catalyst. The reduction of such [Cu-O-Cu]²⁺ species will lead to Cu₂O and the shoulder observed at 360 °C might be attributable to Cu₂O reduction.

Considering that the cationic copper species, bearing an extra-lattice oxygen [Cu-O-Cu]²⁺, are more easily reduced than isolated Cu²⁺,¹⁰ the shoulder which appears at around 180 °C in the H₂-TPR profile of [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI, might be attributed to the reduction of [Cu-O-Cu]²⁺ to Cu₂O. The higher intensity of the peaks attributed to [Cu-O-Cu]²⁺ and Cu₂O reduction in [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI in comparison with [Cu_{0.49}][Si₁₂Al]-MFI shows that the ion exchange of Cu²⁺ by Ca²⁺ in a solution with a pH slightly higher than seven (see Table 1) favours the formation of Cu(OH)⁺ cations.¹¹ These cations, which are compensate the negative charge of the zeolite, generate [Cu-O-Cu]²⁺ species after activation, probably by the mechanism illustrated in Figure 3.

In [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI the peak attributed to the reduction of Cu⁺ to elemental copper shifts to higher temperatures. This is due to the fact that in this sample the Cu cations are in lower amounts and consequently more isolated and better stabilised in the presence of Ca²⁺.¹²

In Table 1 the ratio between the consumed hydrogen and the copper cations for the studied Cu-catalysts is presented. As these ratios are nearly equal to one and considering that the reduction of Ca²⁺ is unlikely under the applied reduction conditions, the TPR-H₂ results confirms the presence of Cu²⁺ cations in the catalysts and their complete reduction. It is worth pointing out that the formation of Cu³⁺ and Cu⁴⁺ cations during the preparation procedure employed here is also unlikely.

H₂-TPR profiles for [Co_{0.58}][Si₁₂Al]-MFI, [Co_{0.29}][Si₁₂Al]-MFI and [Co_{0.53}Ca_{0.055}][Si₁₂Al]-MFI catalysts (Figure 2b) present a main peak at around 760 °C and a less intense reduction peak at around 330 °C, which might be attributed to the reduction of Co²⁺ to Co⁰ and to well dispersed cobalt oxide in the zeolite channels,

**Figure 2.** H₂-TPR profiles of the catalysts containing (a) copper and (b) cobalt.

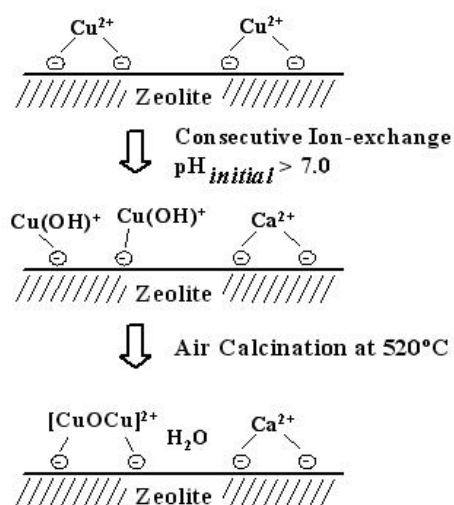


Figure 3. Mechanism proposed for the formation of $[\text{Cu-O-Cu}]^{2+}$ during preparation by ion exchange of Cu-catalysts.

respectively.¹³ For these samples, H_2/TM ratios higher than 1 indicate the presence of Co^{3+} . The oxidation of Co^{2+} into Co^{3+} might occur under the activation conditions, generating $\text{CoO}(\text{OH})$ which is already indicated by the brownish colour of the activated samples.⁸

In order to obtain further information about the species present in the cobalt catalysts, Raman measurements were performed. Figure 4 shows the spectra obtained from $[\text{Co}_{0.58}][\text{Si}_{12}\text{Al}]\text{-MFI}$ and $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts together with a reference Co_3O_4 and the zeolite used as precursor. As can be seen, the bands at 303 and 385 cm^{-1} correspond to the zeolite framework and they are not related to Co species.¹⁴ In addition to the band related with the zeolite framework, bands at 197, 483, 529, 616 and 692 cm^{-1} are observed in the spectra of the zeolite containing cobalt. These bands are attributed to Co_3O_4 agglomerates, which must be smaller than 3 nm, as they

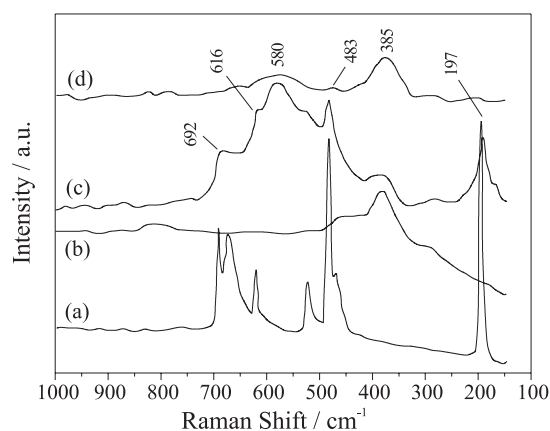


Figure 4. Raman spectra of Co containing catalysts: (a) Co_3O_4 , (b) $[\text{Na}_x][\text{Si}_{12}\text{Al}]\text{-MFI}$, (c) $[\text{Co}_{0.58}][\text{Si}_{12}\text{Al}]\text{-MFI}$ and (d) $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$.

were not detected by XRD. In the same spectra, a band at around 580 cm^{-1} is also observed. As this band can not be attributed to zeolite framework nor to Co_3O_4 , it is suggested that it corresponds to a loaded cobalt species other than Co_3O_4 (e.g. $\text{CoO}(\text{OH})$).¹⁴ On the other hand, the $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalyst shows lower intense peaks in the region between 450 – 700 cm^{-1} . This is indicative that the species discussed above are present in small amounts, consistent with the results obtained in the H_2 -TPR measurements.

Figures 5a and 5b show the spectra obtained in the UV-Vis region by diffuse reflectance for the catalysts containing copper or cobalt, respectively. In agreement with the results presented by Itho *et al.*,¹⁵ the band at 212 nm, which appears in all spectra, is related to the zeolitic structure and not to the cationic species present. For the $[\text{Cu}_x][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts (Figure 5a), the band at 256 nm is attributed to Cu^{2+} species interacting with the oxygen of the zeolitic structure. The shift of this band to 262 nm in $[\text{Cu}_{0.38}\text{Ca}_{0.086}][\text{Si}_{12}\text{Al}]\text{-MFI}$ might be attributed to the presence of the $[\text{Cu-O-Cu}^{2+}]$ cationic species, as suggested by the H_2 -TPR results. The broad band between 600 and 850 nm is attributed to Cu^{2+} cations in octahedral coordination and shows no significant difference when all the catalysts are compared.

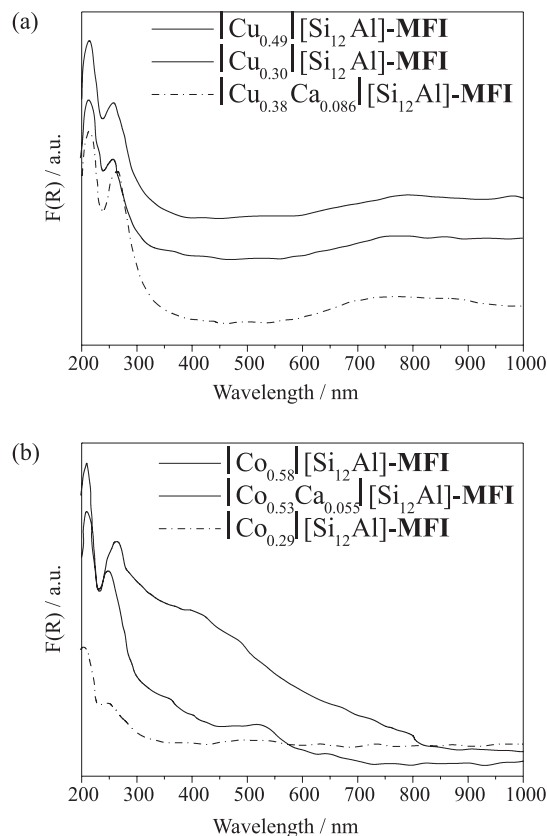


Figure 5. DRS-UV-Vis spectra of the catalysts containing: (a) copper and (b) cobalt.

For cobalt-containing catalysts (Figure 5b), more defined bands at 250-270 and 350-560 nm are observed, which correspond to tetrahedrally co-ordinated Co^{2+} and Co^{3+} ions or Co-complexes in octahedral symmetry, respectively.^{16,17} It is suggested that Co^{3+} species Co_3O_4 , and probably $\text{CoO}(\text{OH})$, are formed during the catalyst activation through the oxidation of precipitated $\text{Co}(\text{OH})_2$ in the zeolite channels and also by the partial oxidation of charge-compensating Co^{2+} cations. From Figure 5b it can further be seen that for the bicationic $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalyst, the intensity of the band near to 355 nm is lower than that for its precursor (monometallic $[\text{Co}_{0.58}][\text{Si}_{12}\text{Al}]\text{-MFI}$), which confirms that the Co-Ca catalyst possesses a smaller amount of the Co^{3+} species. This is in agreement with the lower H_2/TM ratio observed in the H_2 -TPR experiment and Raman measurements. Probably the presence of Ca^{2+} hampers Co^{2+} oxidation. For the bicationic Co-Ca catalyst the relatively intense band at around 550 nm suggests the presence of a higher amount of Co-complexes or Co-Ca-mixed oxides than in the monometallic Co-catalyst.^{4,15} For the $[\text{Co}_{0.29}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalyst the band near 350 nm, which is attributed to Co^{3+} , possesses a very low intensity and this indicates that here Co^{2+} is predominant, as observed from the lowest H_2/TM ratio in the H_2 -TPR measurement (Table 1).

The EPR spectra of $[\text{Cu}_x][\text{Si}_{12}\text{Al}]\text{-MFI}$ and $[\text{Cu}_{0.38}\text{Ca}_{0.086}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts, shown in Figure 6 (curves a, b and c), are similar to those reported by Yan *et al.*¹⁸ and can be attributed to the presence of hydrated Cu^{2+} cations in octahedral symmetry. This confirms the conclusions drawn from the H_2 -TPR and DRS-UV-Vis measurements.

Consistent with the DRS-UV-Vis and H_2 -TPR data for $[\text{Co}_x][\text{Si}_{12}\text{Al}]\text{-MFI}$ and $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts, their EPR spectra shown in Figure 6 (curves d, e and f), are typical for d^7 high spin Co^{2+} ions.¹⁹

Reduction of NO to N_2

In a previous study,²⁰ it was verified that $[\text{Cu}_x][\text{Si}_y\text{Al}]\text{-MFI}$ catalysts are more active for NO reduction in the presence of propane, while $[\text{Co}_x][\text{Si}_y\text{Al}]\text{-MFI}$ display higher activity when methane is employed as a reducing agent. Adelman *et al.*²¹ found that in the presence of NO and O_2 , nitro and/or nitrate complexes ($[\text{Cu}(\text{NO}_2)_y]^{2+}$ or $[\text{Cu}(\text{NO}_3)_y]^{(2-y)+}$) are predominantly formed on $[\text{Cu}_x][\text{Si}_y\text{Al}]\text{-MFI}$, while nitrite complexes ($[\text{Co}(\text{ONO})_y]^{2+}$) are predominant with $[\text{Co}_x][\text{Si}_y\text{Al}]\text{-MFI}$ catalysts. The latter are reduced upon exposure to CH_4 , which leads to the formation of N_2 and CO_2 , while the nitro and/or nitrate complexes are chemically reduced to N_2 upon exposure to C_3H_8 and remain inert to CH_4 .

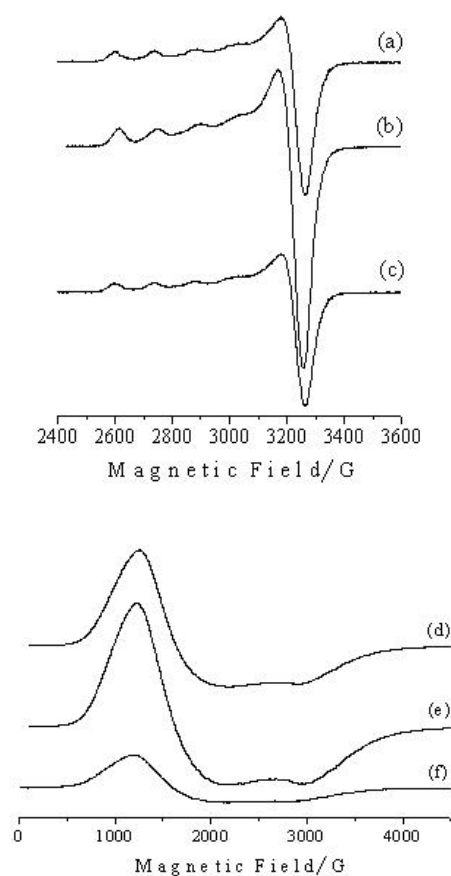


Figure 6. EPR spectra of (a) $[\text{Cu}_{0.38}\text{Ca}_{0.086}][\text{Si}_{12}\text{Al}]\text{-MFI}$, (b) $[\text{Cu}_{0.49}][\text{Si}_{12}\text{Al}]\text{-MFI}$, (c) $[\text{Cu}_{0.30}][\text{Si}_{12}\text{Al}]\text{-MFI}$, (d) $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$, (e) $[\text{Co}_{0.58}][\text{Si}_{12}\text{Al}]\text{-MFI}$ and (f) $[\text{Co}_{0.29}][\text{Si}_{12}\text{Al}]\text{-MFI}$.

Therefore the copper containing catalysts were tested only with propane and the cobalt containing catalysts only in the presence of methane. The specific activity in the reduction of NO (number of nitrogen molecules formed per mol of transition metal per hour) and in the alkane oxidation (number of alkane molecules consumed per mol of transition metal per hour) as a function of the reaction temperature is shown for the copper containing catalysts in Figure 7 and for the cobalt containing catalysts in Figure 8.

Figure 7a reveals that for nitrogen formation the specific activity of the bicationic $[\text{Cu}_{0.38}\text{Ca}_{0.086}][\text{Si}_{12}\text{Al}]\text{-MFI}$ is significantly higher than that observed for the monocationic $[\text{Cu}_{0.49}]$ and $[\text{Cu}_{0.38}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts, whose activity does not differ significantly. The higher specific activity of copper cations in $[\text{Cu}_{0.38}\text{Ca}_{0.086}][\text{Si}_{12}\text{Al}]\text{-MFI}$, which contains the highest amount of $[\text{Cu-O-Cu}]^{2+}$ species, indicates that these species, in which each copper cation is co-ordinated to one negative framework charge and one extra-framework oxygen, are more active for NO reduction than isolated Cu^{2+} cations. On the other hand, a minor improvement in the specific catalytic activity of the Cu^{2+} species in charge compensation sites in the presence of Ca^{2+} , cannot be

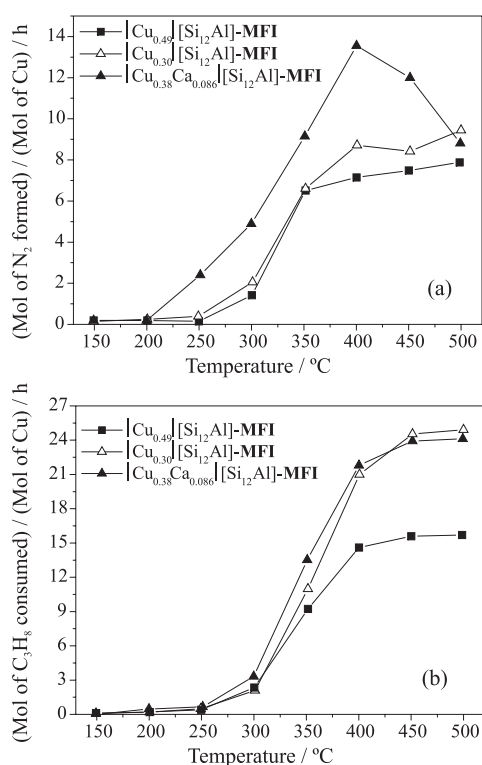


Figure 7. Specific activity of copper containing catalysts at GHSV = 42,000 h⁻¹ as a function of temperature. (a) N₂ formation, (b) propane oxidation.

excluded.³ Kucherov *et al.*¹² showed that during the introduction of a co-cation in a copper exchanged ZSM-5 zeolite, the copper in tetrahedral or octahedral symmetry are preferentially removed maintaining the amount of square-planar Cu²⁺ ions. According to these authors the specific activity of the Cu cations in ethane oxidation was enhanced by the consecutive addition of the co-cation. This behaviour can also be, at least partially, responsible for the higher observed catalytic activity of the [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI in the NO SCR-HC.

For the bicationic Cu-Ca catalyst, practically all the fed NO is reduced at 400 °C (conversion of 100%), however, above this temperature the specific activity of the copper cations in [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI decreases rapidly. A possible explanation of this decrease might be the cleavage of the Cu-O-Cu bond by water formed during the propane oxidation. This would result in the formation of less active isolated [Cu(H₂O)₆]²⁺ complexes. Another factor which might decrease the specific catalytic activity in [Cu_{0.38}Ca_{0.086}][Si₁₂Al]-MFI might be a reduced adsorption of NO on [Cu-O-Cu]²⁺ and Cu²⁺ cations at higher temperatures. This latter effect could also explain the slightly lower specific activity of [Cu_{0.49}][Si₁₂Al]-MFI in comparison with [Cu_{0.30}][Si₁₂Al]-MFI, which was observed at temperatures higher than 350 °C. It must be also considered that at temperatures higher than 350 °C the

hydrocarbon is preferentially consumed by oxidation.³

At the temperatures studied no difference in the specific activity for the oxidation of propane, is observed for the [Cu_{0.38}Ca_{0.086}] and the [Cu_{0.30}][Si₁₂Al]-MFI catalysts (Figure 7b). On the other hand, the [Cu_{0.49}][Si₁₂Al]-MFI catalyst shows significantly lower specific activity for the propane oxidation at temperatures higher than 350 °C. At this temperature the total propane conversion is *ca.* 40 % and raises to nearly 90 % at 400 °C on all the studied copper catalysts. With nearly all propane already oxidised, the specific activity observed for the [Cu_{0.49}][Si₁₂Al]-MFI catalyst, which contains much more copper than the other catalysts, does not increase significantly with further temperature increase.

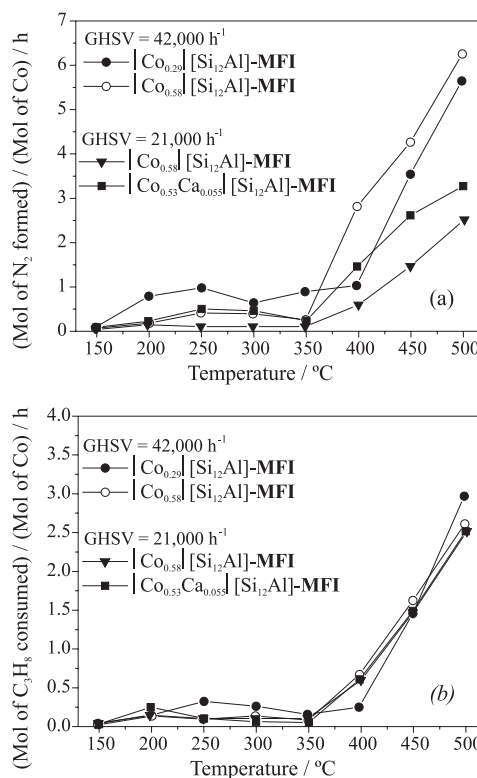


Figure 8. Specific activity of cobalt containing catalysts as a function of reaction temperature: (a) N₂ formation (b) methane oxidation.

Figure 8 shows that for the reduction of NO as well as for methane oxidation at a GHSV of 42,000 h⁻¹, the specific activity of the studied [Co_x] and [Co_xCa_y][Si₁₂Al]-MFI catalysts is considerably lower than that observed for the [Cu_x] or [Cu_xCa_y][Si₁₂Al]-MFI catalysts. At temperatures higher than 450 °C, the specific activity for NO reduction is considerably diminished with decreasing GHSV and does not change for methane oxidation. Under the same GHSV the studied [Co_x] and [Co_{0.53}Ca_{0.055}][Si₁₂Al]-MFI do not show significant differences in the specific activity of cobalt cations.

The observed competitiveness factor for the studied catalysts, which indicates the amount of hydrocarbon effectively used in the NO reduction is shown in Table 2 as a function of reaction temperature. It can be seen that over copper-containing catalysts propane is mainly oxidised by oxygen and that only 7 to 12 % of the consumed propane is used in the reduction of NO. On the other hand, for the cobalt catalysts the relative amount of methane used in the reduction of NO was much higher (up to 82 % of the methane consumed).

Table 2. Competitiveness factors of the $[\text{TM}_x\text{Ca}_y][\text{Si}_{12}\text{Al}]\text{-MFI}$.

$[\text{TM}_x\text{Ca}_y]$	Temperature [°C]		
	400	450	500
$[\text{Cu}_{0.49}]^{\text{a,b}}$	10.4	10.8	11.7
$[\text{Cu}_{0.30}]^{\text{a,b}}$	8.3	6.8	7.5
$[\text{Cu}_{0.38}\text{Ca}_{0.09}]^{\text{a,b}}$	12.5	10.0	7.2
$[\text{Co}_{0.29}]^{\text{a,c}}$...	28.8	22.6
$[\text{Co}_{0.58}]^{\text{d,c}}$	45.8	82.3	49.0
$[\text{Co}_{0.53}\text{Ca}_{0.06}]^{\text{d,c}}$	48.3	72.5	54.2

^aGHSV = 42,000 h⁻¹; ^bC₃H₈; ^cCH₄; ^dGHSV = 21,000.

Conclusions

After ion exchange copper is present as Cu²⁺ and [Cu-O-Cu]²⁺ in ion exchange sites in the zeolite. The amount of the latter species increases both with increasing copper content and in the presence of Ca²⁺ cations. The [Cu-O-Cu]²⁺ species showed higher activity for the reduction of NO. However at temperatures higher than 400 °C its activity decreases markedly, which might be due to the hydrolysis of the Cu-O-Cu bond or to a reduced adsorption of NO on the active sites at temperatures higher than 400 °C.

For $[\text{Co}_x]$ and $[\text{Co}_{0.53}\text{Ca}_{0.055}][\text{Si}_{12}\text{Al}]\text{-MFI}$ catalysts, cobalt is probably present in the form of Co²⁺ in charge-compensating sites or as Co³⁺ in extra-framework precipitates. The amount of Co³⁺ increases with the cobalt content and is diminished in the presence of Ca²⁺. For the different cobalt containing catalysts no significant difference in their specific activity for the reduction of NO and methane oxidation was observed.

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