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The effect of pretreatments on different copper exchanged ZSM-5 for the decomposition of NO

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

Copper exchanged zeolites are proving to be very important in decomposing NO into its elements. This work compares the activities of under and over exchanged copper ZSM-5 catalysts and their properties when treated in reducing atmospheres. The copper in the under exchanged samples was shown to be relatively stable to reduction in reducing atmospheres. However, the copper in over exchanged Cu-ZSM-5 was easily reduced and seemed to migrate forming aggregates on the surface detectable by XPS. This aggregate formation was shown to be reversible. A proposal on the state of copper within the zeolite is presented.

Keywords: Copper; ZSM-5; Nitric oxide decomposition

1. Introduction

Much research surrounds the study of Cu-ZSM-5 as a catalyst for the decomposition or reduction of NO [1-4]. Of particular interest is its ability to selectively decompose environmentally unacceptable NO into N_2 and O_2. The catalyst has been investigated using several characterization techniques and has been found to possess properties such as easy $Cu^{+} \leftrightarrow Cu^{2+}$ redox [5] and the ability to stabilize different NO species [6].

However, many questions remain unanswered, particularly regarding the active centres and the reaction mechanism. The aim of the work presented herein was to contribute to the answering of these unsolved questions with particular emphasis on copper states in under exchanged and over exchanged ZSM-5 zeolites and their modification and stability in different pretreating atmospheres.

2. Experimental

Copper exchanged ZSM-5 zeolites were prepared following a procedure documented in the literature [7]. In brief, 11 mmoles copper acetate monohydrate (Aldrich) was dissolved in 1 l distilled water. Subsequently, 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. After this time, a dilute solution of ammonia (Merck) was added dropwise, until the desired pH was reached. The solution was stirred for a further hour before centrifuging, thoroughly washing and drying.

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The decomposition of nitrogen monoxide was carried out using a continuous flow system operated at atmospheric pressure. The catalyst (0.5 g) was placed in a quartz glass U-tube reactor. Before testing, the catalyst was subjected to a standard pretreatment in 30 ml $\min^{-1}$ helium overnight at 500°C. Following this pretreatment, the reaction was initiated by introducing nitrogen monoxide (5066 ppm) and helium (balance) at 30 ml $\min^{-1}$. The reaction temperature was kept at 500°C. The on line analysis of the product stream was made possible using a Balzers Quadrupole QMG 311 mass spectrometer.

For pretreatments in hydrogen, the reactor temperature was decreased in a flow of helium and 30 ml $\min^{-1}$ hydrogen introduced at 150°C. After 30 minutes, the hydrogen was replaced by helium and the temperature increased to 500°C at a rate of 10° $\min^{-1}$. At 500°C, the reaction was reinitiated and the product stream analysed at regular intervals as described above.

The treatment of the used catalyst in helium, simply involved substituting the NO/He stream for helium and leaving at 500°C overnight.

Elemental analysis of copper was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

XPS analyses were performed on each catalyst at room temperature with an SSX-100 model 206 Surface Science Instrument (SSI) photoelectron spectrometer, following outgassing overnight at 7×10^{-5} Pa in the preparation chamber. 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 (a flood gun). The binding energies were calculated with respect to the C1s peak set at 284.8 eV. The intensities were estimated by calculating the integral of each peak after subtraction of the "S-shaped" background [8]. Atomic concentration ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scoffield cross sections [9]. The surface copper was calculated from the summation of the contributions of each of the Cu $2p_{3/2}$ peaks observed in the photoelectron spectra. The surface silicon was calculated from the Si 2p line at circa 103 eV.

3. Results

Table 1 lists the prepared zeolites, the pH of the exchanging solution and the corresponding copper contents in wt.% and % exchange. The % exchange was calculated on the basis that one copper ion exchanges with two protons in the H-ZSM-5 and was calculated using the formula, 2 × (no. moles Cu/no moles Al). Increasing the pH resulted in an increase in the overall copper content of the zeolite. No sample presented any XRD peaks characteristic of a crystalline phase containing copper.

Fig. 1 presents NO conversion, NO conversion to nitrogen and NO conversion to oxygen directly following the standard pretreatment in helium for the indicated catalyst. A characteristic of the samples containing an over exchange of copper, i.e., an exchange above 100%, was the complete conversion of NO to nitrogen during the initial stages of reaction (Fig. 1b and Fig. 1c). For Cu-ZSM-5(173), high NO conversion (> 80%) was observed for up to 15 minutes on stream and oxygen did not appear until the 25th minute. The conversion of NO decreased steadily with time, until oxygen was detected in the product stream. With the appearance of oxygen, the overall conversion of NO gradually attained a steady state. A similar trend

Table 1
Cu-ZSM-5 prepared

Sample	Preparation pH	wt.% Copper [a]	% Exchange
Cu-ZSM-5(72)	5.03 [b]	1.30	72.3
Cu-ZSM-5(173)	6.50	3.05	172.7
Cu-ZSM-5(225)	7.50	3.93	225.1

[a] Measured using ICP-AES.

[b] No ammonia added.

was observed for Cu-ZSM-5(225). However, in this case, high conversion of NO continued for up to 30 minutes and oxygen did not appear in the exit stream before 50 minutes. Again, the NO conversion continually decreased until oxygen appeared in the exit stream. With the 72% copper exchanged zeolite, Fig. 1a, steady state was quickly obtained resulting in a conversion of 18%.

A comparison of the overall activities of the zeolites at steady state shows that the under exchanges zeolite (< 100%) exhibits a lower activity compared to the over exchanged samples. However, increasing the copper level above 173% does not result in an overall improvement at steady state, i.e., Cu-ZSM-5(173) exhibited an NO decomposition activity of 55.8% at steady state while increasing the copper content up to 225% exchange resulted in a similar activity of 56.5%.

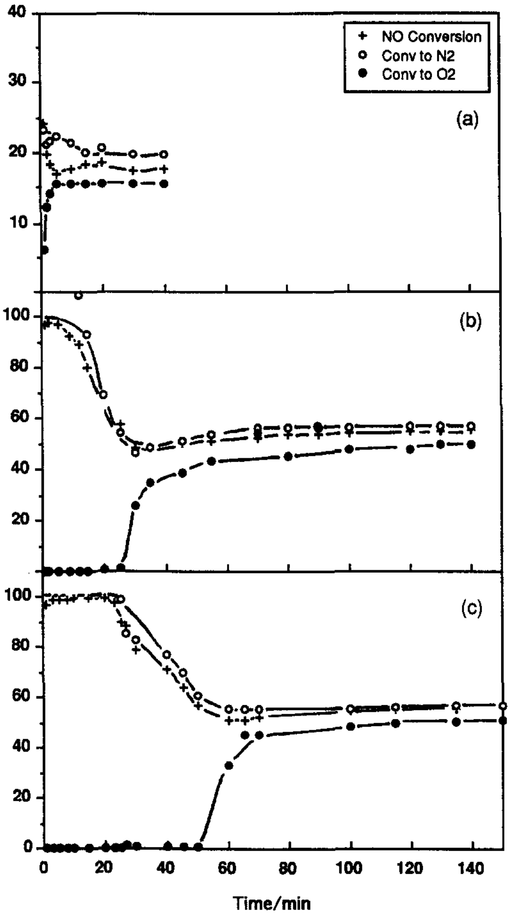

Fig. 1. Conversion of NO (+), conversion to N_2 (O) and conversion to O_2 (●) with reaction time at 500°C directly following the standard pretreatment using (a) Cu-ZSM-5(72), (b) Cu-ZSM-5(173) and (c) Cu-ZSM-5(225). 5066 ppm NO at W/F = 1g s ml^{-1}.

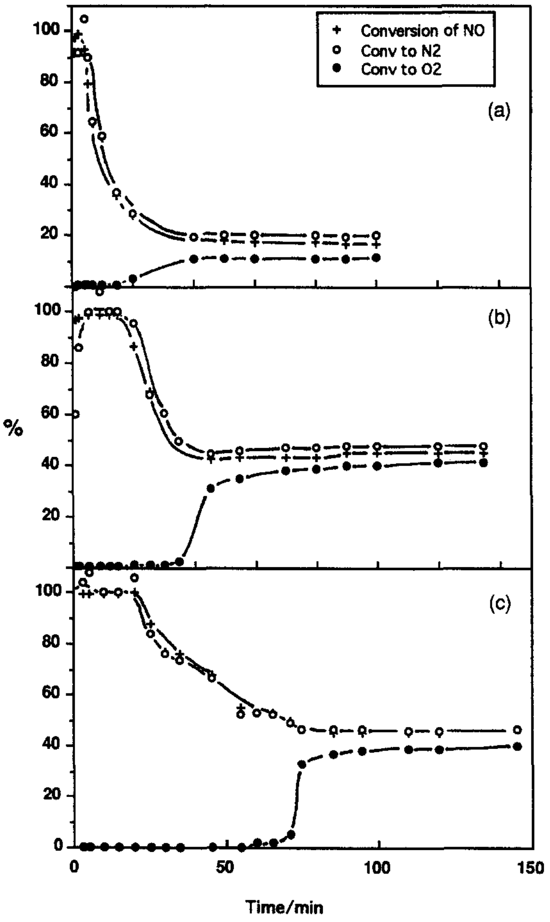

Fig. 2. Conversion of NO (+), conversion to N_2 (O) and conversion to O_2 (●) with reaction time at 500°C following treatment in H_2 at 150°C, using (a) Cu-ZSM-5(72), (b) Cu-ZSM-5(173) and (c) Cu-ZSM-5(225). 5066 ppm NO at W/F = 1g s ml^{-1}.

Once steady state was reached, the samples were subjected to a reductive treatment at 150°C in hydrogen. Fig. 2 presents the evolution of products with time on stream at 500°C directly following this treatment. Each sample presented a high NO conversion and an absence of oxygen at early stages of reaction, the final conversion depending on the level of copper in the zeolite.

A general observation was that the time to acquire steady state was longer than that observed when the standard pretreatment in helium was employed (Fig. 1). The overall activity at steady state was also lower especially for the over exchanged samples.

Following this step the samples were subjected to a pretreatment at 500°C in a flow of helium, overnight. As presented in Fig. 3, the reaction profiles with time, following this pretreatment, did not resemble those observed for the fresh catalysts which were subjected to a similar treatment as in Fig. 1. Steady state appeared quickly and there was little "missing" oxygen. These profiles are similar to those obtained for the samples calcined in air before being subjected to the standard pretreatment overnight in helium.

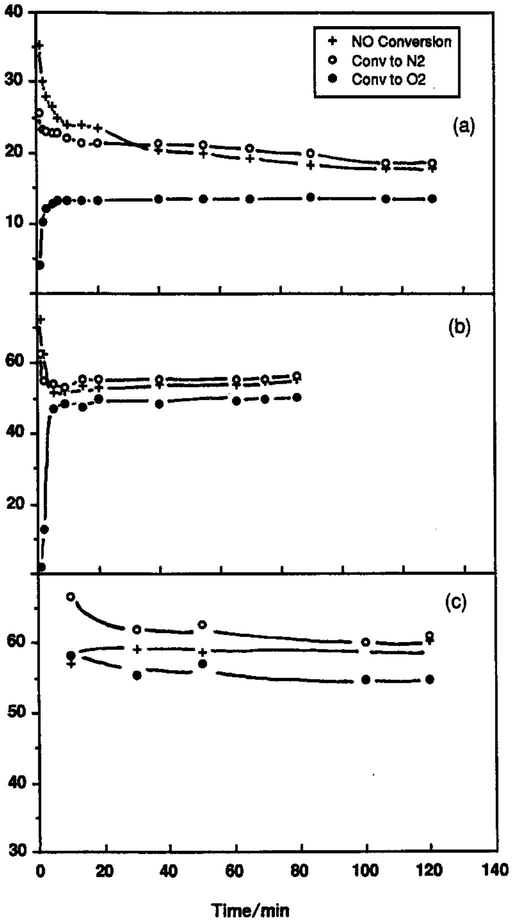

Fig. 3. Conversion of NO (+), conversion to N_2 (○) and conversion to O_2 (●) with reaction time at 500°C using (a) Cu-ZSM-5(72), (b) Cu-ZSM-5(173) and (c) Cu-ZSM-5(225) after pretreatment in helium overnight. 5066ppm NO at W/F = 1g s ml^{-1}.

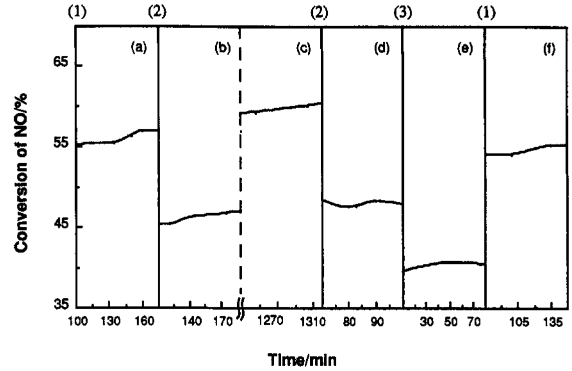

Fig. 4. Conversion of NO after 2–3 hours reaction using Cu-ZSM-5 (255) after the indicated treatments. (1) Helium at 500°C, 30 ml min^{-1}, overnight, (2) hydrogen 150°C, 30 ml min^{-1}, 30 min, (3) oxygen at 500°C, 30 ml min^{-1}, 30 min.

Fig. 4 presents the activity of Cu-ZSM-5(225), in terms of percentage NO converted, following various pretreatments. These pretreatments are indicated by the numerals positioned directly above the plots and explained in the legend. The activity of the zeolite significantly decreased after treatment in hydrogen (sections b and d). However, this activity is recovered by either continually exposing the catalyst to the reaction mixture overnight (Fig. 4c) or pretreating in helium at 500°C. On the other hand, exposing the reduced catalyst to oxygen does not improve the overall catalytic activity and in fact, a decrease is observed (section e). How-

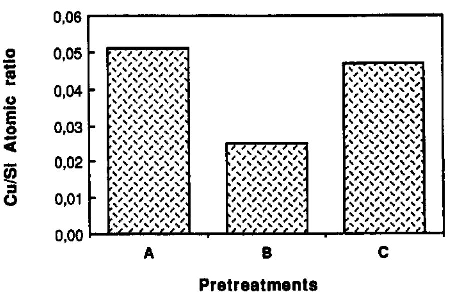

Fig. 5. XPS surface Cu/Si atomic ratio of Cu-ZSM-5(225) measured after (A) reaction at 500°C, (B) treatment in hydrogen followed by (C) reaction at 500°C.

ever, a recovery was observed following treatment in helium, compare Fig. 4a and Fig. 4f.

Fig. 5 presents the surface Cu/Si atomic ratio of the Cu-ZSM-5(225) subsequent to various treatments. Following reaction at 500°C for several hours, the surface Cu/Si atomic ratio was about 0.05. Pretreating this catalysts in hydrogen resulted in a significant lowering of this ratio which was restored when the reduced sample was subjected to reaction conditions for several hours.

4. Discussion

The performance of two types of copper exchanged ZSM-5 zeolites have been examined in this work. One containing an under exchange of copper, i.e., less than 100% exchange and 2 samples presenting an over exchange of copper, Cu-ZSM-5(172) and Cu-ZSM-5(225). Activity at steady state and transient initial activity were different for both kinds of zeolites. The most active were those containing an over exchange of copper. This is in agreement with the results reported by Iwamoto [10] who showed that the highest activity was obtained for Cu-ZSM-5 samples with a Cu/Al ratio exceeding 0.5. A second remark is that these over exchanged samples presented a high NO conversion without the formation of oxygen at early time on stream, following initial pretreatment in helium.

Pretreatment of a freshly prepared, non-calcined, over exchanged Cu-ZSM-5 in helium at 500°C resulted in the transient high NO conversion, low conversion to oxygen, a feature exhibited by all catalysts pretreated in hydrogen at 150°C, (Fig. 1 and Fig. 2). So it would seem that pretreatment in helium or in hydrogen results in the reduction of copper creating oxygen vacancies. Under these circumstances NO can be envisaged as interacting with this vacancy. This interaction would result in lattice stabilisation and consequently weaken the NO bond. With electron transfer it can be envisaged that oxygen remains in the lattice while the nitrogen atoms combine, forming molecular nitrogen which leaves as a gas. The amount of oxygen trapped strongly depends on the amount of copper present in the zeolite and the reducing conditions. This mechanism continues until the complete saturation of the oxygen vacancies created during the pretreatment. More reducing pretreatments, for example in hydrogen, increases the number of reduced sites created but once saturation is achieved the activity towards NO decomposition decreases.

This mechanism of NO decomposition is relatively rapid and has been noted in the literature using copper supported oxides [11]. It was reported that helium induces a slight reduction of copper sites. This creates surface oxygen vacancies that are restored by the oxygen of NO with simultaneous formation of N_2 until all vacancies are filled. More reducing conditions result in an increase in the number of vacancies but for all cases the activity declined to zero after a given time on stream. Copper supported on carriers such as Al_2O_3, SiO_2, TiO_2 and ZrO_2 yielded similar results. In the samples used in this work, the activity did not fall to zero after such a reductive treatment but maintained a certain activity depending on the copper content. So there is an obvious difference between supported oxides and the Cu-ZSM-5 catalysts. In the Cu-ZSM-5, once saturation is achieved the decomposition still proceeds. This may indicate that the copper, within the pores of the zeolite, is arranging itself forming species active for the decomposition of NO. These species could well be very small clusters or some other forms of copper. Indeed in XP spectra of exchanged copper zeolites the binding energies of the $Cu2p_{3/2}$ line is considerably higher than that of bulk Cu compounds and this is thought to indicate the presence of isolated metal ions and small clusters [12]. The decomposition of NO into its elements requires the adsorption of two NO molecules to form a dinitrogen and subsequent desorption of molecular oxygen. This process would be difficult to envisage on exchanged copper ions situated so far apart from each other

Table 2
Atomic ratio of copper to "missing oxygen" following the indicated treatments

Sample	Cu/O ratio	
	He pretreatment	H_2 pretreatment
Cu-ZSM-5(73)	37.0	1.8
Cu-ZSM-5(172)	1.4	1.0
Cu-ZSM-5(225)	1.0	0.8

in a ZSM-5 zeolite of low Al content (Si/Al = 25). Such a reaction, however, may be possible on copper species containing a number of copper atoms.

Table 2 presents the atomic ratio of copper in the prepared zeolites to the "missing oxygen" following the indicated treatments i.e., in hydrogen and helium. The under exchanged Cu-ZSM-5 is more resistant to reduction as is evidenced by the higher Cu/O ratio. Wichterlovà et al. [13] reported results which permitted the identification of two main Cu sites in the ZSM-5 matrix, using Cu^+ luminescence. The conclusion was that one copper ion was located adjacent to two framework Al atoms and the second was a Cu ion associated with one framework Al atom. The latter was reduced more easily and its formation is favoured using copper acetate as the exchanging salt at a high pH. This promotes the formation of the $(Cu^{2+}\text{–}OH)^+$ species, a monovalent entity which is thought to associate with a single Al framework atom. It is this species that is reported to be active for NO decomposition. This could explain the higher stability of the copper species in the under exchanged sample which likely contain copper associated with two framework Al atoms containing no extra framework oxygens. Reduction in this case would require the abstraction of an O^{2-} anion from the zeolitic framework and in helium at 500°C this would not be likely. A stronger reductive treatment in hydrogen was required to reduce this catalyst.

The atomic ratio of copper to "missing oxygen" for the over exchange samples are lower than expected. If it is assumed that during pretreatment in helium, all Cu^{2+} are reduced to Cu^+ with a corresponding formation of oxygen vacancies then the expected amount of oxygen required to transform all Cu^{2+} to Cu^+ or fill the corresponding oxygen vacancies would be 2 in order to satisfy the overall charge balance. However, a much lower ratio is observed in the case of Cu-ZSM-5(225), corresponding to a ratio of one oxygen atom per copper present in the zeolite. This would indicate a more complex process where perhaps extra lattice oxygen species are formed or there is strong adsorption of oxygen. Another explanation would be the formation of other products containing oxygen. However, only trace quantities of N_2O were observed and in no case was any obvious deficit of nitrogen observed in the product stream. It is also possible that the Cu^{2+} is converted to Cu^0. This is probable in the pretreatment involving hydrogen but is unlikely in the case of helium. One thing however is clear, pretreatment of an over exchanged fresh Cu-ZSM-5 in helium overnight at 500°C or treatment in H_2, results in the reduction of the catalyst. Reaction with NO oxidizes this catalyst by leaving behind the oxygen while producing gaseous nitrogen.

An attempt to re-reduce these used catalyst by pretreating overnight in helium at 500°C was not entirely successful, (Fig. 3). All samples quickly reached steady state. A pretreatment in hydrogen for 30 minutes at 150°C, on the other hand, proved successful and a trend similar to that presented in Fig. 2 was observed.

If the samples were calcined in air before the standard pretreatment in helium, the steady state was reached almost immediately and oxygen appeared in the product stream without much delay. Therefore, the pretreatment consisting of calcination followed by treatment in helium does not seem to result in a substantial reduction of the catalyst. It seems, therefore, that impurities remaining in the prepared Cu-ZSM-5 samples directly following preparation may be acting as reducing agents, reducing the copper during the initial pretreatment in helium at 500°C. This could be either acetate, since Cu acetate was used as the exchanging salt or ammonia, since an ammonia solution was used to adjust the pH. In this respect, it should be noted that no ammonia was added to the exchanging solution in the preparation of Cu-ZSM-5(72) and this sample was not reduced after standard pretreatment. This sample did not exhibit the transient phenomenon of the other samples when pretreated in helium (Fig. 1a). Contrary, the over exchanged samples were reduced after pretreatment and ammonia was used in their synthesis.

Kucherov et al. [14] reported, using in situ ESR, that no spontaneous thermal reduction of the cupric ions took place, in a helium flow or in a vacuum, up to 500°C. In these experiments, however, an under exchanged Cu-ZSM-5 was investigated which was calcined in air at 500–520°C for 5 hours before measurements. On the other hand, with the addition of small amounts of hydrocarbon to the helium flow, a drop in the Cu^{2+} signal was observed due to the fast reduction of the copper.

Pretreating in hydrogen resulted in an overall drop in conversion for over exchanged zeolites (compare Fig. 4a and Fig. 4b). This would indicate a rearrangement of the copper within the zeolite during the treatment in hydrogen. However, this effect was reversible. With extended reaction time, the catalyst reverted back to its initial activity. A similar regeneration effect was observed when the treatment gas was helium. Therefore, a flow containing 0.5% NO in helium or pure helium was sufficient to regenerate the active sites ''damaged'' during the pretreatment in hydrogen. This ''damage'' cannot be due to removal of oxygen, extra lattice or otherwise, since a pretreatment in helium also restored activity. Conversely, a pretreatment of this catalyst in oxygen did not restore activity as shown in Fig. 4e. This deactivation could well be because of the formation of aggregates of copper within the zeolite, an effect which must be reversible.

To verify this fact, a more in dept characterisation was carried out using XPS. A measurement of the copper on the surface showed that following hydrogen treatment, the apparent concentration of copper, expressed as a ratio of copper to silica, decreased. This fact, coupled with the change of the binding energy of the copper $2p_{3/2}$ line from 933.7eV to 932.8eV, indicated the modification of copper on the surface of the zeolite. However, the original form of copper was restored after further reaction indicating the reversibility of the effect.

For under exchanged samples, treatment in hydrogen did not result in a lowering of the activity (compare Fig. 1a and Fig. 2a). This emphasises the differences between various species in the under and over exchanged Cu-ZSM-5 samples. In the under exchanged samples, the copper is in the form of well dispersed, isolated ions that interact strongly with two Al atoms in the zeolite. This would explain their stability to reduction in the presence of helium and their resistance to aggregate metal formation in hydrogen treatment. The over exchanged samples, on the other hand, probably some copper cluster species with extra lattice oxygen which are not as stable as the isolated exchanged copper ions in reducing atmospheres, but exhibit more activity towards the decomposition of NO.

5. Conclusion

Under and over exchanged Cu-ZSM-5 zeolites are shown to exhibit different properties when treated in reducing atmospheres. The under exchanged fresh copper zeolite seems to be stable to reduction in reducing atmospheres and there is no loss in activity observed after treatments in hydrogen. The over exchanged copper zeolites, on the other hand, are shown to form aggregates of copper on the surface, following treatment in hydrogen, which is reversed with extended treatment in helium.

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