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NO_x abatement in lean exhaust gas conditions over metal substrated zeolite catalysts

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Abstract

Metal substrated ZSM-5 zeolites ion-exchanged with copper are effective catalysts in the elimination of nitrogen oxides from lean automotive exhaust gases when propene works as a reductant. Some co-cations improve the catalytic activity of Cu-ZSM-5. The critical temperature for the deactivation of Cu-ZSM-5 catalysts is around 700°C where the state of copper begins to change resulting in the decrease of the catalytic activity. The structure of the Cu-ZSM-5 zeolite collapses after thermal aging at temperatures above 800°C. However, the coexistence of chromium in the zeolite increases the thermal stability of Cu-ZSM-5 considerably.

Keywords: Nitrogen oxides; Exhaust gas; Metal substrated zeolite catalysts

1. Introduction

The removal of nitrogen oxides from the exhaust gases of diesel and other lean-burn engines is problematic with three-way catalysts, because in an oxygen-rich atmosphere traditional three-way catalysts work mainly as oxidation catalysts for hydrocarbons and carbon monoxide. Thus, new catalyst solutions have to be developed to solve the NO_x purification problem. One of the most promising deNO_x catalyst is the ZSM-5 zeolite ion-exchanged with transition metal cations (usually Cu).

In the present study the activity of cation-exchanged ZSM-5 zeolites in NO_x reduction by propene and CO in excess of oxygen ($c_{O_2} = 15\%$) was investigated. The zeolite type, SiO_2/Al_2O_3 ratio, ion-exchange procedure, role of different reductants (C_3H_6 or CO), cation and co-cation, and aging were used as variables in the experiments.

2. Experimental

The zeolite catalyst samples were prepared by coating metal foil substrates with washcoats, which contained two different ZSM-5 zeolites as the parent zeolite. The samples were prewashed with a $NaNO_3$-solution and ion-exchanged with transition metals (Cu, Co, Ga, Pt, Pd) according to the methods presented in the literature [1–3]. The ion-exchanges were done either to the zeolite powder or to catalysts supported on a metal foil. Co-cations (Co, Ca, Sr, Cr, Ni, Fe, Pd, Ga, Ce, La) were ion-exchanged to Cu-ZSM-5, either

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before or after the ion-exchange of the main cation. Finally, the catalyst samples were washed, dried and calcined (500°C/2 h). The standard size of the cylindrical test samples was 10.7 cm^3 by volume (length 75 mm, diameter 13.5 mm).

Catalyst samples were tested using a simulated exhaust gas of a diesel engine (NO 1000 ppm, C_3H_6 500/2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO_2 10%, SO_2 0/25 ppm, N_2 bal.) at increasing temperature (from 150 to 550°C, 12°C/min). Some test were also done using a NO/N_2 gas mixture (3000 ppm NO in N_2), with and without the addition of propene and CO. The space velocity was 50 000 h^{-1} in all experiments. The testing apparatus contained gas bottles and mass flow controllers for each gas component, a furnace with a tube reactor and separate gas analyzers for CO/CO_2 (MDIR), O_2 (paramagn.), total hydrocarbon (FID), SO_2 (UV), SO_3 (UV) and NO_x ($NO+NO_2$) (chemiluminescence). The testing apparatus was automatic and controlled by a PC-computer [4]. The catalytic behavior was recorded as the NO_x conversion vs. temperature. Cu-nitr-ZSM-5-33-260[1], Cu-acet-ZSM-5-33-116[2] and Pt-ZSM-5-33-13.6[3] samples were studied also by perturbation tests, where hydrocarbon and O_2 concentrations in the simulated diesel gas were oscillated (HC 0.05 ↔ 1%, O_2 10 ↔ 19%; 0.1 Hz). The concentrations of other gases remained constant during the tests. Perturbation tests were done at four different temperatures (275, 300, 325 and 350°C). To explain the role of the two reducing components in the simulated diesel exhaust gas, tests, by changing the concentrations of propene and carbon monoxide in the exhaust gas at constant temperature, were done. The tests were run by changing the exhaust gas composition after every five minutes according to the six stages presented in Table 1.

Table 1
CO and propene concentrations and the test temperature of 'reductant test' for the Cu-acet-ZSM-5 sample

Sample	Cu-acet-ZSM-5-33-173
Temperature (°C)	350
Stage 1	CO 2000 ppm, C_3H_6 0 ppm
Stage 2	CO 0 ppm, C_3H_6 500 ppm
Stage 3	CO 500 ppm, C_3H_6 500 ppm
Stage 4	CO 2000 ppm, C_3H_6 500 ppm
Stage 5	CO 0 ppm, C_3H_6 2000 ppm
Stage 6	CO 500 ppm, C_3H_6 2000 ppm

Cu-ZSM-5 samples were aged in air at the temperatures of 500, 600, 750, 800, 950 and 1100°C for 3 h or 50 h (750°C) to study the thermal durability in dry conditions. The deactivation of the Cu-ZSM-5 samples was investigated by the NO_x conversion vs. temperature-test with a simulated diesel gas mixture and also by nitrogen adsorption (specific surface area and pore size distribution analyses). The results concerning the hydrothermal treatments will be published in future.

FT–IR studies were done to determine the surface complex formation during the reaction. Separate and simultaneous adsorption of NO, CO and air on Pt-ZSM-5-33-13.6, Pd-ZSM-5-33-29.8 and Cu-ZSM-5-33-116 samples were analyzed. The Perkin–Elmer 1760 FT–IR spectrometer was used in the investigation. In static experiments, the spectra were recorded at successive temperatures in the temperature range of 25 to 400°C whereas in GC–IR experiments, the spectra were recorded at 200 and 300°C using a GC–IR software. The spectra were recorded at 4000–600 cm^{-1} using a resolution of 4 cm^{-1}. The samples were reduced by hydrogen at 300°C and evacuated prior to the FT–IR measurements. The partial pressures of NO, CO and air used in the experiments were 60, 90 and 180 mbar, respectively. NO was introduced into the chamber as a 10% NO/N_2 gas (600 mbar).

3. Results and discussion

The Pt-ZSM-5-33-13.6 catalyst did not show any significant activity in NO_x decomposition,

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[1] E.g. for Cu-nitr-ZSM-5-33-260: ZSM-5 zeolite with the Si/Al ratio of 33, ion-exchanged in Cu-nitrate solution to the ion-exchange level of 260%.

[2] E.g. for Cu-acet-ZSM-5-33-260: ZSM-5 zeolite with the Si/Al ratio of 33, ion-exchanged in Cu-acetate solution to the ion-exchange level of 116%.

[3] E.g. for Pt-ZSM-5-33-260: ZSM-5 zeolite with the Si/Al ratio of 33, ion-exchanged in Pt solution to the ion-exchange level of 13.6%.

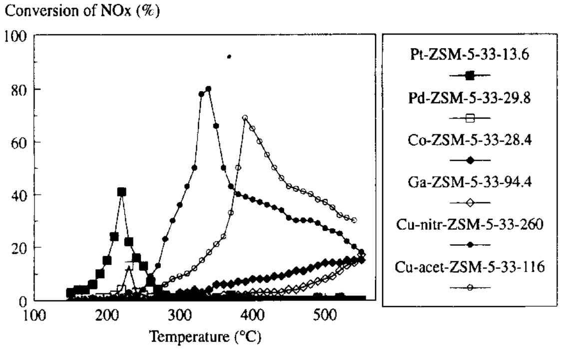


Fig. 1. NO_x conversions of different ZSM-5 catalysts as a function of reaction temperature (light-off tests); NO 1000 ppm, C_3H_6 2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO^2 10%, SO_2 25 ppm, N_2 bal.

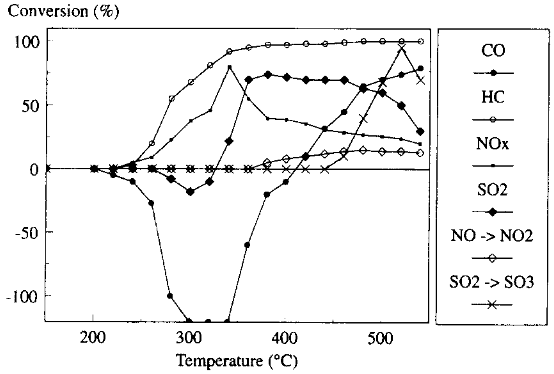


Fig. 2. Conversions of different gas components in a diesel test over Cu-nitr-ZSM-5-33-260 as a function of reaction temperature; NO 1000 ppm, C_3H_6 2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO_2 10%, SO_2 25 ppm, N_2 bal.

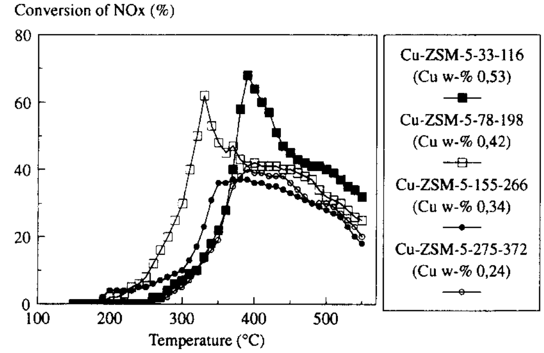


Fig. 3. The effect of SiO_2/Al_2O_3 ratio on the activity of Cu-ZSM-5; NO 1000 ppm, C_3H_6 2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO_2 10%, SO_2 25 ppm, N_2 bal.

when the feed gas contained only NO (3000 ppm) and nitrogen. Addition of propene increased the NO conversion up to 50%, but after the O_2-addition (5%) the NO conversion fell to the level of 0% to 5%. In the tests with simulated diesel gas over Pt-ZSM-5-33-13.6 the NO conversion was 40% at maximum (Fig. 1), but the conversion window was very narrow. The tests with Pd-ZSM-5-33-29.9 were quite similar, only the maximum of NO conversion was lower. Co-ZSM-5-33-28.4 and Ga-ZSM-5-33-94.4 did not show any activity with propene, according to the literature these catalysts prefer methane and ethane as reductants [5,6].

In our coated metal foil substrates Cu-ZSM-5-78-198 was not particularly effective in NO decomposition (3000 ppm NO in N_2 gas). The addition of propene improved NO conversion slightly, but O_2-addition increased it clearly (15%). With the simulated diesel gas mixture Cu-nitr-ZSM-5-33-260 had the highest NO conversion (max. 80%) at the lowest temperature (350°C). The NO conversion was very good also over Cu-acet-ZSM-5-33-116 (max. 70% at 400°C) (Fig. 1). This phenomenon can be explained by the differences in the ion-exchange levels.

The formation of CO was abundant as long as hydrocarbon was detected in the gas phase after catalyst (Fig. 2). The oxidation of NO to NO_2 was not very significant at the test temperatures. The measured NO_x conversion may also include the NO conversion to N_2O which can be significant in cases, when the oxygen concentration is low and in transient conditions [7]. The formation of N_2O is typically higher during the initiation of the deNO_x reactions and thermodynamically favored at relatively low temperatures (<350°C). Almost all of SO_2 was oxidized to SO_3 at temperatures over 500°C.

From Fig. 3 it can be seen that the SiO_2/Al_2O_3 ratio in ZSM-5 structure affects the NO_x conversion. The samples which had lower SiO_2/Al_2O_3 ratios were the most active. This result was expected because the zeolites with small SiO_2/Al_2O_3 ratio have more aluminum, and, thus, more ion-exchange places for Cu in zeolite structure resulting in active sites [8]. However, the different degree in ion-exchange levels may also have an effect on these results. Unfortunately, ZSM-5 zeolite is not stable as a carrier when $SiO_2/$

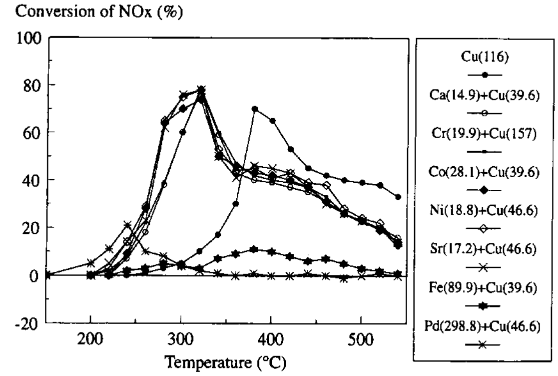


Fig. 4. The effect of co-cation in Cu-ZSM-5 on NO_x conversions; NO 1000 ppm, C_3H_6 2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO_2 10%, SO_2 25 ppm, N_2 bal. The ion-exchange levels are in parenthesis after co-cation, parent zeolite is ZSM-5-33.

$Al_2O_3 < 20$. $NaNO_3$-wash had no effect on the catalytic activity. The purpose of the $NaNO_3$-wash often proposed in the literature is to make the state of the zeolite from the different origins similar before the ion-exchange [9].

The catalytic activity was improved with Ca, Co, Cr, Ni and Sr as co-cations when Cu was ion-exchanged before the co-cation. Fe, Ga and Pd combined with Cu had very low activity. When the catalysts were prepared by ion-exchanging first the co-cation and then copper (three ion-exchange solutions) even more active catalysts could be prepared. This observation is also presented in the literature [10]. The interaction of Cu and a co-cation seemed to disturb the state of the most active Cu sites, when co-cations were ion-exchanged after copper. Ce or La as a stabilizer had no significant effect on the NO removal efficiency. NO_x conversions of Cu-ZSM-5 samples with a co-cation can be seen in Fig. 4 (first co-cation then copper).

In the perturbation tests Cu-nitr-ZSM-5-33-260 converted propene and nitrogen oxides at temperatures higher than 300°C, when there was a lot of propene present (1%). For Cu-acet-ZSM-5-33-116 this temperature was correspondingly 350°C. Pt-ZSM-5-33-13.6 had very high activity towards hydrocarbon and CO oxidation at temperatures between 275–350°C, but the NO_x conversions were low. At this temperature range both Cu-ZSM-5 samples showed high activity for NO_x reduction. The perturbation tests for these three samples at 325°C are shown in Fig. 5.

As mentioned earlier, formation of CO was seen as long as propene was present in the gas phase at the outlet of the reactor. CO concentration had its maximum simultaneously with NO_x conversion. This observation could lead to conclude that CO has some reductive properties in the NO_x abatement. However, the 'reductant tests' showed clearly that carbon monoxide in the gas phase had no promoting effect on NO_x conversion. When only CO was present in the reaction gas, NO_x conversions remained under 10% with both catalyst samples. With 500 ppm of propene deNO_x activity raised to 20% and with 2000 ppm of propene it achieved the level of about 40%. It is obvious that it is primarily propene that causes the improvement in NO_x reduction activity over Cu-ZSM-5, which can also be seen in Fig. 6. For Cu-nitr-ZSM-5 the presence of carbon monoxide with propene caused anyhow high NO_x conversions during the first 30 s before they were established to lower levels. This may be due to the role of CO as a reductant or a promotor during transient conditions, but it can also be caused by a chemisorption effect.

In FT–IR experiments on Cu-ZSM-5 gem-dinitrosyl species were seen at 1840 and 1715 cm^{-1}

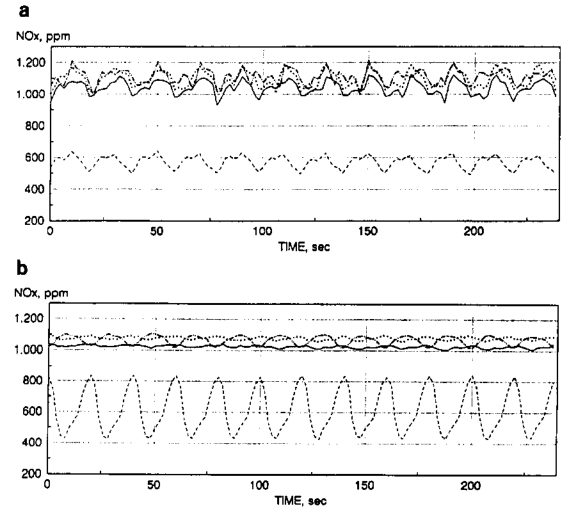


Fig. 5. Perturbation tests for Cu-acet-ZSM-5-33-116 (———), Cu-nitr-ZSM-5-33-260 (- - -) and Pt-ZSM-5-33-13.6 (- · · - · · -) samples at 325°C, 0.1 Hz, inlet NO_x (· · ·); (a) O_2 10 to 19%, HC 1% and (b) HC 0.05 to 1%, O_2 19%.

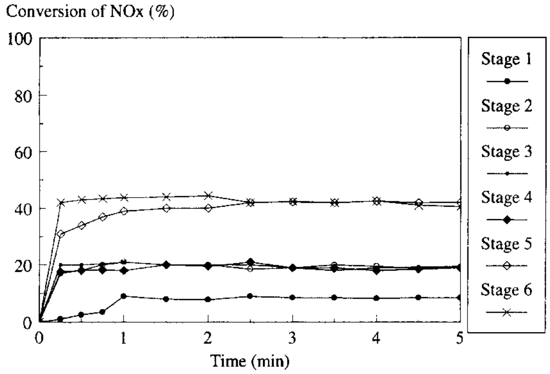


Fig. 6. Comparison of carbon monoxide and propene as reductants in the elimination of NO_x with Cu-acet-ZSM-5-33-173 (concentration of components at different stages are shown in Table 1).

(Cu$^+$-(NO)$_2$). The formation of NO_2 in a NO + CO + air gas mixture was observed by the formation of adsorbed NO_2 species at 1750, 1625, 1605 and 1580 cm^{-1}. Linear adsorption of NO on Cu^{2+} could also be seen at room temperature (1870 cm^{-1}). When air was introduced into the chamber strong absorption bands appeared at around 1630 and 1610 cm^{-1} and weak bands at 1340–1300 cm^{-1}. These bands are assigned [10–12] to asymmetric NO_2 stretching, NO_3^- adsorbed on alumina and symmetric NO_2 stretching, respectively. CO formed a linear complex with copper (Cu$^+$–CO at 2160–2150 cm^{-1}). When Pt-ZSM-5 and Pd-ZSM-5 zeolites were used linear Pd$^+$–CO at 2140 cm^{-1}, Pd–NO at 1780–1750 cm^{-1} and Pt$^+$–CO at 2150 cm^{-1} could be seen. The adsorption of NO_2 at 300°C was not so intense than with Cu-ZSM-5 whereas the formation of a *M*–NCO complex was probable (a strong band at 2270–2260 cm^{-1}) [10].

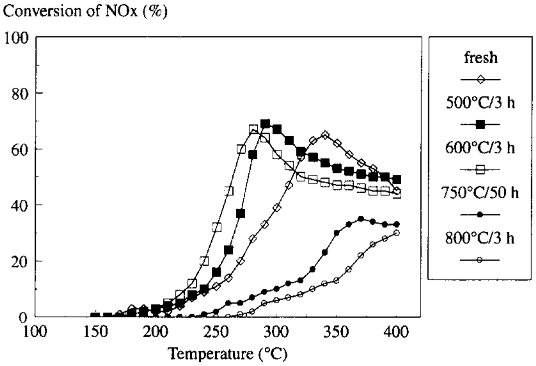


Fig. 7. NO_x conversions of aged Cu-acet-ZSM-5-33-173 catalysts; NO 1000 ppm, C_3H_6 2000 ppm, H_2O 7%, O_2 15%, CO 500 ppm, CO_2 10%, SO_2 0 ppm, N_2 bal.

According to FT–IR studies, CO is not a good reductant when Cu-ZSM-5 is used as a catalyst for NO reduction. The most probable reaction is NO decomposition and reactions of adsorbed NO (gem-dinitrosyl and nitrite species) to form N_2O, NO_2 and N_2. Gaseous NO_2 is formed by desorption of nitrite species. Adsorbed CO reacts with oxygen released from NO decomposition [13,14]:

$$\mathrm{NO} \rightarrow \mathrm{NO(ads)} \tag{1}$$

$$\mathrm{NO(ads)} \rightarrow \mathrm{N(ads)} + \mathrm{O(ads)} \tag{2}$$

$$\mathrm{NO(ads)} + \mathrm{N(ads)} \rightarrow \mathrm{N_2} + \mathrm{O(ads)} \tag{3}$$

$$2\mathrm{N(ads)} \rightarrow \mathrm{N_2} \tag{4}$$

$$\mathrm{NO(ads)} + \mathrm{N(ads)} \rightarrow \mathrm{N_2O} \tag{5}$$

$$\mathrm{N_2O} \rightarrow \mathrm{N_2} + \mathrm{O(ads)} \tag{6}$$

$$\mathrm{CO(ads)} + \mathrm{O(ads)} \rightarrow \mathrm{CO_2} \tag{7}$$

$$\mathrm{NO_2^-(ads)} \rightarrow \mathrm{NO_2} \tag{8}$$

With noble metal zeolites the reaction is more likely to go through isocyanate complex formation at temperatures higher than 300°C [15,16]:

$$\mathrm{NO(ads)} \rightarrow \mathrm{N(ads)} + \mathrm{O(ads)} \tag{9}$$

$$\mathrm{O(ads)} + \mathrm{CO(ads)} \rightarrow \mathrm{CO_2} \tag{10}$$

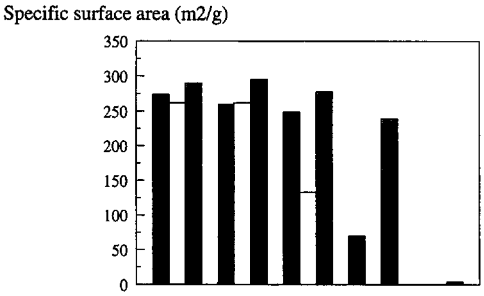
$$\mathrm{N(ads)} + \mathrm{N(ads)} \rightarrow \mathrm{N_2} \tag{11}$$

$$\mathrm{N(ads)} + \mathrm{CO(ads)} \rightarrow \mathrm{NCO(ads)} \tag{12}$$

$$2\mathrm{NCO(ads)} + \mathrm{O_2} \rightarrow \mathrm{N_2} + 2\mathrm{CO_2} \tag{13}$$

To see the reducing effect of propene FT–IR studies should be done with a C_3H_6–NO–O_2 gas mixture.

After aging the catalysts at high temperatures the activity of Cu-acet-ZSM-5-33-173 decreased clearly when the temperature of aging was raised from 600 to 750°C (Fig. 7). Catalysts aged at 500 and 600°C worked as well as the fresh ones, whereas samples aged at higher temperatures (750 and 800°C) were considerably more inactive in NO reduction. Based on this observation, it can be claimed that 700°C is the temperature where a



Sample (temp. of ion-exch.,°C)	fresh	600°C/3 h	800°C/3 h	950°C/3 h	1100°C/3 h
Cu-acet-ZSM-5-33-72.2 (25) ■	274	260	249	70	0
Cu-acet-ZSM-5-33-173 (60) □	262	262	133	0	0
Cu-Cr(58.3)-ZSM-5-33-37.7 (60) ■	290	295	278	239	4

Fig. 8. Specific surface areas (m^2/g) of Cu-acet-ZSM-5 samples aged at different temperatures.

radical reduction in the catalytic activity of Cu-ZSM-5 zeolite occurs.

Cu-acet-ZSM-5 samples did not lose their specific surface area or total pore volume considerably until aged at 950°C (Fig. 8). Samples ion-exchanged at room temperature were more thermally stable than those ion-exchanged at higher temperatures. Cr improved the thermal stability clearly and Cu–Cr(58.3)-ZSM-5-33-37.7 kept its physical properties even after aging at 950°C. The same phenomenon was observed earlier over a Y-zeolite [17]. However, the catalytic activity decreased considerably after aging at 700°C.

Thus, the main reason for the deactivation has to be a phenomenon other than the collapse of the physical structure. It seemed to be modifications in the state of copper. Thermodynamic calculations showed that copper itself is completely in the CuO form in lean conditions (15% O_2) up to 700°C. At higher temperatures Cu preferably forms Cu_2O. As a conclusion it could be assumed that the main reason for the deactivation of Cu-ZSM-5 is the permanent reduction of the oxidation level of copper at temperatures over 800°C, which results in more mobile surface species, out-migration of copper and rapid sintering (agglomeration) [13]. In the case of zeolite catalysts dealumination can play an important role in deactivation [13,18]. Thus, this can also, in our case, be an essential factor for deactivation.

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