NO_2 formation and its effect on the selective catalytic reduction of NO over Co/ZSM-5

A.Yu. Stakheev [1], C.W. Lee, S.J. Park [a] and P.J. Chong [2]

Solid-State Chemistry Laboratory, KRICT, PO Box 107, Yusong, Taejon 305-606, Korea
[a] *Department of Chemistry, Korea University, Korea*

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Catalytic performance of Co/ZSM-5 with different metal loadings and of HZSM-5 was compared in the $NO + O_2$, $C_3H_8 + O_2$, and $NO + C_3H_8 + O_2$ reactions. It was found that Co/ZSM-5 catalysts containing only isolated cobalt ions in cationic positions are inactive in NO_2 formation. To achieve appreciable NO conversion in the SCR process over these catalysts higher reaction temperatures are required. These results make it possible to suggest that NO_2 formation is not a prerequisite for the SCR of NO with hydrocarbons over Co/ZSM-5. With increasing Co loading, however, Co/ZSM-5 begins to exhibit activity in NO_2 formation. This is explained by the formation of cobalt oxide particles on the zeolite carrier, which are active in the NO_2 formation. Increase in NO_2 formation strongly enhances catalytic activity in SCR of NO at lower reaction temperatures. Comparison of the C_3H_8 conversion in the $C_3H_8 + O_2$ and $C_3H_8 + O_2 + NO$ reactions provides evidence that NO_2 activates hydrocarbon molecules resulting in the formation of the reaction intermediates of the SCR process.

Keywords: Co/ZSM-5; selective catalytic reduction of NO_x; propane; NO_2 formation; NO oxidation; cobalt oxide; isolated cobalt cations; temperature-programmed reduction; temperature-programmed desorption of NO

1. Introduction

Recently, selective catalytic reduction (SCR) of nitric oxide with hydrocarbons under oxygen-rich conditions has attracted considerable attention as an alternative to the traditional NH_3-SCR process. Numerous catalysts were proposed for this reaction, which include ion-exchanged zeolites, H-form of mordenite and ZSM-5, transition metal oxides supported on Al_2O_3, etc. [1–7]. Among these catalysts Co/ZSM-5 appears to be one of the most promising due to excellent catalytic performance, high selectivity, and ability to utilize methane as NO reductant [7–10]. However, the reaction mechanism of the SCR process remains unclear, and efforts of many research groups have been directed to clarifying the details of this reaction.

The role of oxygen is one of the most important aspects of the reaction mechanism to be elucidated. Though Co/ZSM-5 exhibits some activity in SCR of NO even without oxygen, this reaction can be remarkably promoted by an excess of oxygen in the feed. Recently, Li and Armor [11,12], and Lukyanov et al. [13] provided strong evidence that the role of oxygen is to convert NO into NO_2, and it is NO_2 that reacts with hydrocarbon. The proposed mechanism appears to be very plausible, because it is well known that nitrogen dioxide ("nitrous fumes") is used as selective oxidizing agent for many organic molecules. The first step of the reaction is the formation of the hydrocarbon radical as a result of hydrogen abstraction [14]:

$$RH + NO_2 \rightarrow R\cdot + HONO \qquad (1)$$

Therefore, it was assumed that the formation of an alkyl radical via hydrogen abstraction on the adsorbed NO_2 is a necessary step for SCR of NO. Cowan et al. [15] demonstrated that the rate determining step of the reaction is the breaking of a carbon–hydrogen bond, which provides additional evidence for the mechanism proposed by Li and Armor. Lately, the important role of the adsorbed NO_2 or NO_x ($x \geqslant 2$) in the SCR of NO was confirmed by Beutel et al. [16], Bethke et al. [17], and Yokoyama and Misono [18,19]. Recently, Shelef et al. [20] and Yokoyama and Misono [18] demonstrated that correlation exists between the activity of catalysts for the NO_2 formation in the $NO + O_2$ reaction and their activity in the SCR process for Cu/ZSM-5 and Ce/ZSM-5.

However, the activity of Co/ZSM-5 in NO_2 formation was not reported so far. In this context, it was important to evaluate the activity of Co/ZSM-5 in the oxidation of NO into NO_2 ($NO + O_2$ reaction), and to correlate this activity with NO and hydrocarbon conversion under conditions of the selective catalytic reduction of NO ($NO + C_3H_8 + O_2$ reaction). Considering the role of NO_2 as a hydrocarbon activator, it was also of interest to compare hydrocarbon conversion over the catalysts that exhibit different activities in the NO_2 formation in the presence and in the absence of NO ($NO + C_3H_8 + O_2$ reaction and $C_3H_8 + O_2$ reactions, respectively).

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[1] On leave from N.D. Zelinskii Institute of Organic Chemistry, Leninskii Pr. 47, Moscow, Russia.

[2] To whom correspondence should be addressed.

However, one should take a complex structure of the Co/ZSM-5 catalytic system into account. Cobalt ions are difficult to exchange into ZSM-5, and to achieve a sufficient exchange level a special ion-exchange procedure has been developed by Li and Armor [7]. It includes ion-exchange of ZSM-5 with cobalt acetate solution for several days at elevated temperature (~80°C). However, experiments with cobalt acetate solutions performed in our laboratory indicated that the heating of the solution inevitably leads to some precipitation of cobalt hydroxide. Thus, one can expect that the calcined catalyst may contain at least two different kinds of Co species: cobalt ions in cationic positions of the ZSM-5 framework, and cobalt oxide particles in the zeolite channels and/or on the external surface of the zeolite microcrystals. These species may exhibit different catalytic properties thus complicating the overall reaction pattern.

The primary aim of this study is to unravel superimposing effects of these species. For this purpose it is attempted:

(1) to prepare two types of Co/ZSM-5 catalysts containing solely isolated Co cations and containing some additional amount of Co oxide particles;

(2) to study the activity of those catalysts for the oxidation of NO into NO_2 and SCR of NO, respectively, and to compare these results with the activity of pure HZSM-5;

(3) to correlate the activity in the oxidation of NO into NO_2 with the activity of the catalysts in the SCR of NO;

(4) to compare the activity of the catalysts in the conversion of propane in the presence and in the absence of NO, and to correlate it with the activity in NO_2 formation.

2. Experimental

2.1. Catalyst preparation

Cobalt-containing zeolites were prepared from NH_4ZSM-5 by a conventional ion-exchange method. NH_4ZSM-5 was obtained by ion-exchanging HZSM-5 ($SiO_2/Al_2O_3 = 30$, PQ Co.) with 0.5 M NH_4NO_3. Two Co/ZSM-5 samples containing cobalt ions only in cationic positions were prepared by addition of 1 g of NH_4ZSM-5 to 200 ml 0.05 M or 0.1 M solution of cobalt acetate. Before performing the ion-exchange the solutions were stored at room temperature for 2 weeks without adding zeolite and it was found that no precipitate was formed under these conditions. The ion-exchange was performed for 4 days with mixing on a mechanical shaker at room temperature. The resulting products contain 0.92 and 1.50 wt% Co, respectively, which was determined by atomic absorption spectroscopy (Perkin-Elmer 2380 AAS).

Two samples containing some additional amount of cobalt in the form of oxide were prepared analogously. For their preparation 0.4 M cobalt acetate solution was used. It was found that storing of the solution at room temperature for 2 weeks results in formation of cobalt hydroxide precipitate. The first sample was prepared according to the above procedure using 0.4 M cobalt acetate solutions. The cobalt content was found to be 1.90 wt%. The second sample was prepared by repetitive ion-exchange with 0.4 M cobalt acetate solution. Between ion-exchanges calcination was performed at 520°C for 4 h. The cobalt content of this sample was found to be 2.33 wt%.

Hereafter the catalysts thus prepared are denoted as e.g. Co(0.16)/ZSM-5, where the number in parentheses corresponds to the Co/Al ratio calculated on the basis of elemental analysis.

For comparative study a NaHZSM-5 sample of similar ion-exchange level as Co(0.16)/ZSM-6 was prepared by stirring the NH_4ZSM-5 with 0.05 M $NaNO_3$ solution for 24 h at room temperature, followed by thorough washing and calcination at 500°C. The Na content was determined by atomic adsorption spectroscopy and found to be 0.76 wt%, which corresponds to approximately 32% ion-exchange level.

For comparative study a Co_3O_4/SiO_2 sample was prepared by incipient wetness impregnation of SiO_2 (Aldrich, 300 m^2/g) with $Co(NO_3)_2$ solution. The sample was dried at room temperature and calcined at 500°C in air.

2.2. Reaction studies

The catalytic reaction was carried out in a quartz glass tubular reactor in a steady-state plug-flow mode. A temperature programmer was used with a K-type thermocouple installed in contact with the catalyst bed. Prior to the catalytic tests, the samples were calcined overnight with the temperature ramped at a rate of 1°C/min with a hold at 600°C for 2 h in a flow of 20% O_2 in He. The catalysts were preconditioned at each temperature for 30 min before the product analysis was commenced.

The reactant gas mixture in use was obtained by blending four different gases (NO/He, O_2/He, C_3H_8/He, and He), each of them controlled by independent flow controllers. The gases (NO, O_2, and C_3H_8) were all of > 99.9% purity and blended with He (> 99.99% purity) to provide the desired gas mixture. All gases except He were used as received. Helium was passed through liquid nitrogen cold trap to ensure removal of traces of water. The resulting mixtures contained:

(1) 900 ppm of NO and 2% of oxygen for the $NO + O_2$ reaction;

(2) 900 ppm of NO, 1000 ppm of C_3H_8, and 2% of oxygen for SCR of NO;

(3) 1000 ppm of C_3H_8 and 2% of oxygen for the $C_3H_8 + O_2$ reaction.

For the reaction studies 0.23 g of each catalyst was loaded with a total gas flow rate of 230 ml/min, which gave a gas hourly space velocity (GHSV) of 30000 h^{-1}, when a zeolite apparent density of 0.5 g/cm^3 was assumed.

An on-line gas chromatograph (HP 5890, series II) with a thermal conductivity detector and a chemiluminescence NO_x analyzer (Kimoto model 272), equipped with a catalytic converter for conversion of NO_2 into NO, were used for analysis of the effluent gases. A MS-13X column was used for separation of O_2, N_2, and C_3H_8. NO and NO_2 + NO concentrations were measured separately by the NO_x analyzer.

The conversion of NO into NO_2 was calculated by the difference between NO + NO_2 and NO, as determined by the NO_x analyzer. Prior to catalytic measurements the analyzer was carefully calibrated using standard gas mixtures. The conversion of NO into N_2 was determined on the basis of N_2 peak areas obtained by gas chromatography, which were verified using NO_x-analyzer data as a difference between NO_x concentrations (NO + NO_2) before and after reactor. NO_x conversions determined by these two methods were found to coincide with the precision of ±8% (relative) at NO_x conversion below 10%, and with a precision of ±4% at NO_x conversion above 10%. C_3H_8 conversion was calculated by a difference between C_3H_8 concentration in the reaction mixture before and after its passage through the reactor.

2.3. Temperature-programmed desorption

TPD measurements were performed with the same reactor unit as used for the catalytic tests. After the catalytic run, the catalyst was calcined at 600°C in a stream of 10% O_2/He mixture in order to remove carbon deposits. Thereafter, the catalyst was cooled down to room temperature in He flow and the nitric oxide adsorption was carried out by flowing the NO/He mixture through the sample under ambient conditions. After adsorption the catalyst was purged with He flow at room temperature to remove weakly adsorbed nitric oxide. When the nitric oxide level, monitored by the NO_x analyzer, returned to the background level, the sample was heated up to 500°C at a rate of 8°C/min in flowing helium (170 cm^3/min). Desorption of nitric oxide was measured continuously by the NO_x analyzer as a function of temperature–time. The amount of nitric oxide desorbed was obtained by integration of the TPD profiles (desorption rate vs. time).

2.4. Temperature-programmed reduction

Temperature-programmed reduction (TPR) experiments were carried out in an AMI-100 system (Altamira Instruments) with a TCD detector using 5.13% H_2/Ar mixture. The heating rate was 8°C/min and the amount of the sample was 0.2–0.4 g. Prior to the measurements the samples were calcined externally as described in section 2.2. After loading to the TPR reactor the samples were calcined in O_2 flow with the temperature ramped at a rate of 1°C/min with a hold at 500°C for 30 min.

3. Results and discussion

3.1. Activity of the catalysts under study in the NO_2 formation

Fig. 1 presents the temperature dependence of the catalytic activities of HZSM-5, NaHZSM-5, Co/ZSM-5 with various Co loadings, and Co_3O_4/SiO_2 in the formation of NO_2 in the NO + O_2 reaction. Under the experimental conditions used in this study HZSM-5 exhibits fairly high activity in the NO_2 formation. The conversion of NO into NO_2 reaches maximum of 15% at 325°C and then decreases with further increase in temperature. These results are consistent with those reported by Sasaki et al. and Shelef et al. for the NO + O_2 →NO_2 reaction over HZSM-5 [20,21].

Our data indicate that Co(0.16)/ZSM-5 and Co(0.25)/ZSM-5 do not exhibit any appreciable activity in the NO_2 formation (fig. 1). However, HZSM-5 exhibits fairly high activity in NO_2 formation. It was proposed that zeolite acid sites are responsible for this reaction [22]. The cobalt-exchange levels for Co(0.16)/ZSM-5 and Co(0.25)/ZSM-5 are significantly lower than the exchange capacity of the zeolite. Therefore, we can expect that a number of acid sites remain on the zeolite

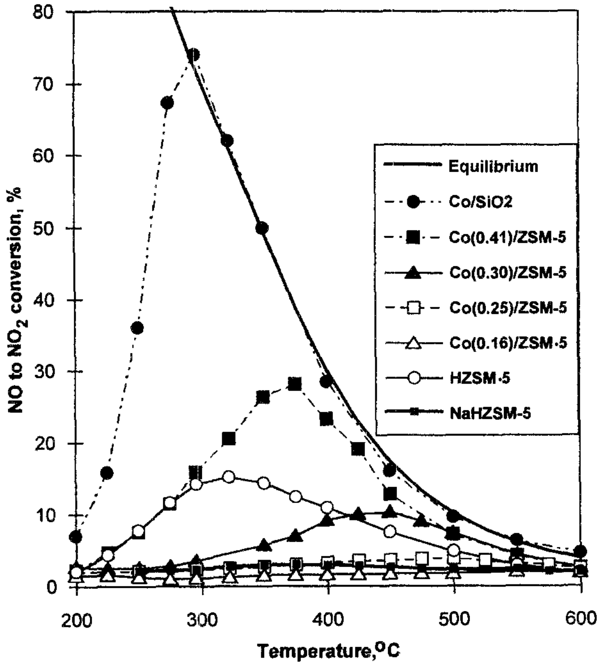

Fig. 1. NO_2 formation during the NO + O_2 reaction over HZSM-5, NaHZSM-5, Co/ZSM-5 with various Co loadings, and Co_3O_4/SiO_2. NO to NO_2 conversion under equilibrium is calculated according to ref. [35].

after ion-exchange and zeolite should exhibit some activity in NO_2 formation after ion-exchange.

To verify this experimental result the activity on partially exchanged NaHZSM-5 in NO_2 formation was studied. These data (fig. 1) also demonstrate that even partial substitution of protons with Na^+ ions almost completely suppresses the ZSM-5 activity in the NO_2 formation. In order to interpret these experimental results it should be noted that the nature of the active sites on HZSM-5 responsible for NO_2 formation was not studied in detail. In general, it was proposed that Brønsted acid sites are active in this reaction. However, many researchers reported the heterogeneity of the Brønsted acid sites on HZSM-5 [23–25]. The activity of different types of acid sites in NO_2 formation was not studied, and the effect of partial ion-exchange on their substitution is also unknown. Our results might be tentatively explained by the assumption that only certain types of the acid sites in HZSM-5 are active in the NO_2 formation, and ion-exchange results in the preferable removal of these sites. However, at present this is only a speculation, and additional studies are needed to clarify the observed phenomenon. Nevertheless, experimental result shows obviously that even partial ion-exchange effectively suppresses the intrinsic ZSM-5 activity in the NO_2 formation.

However, with increasing Co loading Co(0.30)/ZSM-5 and Co(0.41)/ZSM-5 samples begin to show activity in the NO_2 oxidation. The appearance of the activity for these samples may be attributed to the formation of the Co-oxide particles on the zeolite carrier. Indeed, Co oxide was found to be very active in the NO_2 formation (fig. 1). TPR results reveal the appearance of two peaks for these samples at 260°C and above 700°C with a shoulder at 550°C (fig. 2). These peaks were assigned to the reduction of Co-oxide particles and Co^{2+}, respectively [26,27].

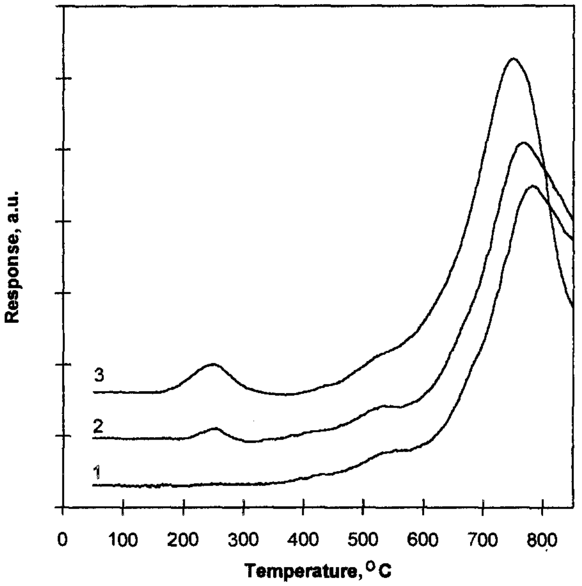

Fig. 2. TPR profiles of Co/ZSM-5 with different Co loadings. (1) Co(0.25)/ZSM-5; (2) Co(0.30)/ZSM-5, (3) Co(0.41)/ZSM-5.

The formation of Co oxide is not astonishing because cobalt acetate exhibits a strong tendency for hydrolysis since it is a salt of a weak acid and a weak base [28]. For the preparation of Co(0.30)/ZSM-5 and Co(0.41)/ZSM-5 the concentrated (0.4 M) cobalt acetate solution was used, which shows a tendency for the formation of cobalt hydroxide (see Experimental section). Therefore, it is conceivable that the sample might contain some amount of cobalt hydroxide. When the resulted material is calcined, the highly dispersed cobalt oxide, or cobalt oxide clusters may be formed, which exhibit activity in the NO_2 formation.

It should be noted, that the TPR profile of Co(0.25)/ZSM-5, which is not active in the NO_2 formation, exhibits only the peak characteristic of Co^{2+} ions and does not exhibit the peak characteristic of Co oxide. Thus we may assume that Co^{2+} ions in the cationic positions of ZSM-5 framework do not contribute significantly to the NO_2 formation, and the NO_2 formation over higher Co-loaded samples might be attributed to the presence of Co-oxide particles.

In this respect it is noteworthy to consider the data on NO adsorption on the catalysts thus prepared. Table 1 discloses the amount of the adsorbed NO and NO/Co ratios obtained from the TPD results. The NO/Co ratio is close to the values reported by Li and Armor [9] and Zhang et al. [29,30], but slightly decreases with the increase in Co loading. Hence, we can suppose that only a minor part of cobalt forms cobalt oxide particles and that these particles are highly dispersed. This is in agreement with the TPR data (fig. 2). Indeed, the peak at 260°C is not very intensive even for Co(0.41)/ZSM-5. A rough estimation of the ratio of the Co existing in the form of Co oxide and Co ions on the basis of the hydrogen consumption shows that only 5–6% of the total amount of the Co exists in the form of Co oxide.

3.2. *SCR activity*

3.2.1. *HZSM-5*

Activities of HZSM-5 catalyst in NO removal and propane conversion under SCR conditions are shown in figs. 3a and 3b, respectively. For the sake of comparison, propane conversion in the absence of NO is also presented therein. As evidenced, the temperature of maxi-

Table 1
The amounts of NO adsorbed on Co/ZSM-5

Co/Al	Co content (mmol/g)	NO adsorbed (mmol/g)	NO/Co
0.16	0.15	0.26	1.67
0.25	0.24	0.39	1.66
0.30	0.29	0.44	1.54
0.41	0.40	0.57	1.43

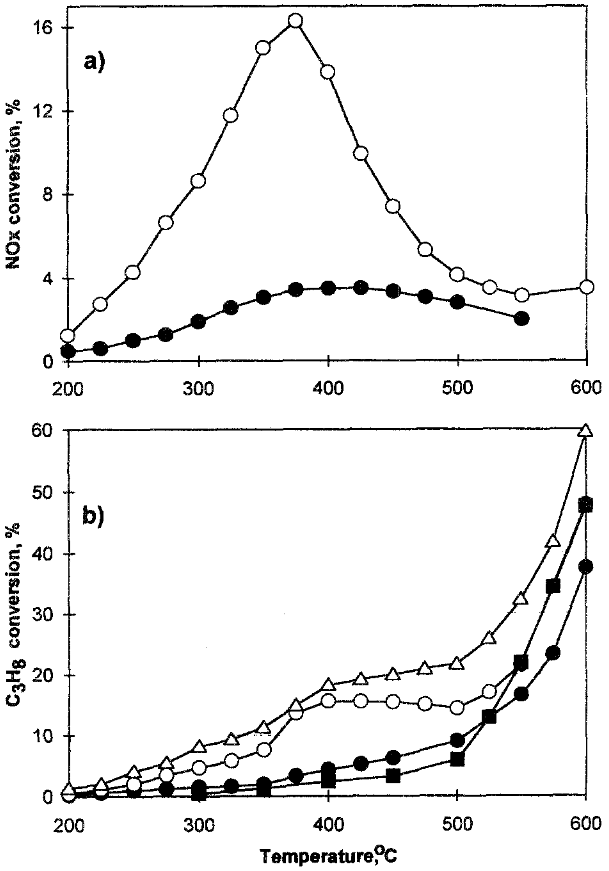

Fig. 3. NO and C_3H_8 conversion over HZSM-5 and NaHZSM-5. (a) NO_x conversion in selective catalytic reduction of NO: (○) HZSM-5,(●) NaHZSM-5; (b) C_3H_8 conversion: (○) HZSM-5, SCR of NO, GHSV = 30000 h^{-1}; (△) HZSM-5, SCR of NO, GHSV = 15000 h^{-1}; (■) HZSM-5, the $C_3H_8 + O_2$ reaction; (●) NaHZSM-5, SCR of NO.

mum conversion (fig. 3a) almost coincides with that for NO_2 formation (fig. 1). NO conversion in SCR reaction increases with increasing yield of NO_2 in the NO oxidation. While NO_2 formation in the NO oxidation passes through a maximum and decreases with increasing temperature (fig. 1), NO conversion in the SCR also declines (fig. 3a). It is noteworthy that NO conversion into NO_2 ($NO + O_2$ reaction, fig. 1) is quite close to the NO conversion into nitrogen under SCR conditions (~ 15 and 16%, respectively).

It is of interest to denote that the C_3H_8 conversion over HZSM-5 under SCR conditions (fig. 3b) follows the similar trend. While in the absence of NO HZSM-5 does not show any appreciable activity at the temperature below 450–500°C, in the presence of NO HZSM-5 shows significantly higher activity in hydrocarbon conversion. The variation of C_3H_8 conversion with the reaction temperature follows the dependence of NO_2 formation on the temperature in the $NO + O_2$ reaction (fig. 1). With increasing NO conversion into NO_2, C_3H_8 conversion increases rapidly. However, while NO_2 formation declines with increasing temperature, a plateau on the C_3H_8 conversion–temperature curve appears, and in the temperature range 400–500°C one can observe even a slight decrease in C_3H_8 conversion. Only at reaction temperatures higher than 500°C C_3H_8 conversion increases. Presumably, this reaction pattern stems from the superimposing two reaction mechanisms, which operate in the presence and the absence of NO. It should be noted that NO reduction with propane over HZSM-5 was studied by Sasaki et al. [21] and Yogo et al. [31,32]; however, they did not observe a plateau on the conversion curve. The possible reason of this discrepancy is the significantly lower flow rate used in their study, $< 2000\ h^{-1}$ versus 30000 h^{-1} used in our experiments. Our results indicate that decrease in flow rate makes the observed plateau less pronounced (see fig. 3b). Besides that, in refs. [21,31,32] the propane conversion was measured with a step of 100°C, which also complicates the observation of the plateau on the C_3H_8 conversion curve.

As it was shown earlier, partial ion-exchange with Na effectively suppresses the NO_2 formation over NaHZSM-5. Interestingly, activities of this sample in the NO_x and C_3H_8 conversion under SCR conditions are also strongly decreased (figs. 3a, 3b), though it possesses a number of acid sites.

The results obtained for SCR of NO over HZSM-5 are in a good agreement with the general viewpoint proposed in refs. [21,31,32] that the NO_2 formation plays an important role for NO reduction over solid acid catalysts. The correlation between NO and C_3H_8 conversion in the SCR of NO and NO_2 formation in the NO oxidation allow us to infer that the first step of the SCR process over HZSM-5 is the formation of NO_2. NO_2 presumably reacts further with hydrocarbon, forming intermediates which eventually produce N_2. Thus, the selective catalytic reduction of NO over HZSM-5 appears to be governed mainly by the NO_2 formation.

3.2.2. Co/ZSM-5

NO conversions in SCR versus reaction temperature are depicted in fig. 4. Interestingly, Co(0.16)/ZSM-5 and Co(0.25)/ZSM-5 that are not active in NO_2 formation (fig. 1) exhibit high activity in the SCR of NO. However, these catalysts show maximum conversion at higher temperature than Co(0.30)/ZSM-5 and Co(0.41)/ZSM-5. The increase in Co loading results in the marked shift of the maximum activity toward lower temperature. This shift is particularly pronounced for Co(0.41)/ZSM-5, which also exhibits relatively high activity in NO_2 formation in the $NO + O_2$ reaction. However, it is necessary to distinguish between the activity gain due to the increase in the Co loading and that due to the NO_2 formation.

In order to do that, the activity in SCR expressed as turnover frequencies (TOF) – the number of nitric oxide molecules converted into N_2 molecules per cobalt cation per second – is compared for the catalysts exhibiting different activity in the NO_2 formation (table 2). If the

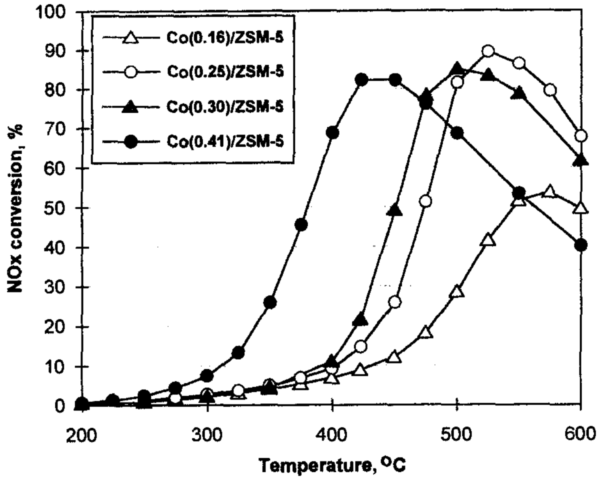

Fig. 4. NO conversion in the selective catalytic reduction over Co/ZSM-5 catalysts with different Co loadings.

activity gain is caused only by increasing Co loading, the TOF values should remain constant for all the catalysts, as it was demonstrated by Li and Armor [9]. Indeed, for Co(0.16)/ZSM-5 and Co(0.25)/ZSM-5, which do not show activity in the NO + O_2 reaction, the TOFs remain essentially constant. However, it is obvious that for Co(0.30)/ZSM-5 and Co(0.41)/ZSM-5 the increase in NO_2 formation strongly enhances the activity in SCR and the TOFs for these catalysts.

This is in a good agreement with the results of other research groups. It was reported that NO_2 is much more active in the selective catalytic reduction of NO_x than NO over the catalysts that are not active in the NO_2 formation [18]. Since cobalt ions themselves appear to be inactive in the NO oxidation, Co-oxide species presumably serve as active centers for NO_2 formation.

As to the possible role of NO_2 as a hydrocarbon activator, it is noteworthy to compare hydrocarbon conversion in the presence and absence of NO over the catalysts that exhibit various activities in the NO_2 formation. Figs. 5a–5d compare propane conversion with NO present in the feed (SCR conditions) and in the absence of NO (conditions of the conventional hydrocarbon combustion) over the catalysts under study. For the catalysts which are not active in NO_2 formation (Co(0.16)/ZSM-5 and Co(0.25)/ZSM-5) addition of NO to the feed does not improve overall propane conversion, and even inhibits it at lower temperature. Probably, for the catalysts which are not active in NO_2 formation NO inhibits C_3H_8 oxidation due to the strong adsorption on the cobalt ions. Fig. 6 displays TPD profiles of NO for some catalysts under study. As can be seen from this figure, NO strongly adsorbs on the Co ions and high temperature is required for NO desorption. These results are consistent with the data reported by Li and Armor [11], and Zhang et al. [29,30]. Moreover, FTIR data reported by Li and Armor [10] indicate that NO adsorbed on Co/ZSM-5 is fairly inactive compared to Cu/ZSM-5. These two factors, probably, cause the inhibitory effect of NO on the C_3H_8 oxidation over the Co/ZSM-5 catalysts that are not active in NO_2 oxidation. However, a detailed discussion of the inhibiting effect of NO is beyond the scope of this paper and will be reported in a forthcoming communication.

Table 2
Turnover frequencies of Co/ZSM-5 for the nitric oxide reduction

Catalyst	TOF (s^{-1} × 1000)	
	400°C	450°C
Co(0.16)/ZSM-5	0.25	0.49
Co(0.25)/ZSM-5	0.24	0.51
Co(0.30)/ZSM-5	0.36	0.78
Co(0.41)/ZSM-5	1.11	1.36

However, for the catalysts which are active in NO_2 formation propane conversion is significantly enhanced in the presence of NO (fig. 5). This effect is very pronounced for Co(0.41)/ZSM-5, which shows appreciable activity in NO_2 formation. For this catalyst, the addition of NO strongly enhances propane conversion within the whole temperature range studied. This result can be explained on the basis of the reaction mechanism proposed by Li and Armor [10]. Adsorbed NO_2 activates hydrocarbon molecule more effectively than oxygen does. This enhances hydrocarbon conversion at lower reaction temperature. Interaction of NO_2 with hydrocarbon may result in the formation of nitro-organic intermediates. Their further transformation leads to nitrogen formation as a final product of the SCR process. Therefore, catalysts showing higher activity in NO_2 formation exhibit activity in SCR at lower reaction temperature (vide supra).

Interestingly, the catalysts that are active in NO_2 formation do not show any color change after SCR reaction. The catalysts that are not active in NO oxidation become darker after reaction, presumably due to carbon deposits. This observation indicates that NO_2 may also play a role as an effective "scavenger" for coke precursors due to its high oxidizing activity.

The data obtained allow us to hypothesize on some aspects of the SCR reaction mechanism over Co/ZSM-5. Our results indicate that NO_2 formation plays an important role in the selective catalytic reduction of NO. In hydrocarbon activation NO_2 is more active than NO. Catalysts active in the NO_2 formation exhibit significantly higher activity for NO and C_3H_8 conversion in the lower temperature region. However, NO_2 formation does not seem to be a necessary step in the SCR of NO. Catalysts that are not active in the NO oxidation exhibit relatively high activity in SCR of NO, albeit at higher reaction temperature. This assumption does not contradict the reaction mechanism that implies the formation of alkyl radicals as a rate-determining step. Alternatives to reaction (1) have been discussed by Lukyanov et al. [13]. It was shown that NO as a stable free radical can

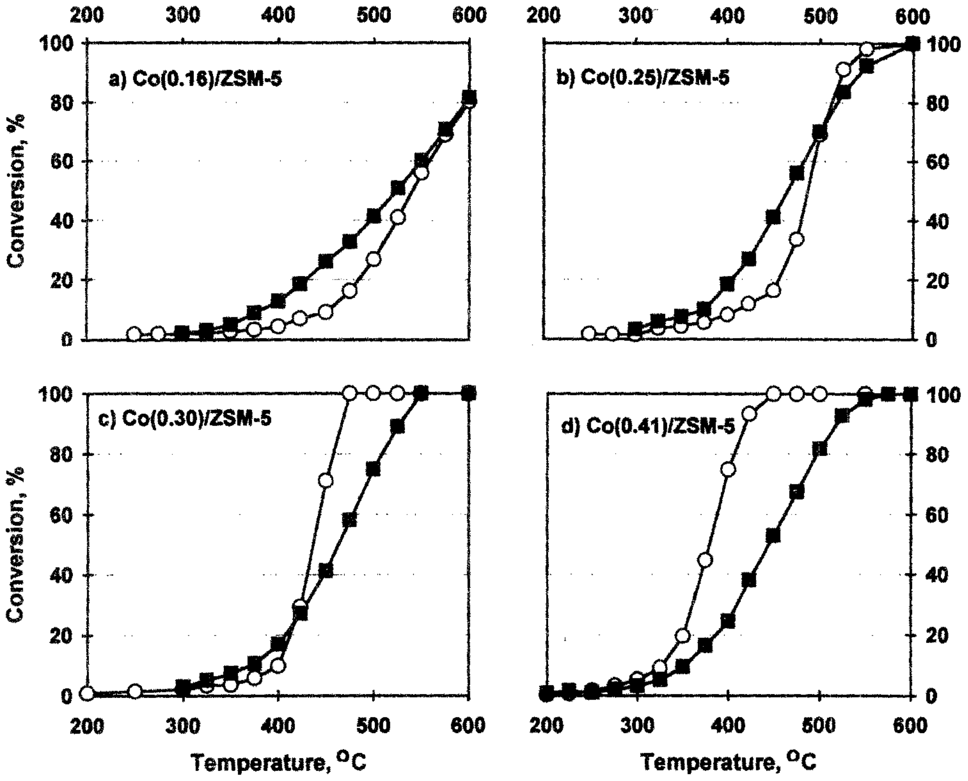

Fig. 5. Comparison of C_3H_8 conversion in the presence and absence of NO over Co/ZSM-5 catalysts: (a) Co(0.16)/ZSM-5; (b) Co(0.25)/ZSM-5; (c) Co(0.30)/ZSM-5; (d) Co(0.41)/ZSM-5. (■) $C_3H_8 + O_2$; (○) $C_3H_8 + O_2 + NO$.

also abstract a hydrogen atom from a hydrocarbon molecule [33]:

$$RH + NO \rightarrow R\bullet + HNO \qquad (2)$$

Another possible route includes the alkyl radical formation via hydrogen abstraction by interaction with an oxygen molecule [34]:

$$RH + O_2 \rightarrow R\bullet + HO_2 \qquad (3)$$

Our results do not show that NO is more active in hydrocarbon activation. For the catalysts that are not active in NO_2 formation (Co(0.16)/ZSM-5, Co(0.25)/ZSM-5) the introduction of NO into the reaction mixture even suppresses the rate of the propane conversion (fig. 5). However, taking into account that the TPD data revealed the high stability and concentration of the NO adsorbed species on the Co/ZSM-5, reaction (2) appears to be more probable. This assumption seems to be feasible, because it was reported repeatedly that NO reduction by hydrocarbons over Co/ZSM-5 is possible even in the absence of oxygen [11,27].

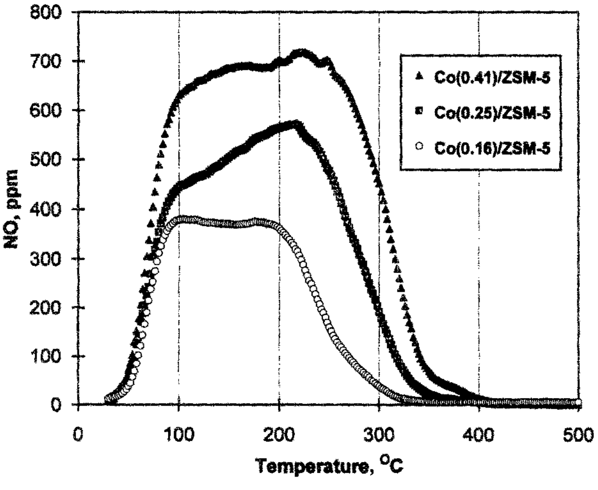

Fig. 6. TPD profiles of NO on various Co/ZSM-5.

4. Conclusion

From the above discussion the following conclusions may be drawn on the catalytic performance of Co/ZSM-5 in the SCR of NO:

(1) For HZSM-5 NO_2 formation appears to be a necessary step in the selective catalytic reduction of NO with hydrocarbons.

(2) Isolated Co ions in cationic positions of the ZSM-5 framework are not deemed to be active in the NO_2 oxidation. However, cobalt oxide particles, formed due to Co-acetate hydrolysis, may serve as centers of NO_2 formation in Co/ZSM-5.

(3) NO_2 formation does not seem to be a *prerequisite* for the selective catalytic reduction of NO by hydrocar-

bons over Co/ZSM-5. Catalysts that are not active in the NO_2 formation also exhibit high activity in the SCR of NO, albeit at higher reaction temperatures.

(4) NO_2 formation definitely improves SCR activity of Co/ZSM-5, particularly at lower reaction temperatures. The NO_2 role presumably involves the efficient activation of hydrocarbons that results in the formation of the reaction intermediates for the SCR process.

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