Catalysis Letters Vol. 112, Nos. 1–2, November 2006 (© 2006)
DOI: 10.1007/s10562-006-0170-3

Catalytic reduction of NO over the modified MFI metallosilicalites

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Received 6 August 2006; accepted 30 August 2006

The metallosilicalites (MFI) containing copper ([Cu,Si]), zinc ([Zn,Si]) or both elements ([Cu,Zn,Si]) were prepared and modified as potential catalysts for the NO reduction with propene. The H-[Cu,Si] samples showed the highest activity, which was initially comparable to that of Cu-ZSM-5, but contrary to the latter, it increased with time. The framework Cu or Cu released from the framework probably act as active sites.

KEY WORDS: metallosilicalites; [Cu,Zn,Si]; [Zn,Si] MFI; synthesis; characterization; catalysts for NO reduction.

1. Introduction

Zeolites ZSM-5 belong to a group of zeolites of great industrial importance and they are applied as very efficient and selective catalysts. The MFI structure can be attained not only as aluminosilicate with very broad Si/Al ratio (including pure silica silicalite-1) but also as metallosilicalites with various kind of metals. The isomorphous substitution of the framework aluminum for other metals results in substantial changes in the properties of internal surface and subsequently in the nature, concentration and strength of catalytic active sites generated in obtained MFI metallosilicates [1].

The nitrogen oxide abatement has been one of the most challenging environmental problems in recent decades. The selective catalytic reduction of NO_x [2–4] is considered the most promising approach to this problem. The works of Iwamoto [5] evoked a great hope that the catalytic decomposition of nitrogen oxides over Cu-ZSM-5 could be the easiest way to eliminate these air pollutants. The high activity and selectivity of Cu-ZSM-5 appeared, however, not stable, and therefore this catalyst never attained any industrial application. The Cu modified zeolites are still investigated as catalysts for selective catalytic reduction of NO_x. The role of MFI structure as well as that of Cu cations seems to be crucial, although the details remain still not quite clear.

It is interesting to study, whether the copper atoms introduced into the framework of the MFI metallosilicalite could also result in catalytic activity for NO_x reduction, and whether a potential activity would be more stable than that of Cu cation modified aluminosilicate ZSM-5.

The following study presents the synthesis of [Zn,Si] MFI, [Cu,Si] MFI and [Cu,Zn,Si]MFI and their cation modifications with Cu^{2+} and H^{+}. The resulting metallosilicalites were characterized with physicochemical methods. Their catalytic activity was first examined for the propan-2-ol decomposition in order to assess the presence and the efficiency of acid and red-ox active sites. The selected samples presenting both active centers were used as catalysts for the reduction of NO with propene. The main aim of the catalytic examination was to assess, whether the metallosilicalites containing the framework Cu can show any activity for this reaction. The activity and stability was compared with those of zeolite Cu-ZSM-5 known as efficient catalyst for this reaction [5]. Even if a part of introduced metal atoms could be removed from the framework upon the thermal treatment, the released Cu species could act as catalytic sites quite differently than the Cu cations introduced into zeolite ZSM-5.

2. Experimental

The MFI metallosilicates [Cu,Si] and [Cu,Zn,Si] with atomic ratio Me/Si = 0.01–0.08 and [Zn,Si] with Me/Si = 0.001–0.03 were prepared similarly as aluminosilicate ZSM-5 [6], but instead of aluminum source, the chosen metal (i.e. Cu or Zn) compounds were added to the starting mixture. The water glass (supplied by Prayon-Rupel, Belgium) was used as silicon source. Zinc was admitted into the gel as sodium zincate (the latter was obtained by dissolving ZnO in NaOH solution), whereas ammonium complex of Cu salt ($CuSO_4$ dissolved in aqueous ammonia) was used as Cu source. The samples containing both Zn and Cu always contained equimolar content of the metals. Tetrapropylammonium bromide (TPABr) (Lancaster) was used as a template. The pH of the initial solution mixture was always very high (pH = 14). The gel was formed after

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adjusting the pH to the value 11 by adding some amount of H_2SO_4. Crystallization was conducted at 170 °C for 46 h. The products were washed with water, dried and calcined at 450 °C overnight in order to remove the organics. The samples were modified with cations by means of conventional ion-exchange with aqueous solutions (0.1 M) of respective salts (NH_4Cl, $CuCl_2$). The procedure was always repeated three times to attain a high exchange degree. The ammonium modification of the samples was transformed into H-form by conventional thermal decomposition of NH_4^+ cation. The obtained samples were characterized by means of XRD (TUR M-62), SEM (Philips SEM 515), FTIR (Bruker FTIR Vector 22) with KBr pellets. The spectra of adsorbed NO were recorded in a vacuum cell. The self-supported wafers were first evacuated at 400 °C for 2 h and then NO was adsorbed (20 torr) at the room temperature. The samples with adsorbed NO were then evacuated at different temperatures. The presented spectra, recorded at room temperature, contain the bands remained after subtraction of the spectra of the activated samples from those of the samples with adsorbed NO. The DRIFT spectra were recorded on Bruker Equinox 55 spectrometer with the diffusive reflection arrangement equipped with vacuum chamber (Harrick). The other characterization methods included ^{29}Si MAS NMR (Bruker AMX300 WB), DTA and DTG (SETARAM SETSYS 12). The samples were first examined as catalysts for propan-2-ol decomposition in a pulse micro-reactor attached to the GC system. The catalyst powder samples (0.015 g) were activated in helium stream prior to reactions at 400 °C for half an hour and then the test was conducted at 230 °C in helium flow (50 cm^3/min). The 1μl pulses of substrate were injected. The NO reduction reaction was carried out in a flow reactor at 400 °C usually for 4 h. The catalyst (0.1 g) was purged with helium prior to reaction at 400 °C for 2 h. The feeding mixture contained 1% vol. NO, 1% vol. C_3H_6 and 5% vol. O_2 diluted in helium. The total flow rate was 35 ml/min. The *R* coefficient calculated according to formula given by Tanaka et al. [7] was 0.33. No water vapors were used in the mixture applied for these preliminary experiments. The products were analyzed periodically with GC, each 60 minutes. The 2 m column was filled with zeolite 13X (2/3) and chromosorb 104 (1/3). The TCD was used as detector. The N_2 and unconverted NO were the only nitrogen bearing compounds detected. The conversion was estimated by comparison of the NO concentration in the products and in the feeding mixture.

3. Results and discussion

The obtained metallosilicalites show the MFI structure, although the samples with highest Me/Si ratio always exhibit lower crystallinity, particularly in the case of [Zn,Si] series (figure 1) and some admixtures of amorphous impurities. A small reflection at 6.9 ° (2P) is noticeable for the as synthesized Cu bearing samples, but it disappears after calcination. It could result from some organic impurity, that decomposes on heating. The unit cell volumes of the samples increases slightly with growing metal content, which results from the framework localization of the introduced metals (figure 2). The thermal removal of the template remnants does not affect the crystallinity of the samples. Nevertheless, the calcination at higher temperatures

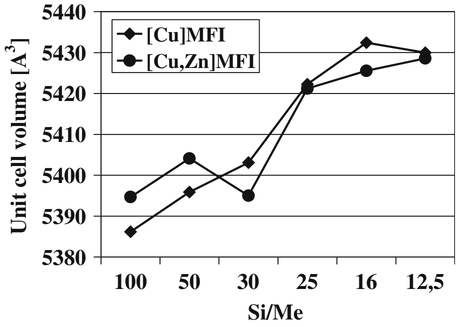


Figure 2. Correlation between the Si/Me ratio and the unit cell volume (for *as prepared* samples).

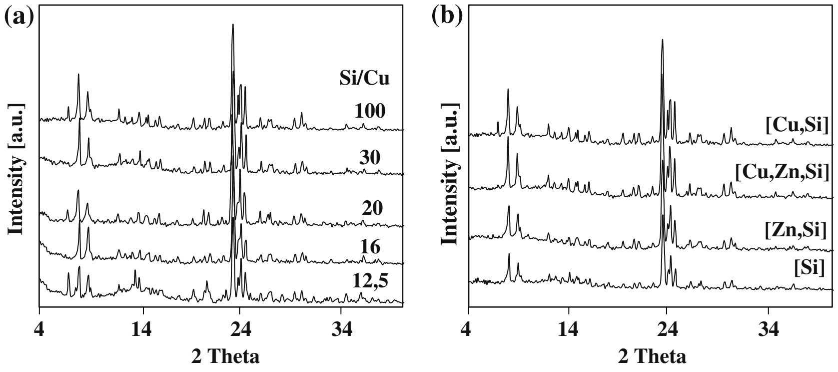


Figure 1. XRD patterns of the indicated samples. (a) series [Cu,Si] with various Si/Cu ratio, (b) silicalite (bottom patterns) and indicated metallosilicates with Si/Me = 100.

(600–900 °C) causes a recrystallization to condense phase of crystobalite. The DTA and TG data (figure 3) indicate very similar course of the curves for the studied metallosilicalites and silicalite-1. The main thermal effects reflect the oxidation of organics (exothermic peak at ~400 °C) and subsequent desorption of the oxidation products (endothermic peak at ~420 °C). The morphology and size of crystallites in the prepared series depend on nature and concentration of the introduced metals (figure 4). Generally, the low metal loaded samples show well separated, uniform crystallites with the shape typical of heteroatom bearing silicalites [8,9]. The metal rich samples usually form the larger shapeless aggregates. The FTIR spectra (KBr) of the samples (figure 5) do not indicate any distinct bands which could be attributed to the framework *heteroatoms*. Small shoulders at ~960 cm^{-1} (noticeable in presented spectra) are sometime assigned to the framework metal–oxygen bond [1]. An interesting feature of recorded spectra (mainly those of the Cu-bearing samples) is a splitting of the main asymmetric stretching band at about 1100 cm^{-1}. Such splitting is never seen in the spectra of silicalite, thus, it could be tentatively attributed to the introduced framework Cu. The DRIFT spectra of the hydrogen forms of the Cu bearing samples (figure 6) show the bands at 3730 and 3600 cm^{-1}. The bands reflect the presence of terminal SiOH and bridging Si(OH)Cu hydroxyl groups, respectively. The latter play a role of acid sites. The ^{29}Si MAS NMR analysis of the [Cu,Si] and [Cu,Zn,Si] samples indicates two signals

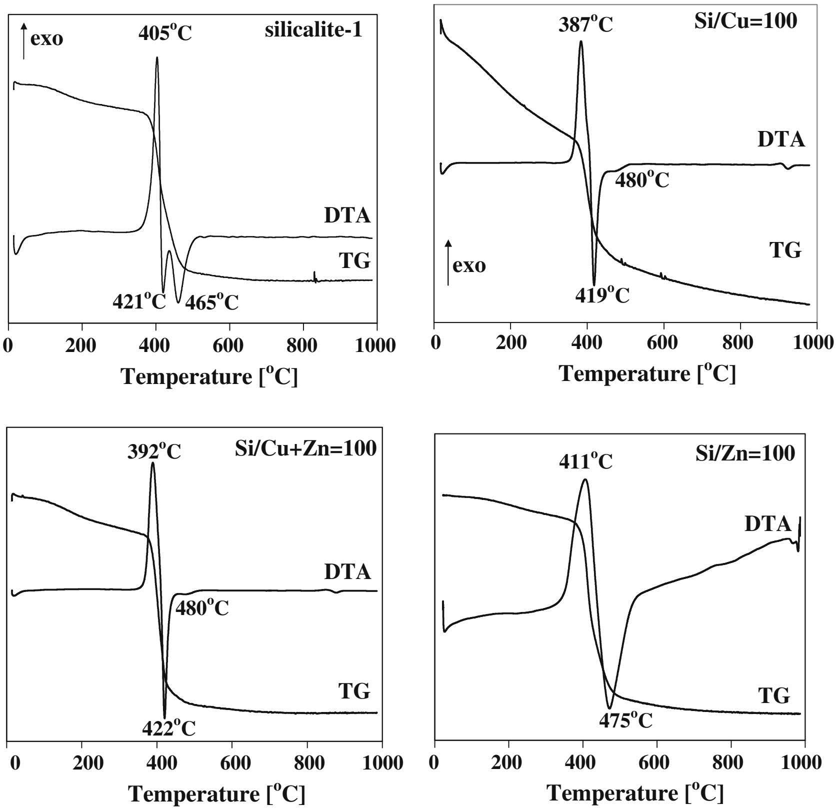
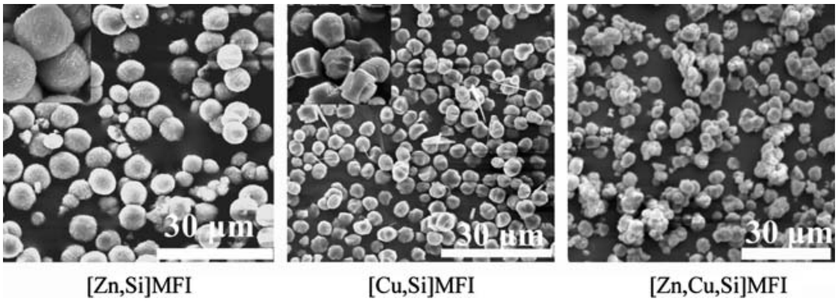


Figure 3. DTA, TG curves for the indicated samples.



[Zn,Si]MFI [Cu,Si]MFI [Zn,Cu,Si]MFI

Figure 4. SEM photographs of the selected samples.

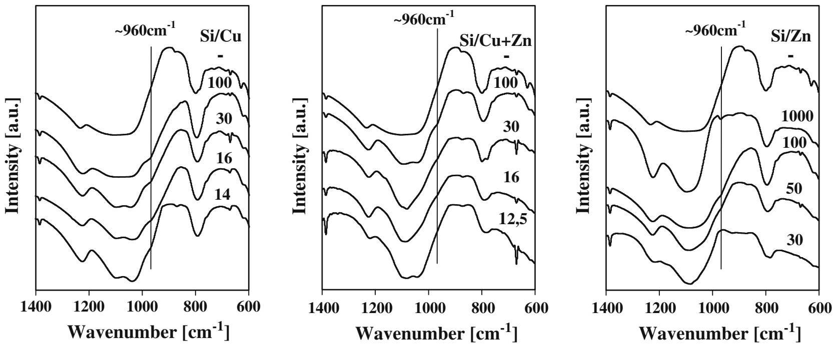


Figure 5. FTIR spectra (KBr) of the indicated samples (the upper spectra for the metal-free silicalite).

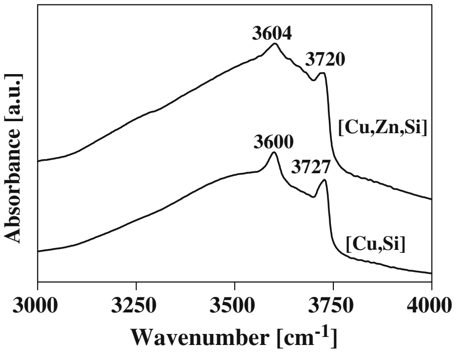


Figure 6. DRIFT spectra of H forms of indicated samples with Si/Cu ratio of 100.

at -114 and at -102 ppm (figure 7), similarly as that of [Zn,Si] [10], which are attributed to Si(4Si) and to Si(3Si,1Cu,Zn), respectively [11,12]. The intensity of the latter signal decreases after thermal treatment, which can suggest a migration of a part of metal atoms from the framework. The released metal moieties can play an important role in catalytic processes. A substantial part of metal atoms still must maintain their framework localization, since the calcined samples exhibit a distinctive cation-exchange ability.

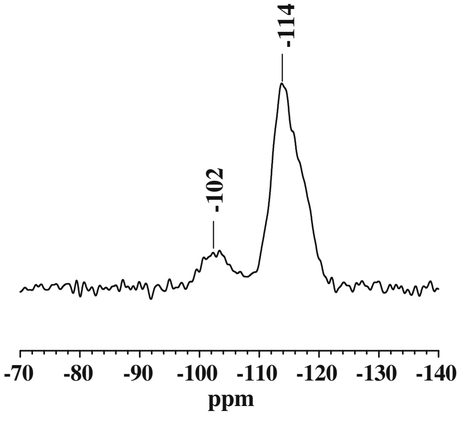


Figure 7. Typical ^{29}Si SS MAS NMR of the as synthesized sample [Cu,Si] with Si/Cu = 100.

The metallosilicalites under study show a noticeable activity for the propan-2-ol decomposition (figure 8). The prepared samples show some activity after thermal removal of template (figure 8a) due to forming the protons as a result of the amine cations (template) decomposition. The samples modified with Cu cations show rather low activity, similarly as the unmodified samples. The H-forms obtained via the NH_4^+ modification are always the most active. Their activity depends markedly on metal loading (figure 8b). The correlation between metal content and activity is different for each series. It increases with rising metal content for the copper-silicalites (figure 8b, c). Some decrease in activity of the metal richest samples can result from their lower crystallinity. The series containing both Cu and Zn is distinctly more active (figure 8d) than the coppersilicates [Cu,Si] MFI. The samples with the extreme metal loading (the lowest and the highest) are the most active. The activity of the H-[Zn,Si] series declined drastically (figure 8e) with rising Zn number. The composition of samples affects very much their selectivity. Although it may be expected that the H-forms should initiate the alcohol dehydration due to the action of acid sites, it is true only for the samples with low metal content. The contribution of acetone in products (as a result of alcohol dehydrogenation) always become prevailing for the metal-rich samples (figure 8c–e). It results from catalytic action of the extra-framework metal moieties.

The nature of the extra-framework metal species remains still not quite clear. The XRD data do not indicate any presence of crystalline oxides (CuO, ZnO). The IR spectra (figure 9) of NO adsorbed on the samples H-[Cu,Si] indicate two predominant bands at 1880 and 1630 cm^{-1}. The first one (with a shoulder at 1900 cm^{-1}) can be attributed to Cu^{2+} NO species. The above interaction is always reflected in the band at above 1900 cm^{-1} in aluminosilicate ZSM-5 modified with Cu [13], but the shift of the band to the value of 1880 cm^{-1} was already recorded for the niobiosilicate MFI modified with Cu cations [14]. It is likely that similar shift takes place in our metallosilicates. The band at 1630 cm^{-1} can be assigned to Cu^{2+} combined with NO_2^- or NO_3^- anions [15,16]. It

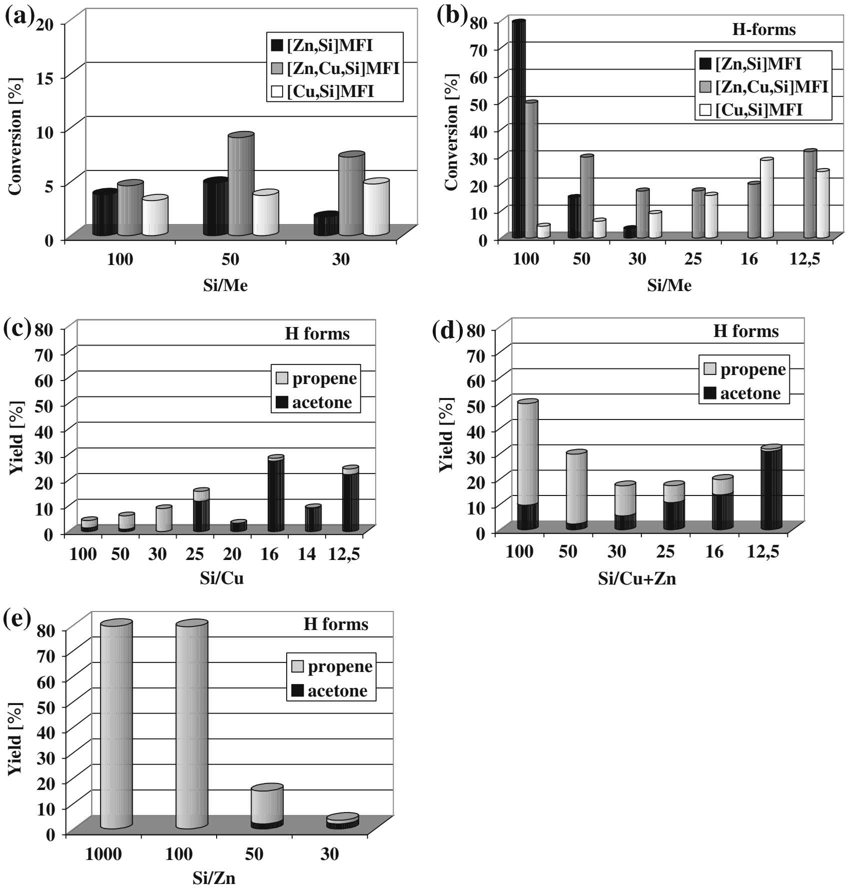


Figure 8. Catalytic activity for propan-2-ol decomposition (a) Conversion of propan-2-ol over selected unmodified samples (i.e. calcined, but not modified with any cation). (b) Conversion of propan-2-ol over H-forms of indicated samples. (c) Yield of propane/acetone over the [CuSi] series with various, indicated Si/Cu ratios. (d) Yield of propane/acetone over the [Cu,Zn,Si] series with various, indicated Si/Cu + Zn ratios. (e) Yield of propane/acetone over the [ZnSi] series with various, indicated Si/Zn ratios.

is interesting to notice that the band at 1810 cm^{-1} usually assigned to the Cu^{+} complex with NO [13] has never been recorded in our samples. It is in contrast to Cu-ZSM-5 (Cu^{2+}-modified zeolites), where Cu^{2+} cations always undergo reduction upon thermal evacuation. The additional band at 2008 cm^{-1} of unknown origination is always recorded in the spectra of NO adsorbed on H-[Cu,Si]. Perhaps, it could result from the interaction between NO and the framework Cu. The above data reflect the different nature of the copper moieties in metallosilicate MFI compared to Cu^{2+}-modified zeolites [13]. The catalytic examination of the studied metallosilicalites in the NO reduction with propene showed a considerable activity of the samples modified with H^{+} (figure 10a). The initial activity (after 1 h) of the samples [Cu,Si] MFI with medium Cu content was similar as that of Cu-ZSM-5, but contrary to the latter the activity of the copper-silicalites increased with time. The sample H-[Cu,Si] MFI (Si/Cu = 16) indicated the most significant increase in activity and after 4 h its activity was distinctively higher than that of Cu-ZSM-5. The samples with the highest Cu loading are usually less active than those with medium Cu content (figure 10b). A modification of copper-silicalite samples with additional Cu^{2+} cations by means of ion-exchange did not improve the activity, but on the contrary it resulted in drastic decrease in activity (figure 10c). It suggests that the role of the framework Cu atoms or the moieties released from the framework is more significant for catalytic reduction of NO than that of introduced Cu^{2+} cations. The decrease in activity can also result from diminished acidity of the catalyst in comparison to H-form. The H-metallosilicalites containing both Cu and Zn exhibited a considerable activity for the NO reduction, particularly when the metal loading was relatively high (figure 10d). However, the activity of these samples declined slightly with time on stream. On the other hand, the samples with low Me/Si ratios were much less active at the beginning of the process, but their activity rose in time. The H-forms of [Zn,Si] metallosilicalites indicated very low activity for the NO reduction (figure 10e), but contrary the series containing the framework Cu they improved their activity after introduction of Cu cations.

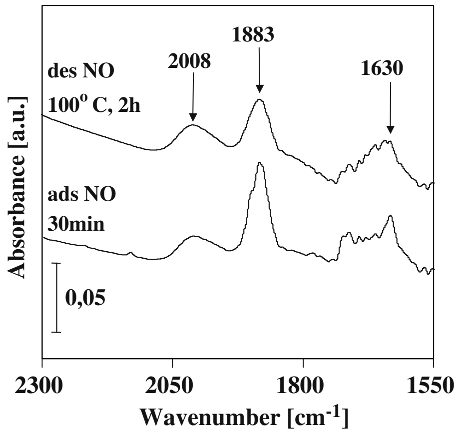


Figure 9. Subtracted FTIR spectra of the NO adsorbed on the sample H-[Cu,Si] (Si/Cu = 16).

Summing up we would like to underline that the conventional hydrothermal synthesis can be applied to obtain the MFI metallosilicalites (with Cu, Zn or both elements) and a relatively high metal loading can be attained (up to Me/ Si = 0.08). It is possible that a part of the metal atoms used for syntheses occupy the extra-framework positions (especially at high metal loading), but the products always indicate the ion-exchange properties which results from negative framework charge located at the metal atoms.

The samples show a considerable catalytic activity in propan-2-ol decomposition. The Zn containing samples are always more active (particularly at low metal loading) than the Cu bearing catalysts, which is caused by generated acid sites. The activity of [Cu,Si] series is lower and it increases with raising metal content. The propene prevails in products over lean metal loaded samples, whereas the dehydrogenation towards acetone becomes predominant in tests catalyzed by metal-rich samples, which results from an action of extra-framework metal species.

The metallosilicalites (particularly [Cu,Si]MFI) show a remarkable catalytic activity for the reduction of NO

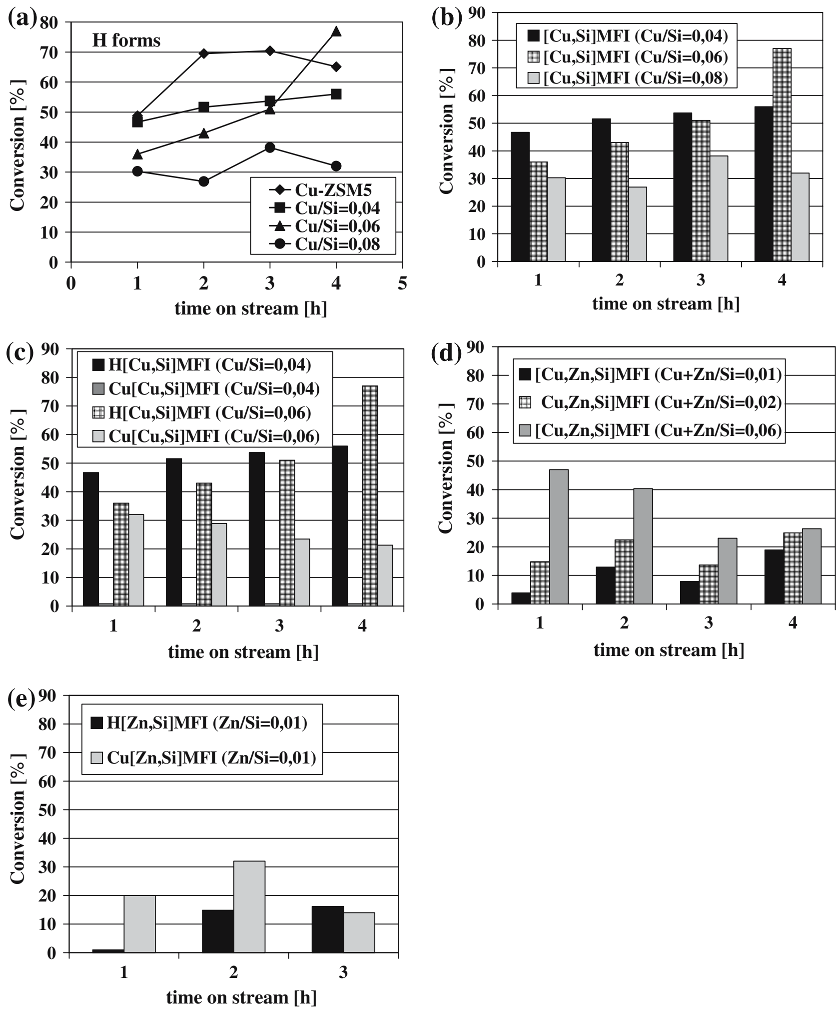


Figure 10. Catalytic activity of selected samples for NO reduction with C_3H_6: (a) activity of H [Cu,Si] samples in comparison to Cu-ZSM-5, (b) conversion over samples H-[Cu,Si] with various Cu loading as a function of time, (c) conversion over the H-and Cu-forms of [Cu,Si] with two different Cu loadings, (d) conversion over samples H-[Cu,Zn,Si] with various metal loading as a function of time (the inactive samples are omitted), (e) conversion over the H and Cu forms of [Zn,Si]MFI (Si/Zn = 100) as a function of time.

with propene. Although our catalytic examination was only exploratory and the applied conditions were not comparable with the real practical parameters (e.g. lack of water vapor) the obtained results are promising. The [Cu,Si] samples (particularly with medium metal loading) show the activity similar to that of Cu-ZSM-5, and moreover, the activity increases with time (at least in recorded period). The nature of active sites in metallosilicalites is not clear, but the presence of the framework Cu or some released Cu moieties seems crucial. Thus, the samples with lower Cu content ([Cu,Zn,Si]) or without any Cu (i.e. [Zn,Si]) are less active than the series [Cu,Si]. Some acidity of the samples is also important to facilitate the process. The samples [Cu,Si] modified with Cu^{2+} show much lower activity than the H-modification because of lower acidity.

Acknowledgment

E. Janiszewska expresses her gratitude to the Foundation for Polish Science for the financial support.

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