

Effect of Pretreatments in Various Atmospheres on the Transient DeNO_x Activity of a Cu-MFI Catalyst

C. Gaudin,* D. Duprez,*¹ G. Mabilon,† and M. Prigent†

*Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers, Cedex, France; and

†Institut Français du Pétrole, 92506 Rueil Malmaison, Cédex, France

Received January 27, 1995; revised November 21, 1995; accepted December 28, 1995

Steady-state and transient activities of a 1.47 wt% Cu-MFI (Si/Al = 27) catalyst in the selective catalytic reduction of NO_x with hydrocarbons (HC) were investigated in the 473–723 K temperature range with propene and propane as reducers. Under steady-state conditions (1000 ppm NO + 1700 ppm HC + 5% O₂), propene gives the highest NO conversion at 673 K while propane is a reducer which is much better at 573–623 K. Transient activities were also investigated by comparing the NO conversion in the presence of O₂ after different pretreatments in HC or HC + NO. On the fresh, non-pretreated catalyst, a NO uptake can be observed without any formation of N₂. Reacting the pretreated catalyst with NO + O₂ leads to transient formation of N₂ and CO₂ with the following efficiency of the hydrocarbons: propene > propane. The pretreatment in HC + NO is significantly better than in HC alone and leads to formation of nitrogen-containing species which are further decomposed into N₂ and CO₂, but only in the presence of O₂. These nitrogen-containing species cannot react with NO alone. © 1996 Academic Press, Inc.

INTRODUCTION

Selective catalytic reduction with hydrocarbons (HC-SCR) is at present the purpose of intensive research to develop a catalytic system capable of removing nitrogen oxides (NO_x) from the exhaust gases of diesel and spark ignition lean-burn engines. Due to the large excess of oxygen in the exhaust gases, typical three-way catalysts are inefficient. Although catalysts which are more resistant to sintering and to poisoning and more active at low temperatures are being developed, copper-exchanged MFI zeolite catalyst remains a reference HC-SCR catalyst (1–5). However, the role of the hydrocarbon added as NO reducer is not yet fully elucidated. Some authors have suggested that hydrocarbon removes adsorbed oxygen when the reaction proceeds through NO decomposition (6–8). Different mechanisms of NO reduction have also been proposed in which the hydrocarbon molecule was considered to be a precursor of:

(i) nitrogen-containing compounds formed from NO₂ with an oxidation degree of the N atom greater than 2 (9–11) or from isocyanate or nitrile with an oxidation degree of the N atom smaller than 2 (12–15) (these compounds then decomposed into N₂ and carbon oxides (16, 17));

(ii) more active oxygenated compounds than the starting hydrocarbon (16, 18–20);

(iii) CH_x deposits on the catalyst participating in the NO_x reduction (21, 22).

In the present work, we compare the steady-state activities of propene and propane of a 1.47 wt% Cu-MFI catalyst and examine the relationship between hydrocarbon reactions and NO reduction. A search for possible intermediates has been carried out in the study of steady-state and transient activities in order to investigate the mechanism.

EXPERIMENTAL

The Cu-MFI catalyst was prepared in the conventional way by cationic exchange with a Cu(NO₃)₂ solution on a MFI zeolite of atomic ratio Si/Al = 27. It contains 1.47 wt% copper which corresponds to an exchange level of 79%. Copper dispersion determined by NO thermodesorption amounted to 42% (23).

Catalytic tests were carried out in a dynamic reactor under temperature programmed conditions. The reactant mixture was composed in volume of 1000 ppm NO, 1700 ppm HC (propene or propane), 5% O₂ and as a make-up gas, helium. High purity gaseous components nitrogen oxide (1.5% in He), propene (1% in He), propane (3% in He), dioxygen (10% in He), and helium were obtained from Air Liquide. Gas flow rates were monitored by mass flow controllers.

The experiments were carried out at a space velocity of 10,000 h⁻¹ calculated with respect to the zeolite volume. The catalyst (100 mg portion) was used for the reaction after overnight oxidation in air at 723 K and cooling to 473 K under He flow. Steady-state activity was studied between 473 and 723 K by increasing the temperature in intervals of 20 K.

¹ To whom correspondence should be addressed. Fax: (33) 49 45 34 99.

Continuous analysis of the effluent was performed on-line with three chromatographs: one TCD with a Chrompack molecular sieve 13X column to separate N₂, O₂, CO, a second TCD with an Interchim Porapak Q column to evaluate CO₂ and N₂O (no N₂O was observed in our reaction studies), and a FID with a Chrompack Poraplot Q to separate hydrocarbons from C₁ to C₆. NO conversion and NO₂ formation were determined by coupling the gas outlet to a QMA 120 Balzers quadrupole mass spectrometer. Care was taken to carry out the experiments in such a way as to avoid saturation by helium since this gas was an internal standard for quantification of reactants and products. The background levels for the N₂ and O₂ which were always present were considered in the analysis.

Attempts to detect oxygen- or/and nitrogen-containing compounds have been carried out using mass spectrometry coupled to gas chromatography (GC-MS). Products from the reaction C₃H₆ + NO + O₂ were trapped in liquid N₂ for 1 h, separated on a Chrompack Poraplot Q capillary column with a temperature program from 310 K (5 min) to 510 K (5 K min⁻¹), and detected on an Inco 500 Finnigan quadrupole mass spectrometer.

The reaction mechanism of NO reduction was investigated by means of a transient response method. The influence of three different treatments, HC, HC + NO, and NO + O₂/HC, on NO conversion in the presence of O₂ was studied by step-change experiments. The procedure is described in Fig. 1. For these experiments, 100 mg of catalyst was oxidized under air at 723 K for 1 h and cooled down under He to the temperature of reaction (673 K).

Products and unconverted NO were collected in the QMA 120 Balzers mass spectrometer during the transient reaction test. Results are given as the percentage of NO converted (mass 30 minus the contribution of NO₂), the relative intensities of the N₂ (mass 28 minus the contribution of CO₂) and CO₂ (mass 44) formed. NO₂ formation was also followed (mass 46). By chromatography the absence of CO (mass 28) and N₂O (mass 44) was checked during the NO + O₂ response. Blank experiments were carried out to determine the outlet profiles of NO and HC corresponding

to the purging of the dead volume gas initially filled with pure He.

RESULTS

Steady-State Activity

Figure 2 shows the NO conversion into N₂ and the hydrocarbon conversion into CO and CO₂ in the above-mentioned temperature range studied. Propene displays a slightly better performance (maximum NO conversion of 85% at 638 K for C₃H₆) than propane (80% at 583 K for C₃H₈).

The onset temperature of NO reduction is around 623 K for propene, while for propane the reaction starts at 523 K.

Propene also differs from propane with respect to its temperature of the maximum activity window: propane maintains 80% of NO conversion over a large window from 593 to 723 K, while for propene there is a definite maximum at 683 K. The decrease in activity observed with propene at high temperature could be due to a negative effect of coke (24). Indeed, the catalyst sample after a catalytic test with propene turned dark gray, while like the fresh oxidized catalyst it remained light blue with propane. Under our experimental conditions, the uptake of coke by the catalyst (determined by TPO) reached 200 μmol C/g. Dealumination and sintering involved by steam produced in the reaction could be another cause for the change in color (25). This was unlikely since there was no hysteresis in the activity when the temperature was decreased from 723 to 453 K.

With respect to hydrocarbon conversion, propene shows a rather complex behavior. At low temperature (< 523 K) the hydrocarbon is strongly adsorbed on the catalyst: there is a significant HC disappearance, yet no CO_x product is formed and a negligible NO reduction is noticed. At an average temperature (523 K < T < 573 K), propene begins to be converted by homologation and cracking (Fig. 3) with no NO reduction. NO reduction and HC oxidation both start

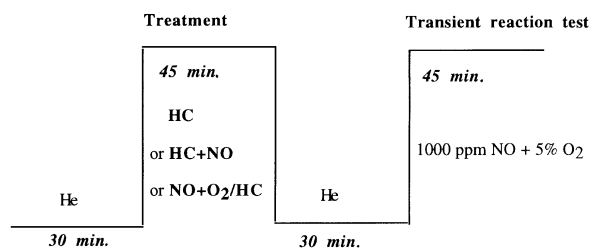


FIG. 1. Conditions of transient activity measurements (673 K, GHSV 10,000 h⁻¹). Pretreatment: 5000 ppm C/45 min (HC) or 5000 ppm C + 1000 ppm NO/45 min (HC + NO) or 1000 ppm NO + 5% O₂/45 min (NO + O₂/HC).

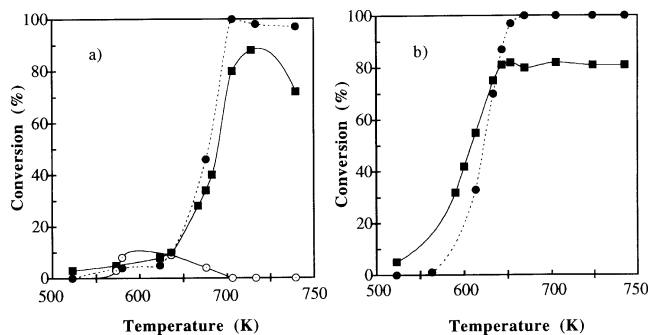


FIG. 2. Conversion of NO into N₂ and conversion of hydrocarbon into CO, CO₂ as a function of temperature over Cu-MFI. (a) GHSV 10,000 h⁻¹; 1000 ppm NO, 1700 ppm C₃H₆, 5% O₂; (b) GHSV 10,000 h⁻¹; 1000 ppm NO, 1700 ppm C₃H₈, 5% O₂.

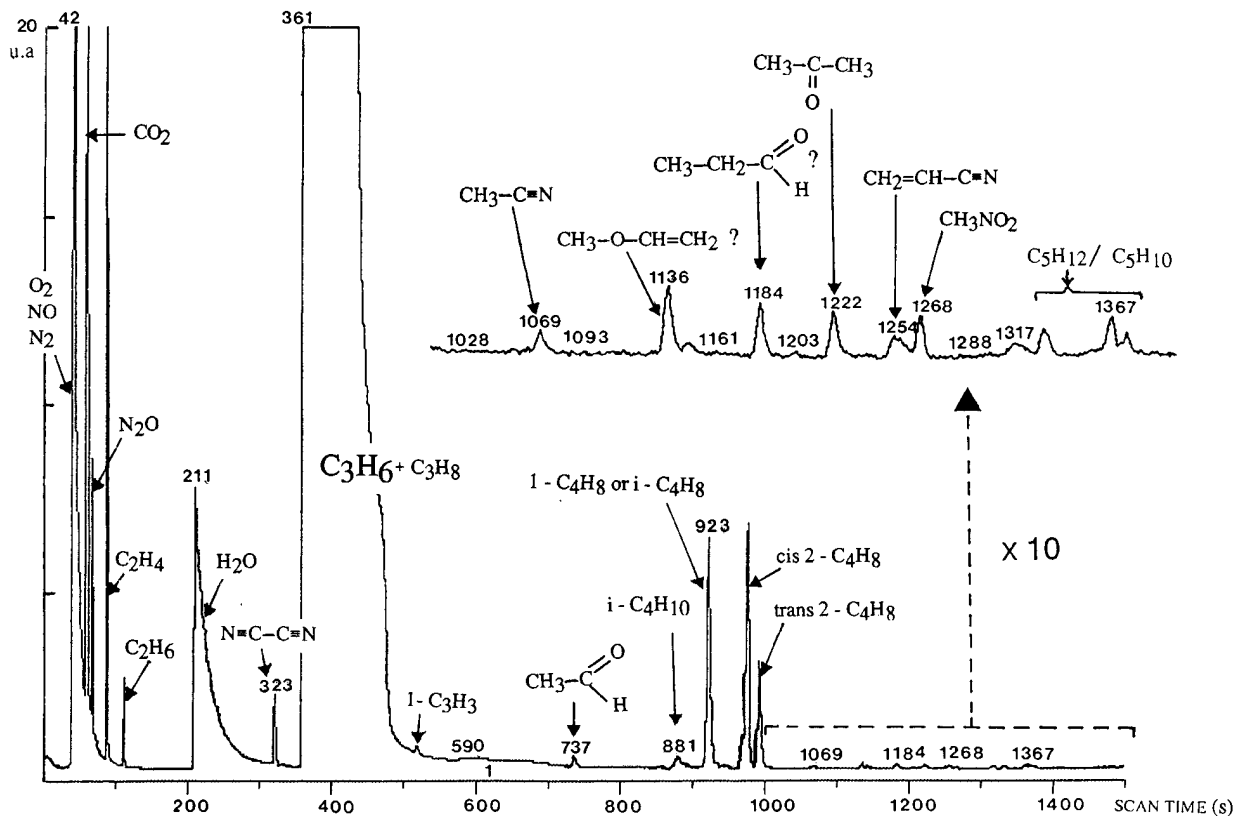


FIG. 3. GC-MS chromatogram of products in $C_3H_6 + NO + O_2$ reaction at 573 K. GHSV $10,000\text{ h}^{-1}$; 1000 ppm NO, 1700 ppm C_3H_6 , 5% O_2 .

at 570 K. A temporary event occurred at about 623 K. Excess of N_2 was formed for 20 min accompanied by a release of CO and CO_2 . It is clear that the excess of N_2 was due to a deposit containing carbon and nitrogen. This transient phenomenon was reported by Hayes *et al.* (14). Nevertheless, as no hysteresis in the activity was found by increasing and decreasing the reaction temperature, the deposit formed at low temperature did not appreciably bias the results obtained with propene.

However, with propane we have a different behavior. Neither retention nor fragmentation of the hydrocarbon are observed at low temperatures. The rise in NO conversion occurs at 523 K accompanied by the beginning of propane oxidation. No CO appears in the gas phase.

Analysis by GC-MS of the products of the reaction with propene at 573 K (Fig. 3) allowed us to detect traces of oxygenated products (acetaldehyde CH_3CHO , acetone $(CH_3)_2CO$, propanal C_2H_5CHO), nitro-products (nitromethane CH_3NO_2), and nitrile products (ethane dinitrile C_2N_2 , acetonitrile CH_3CN , acrylonitrile C_2H_3CN). Higher hydrocarbons (benzene, toluene, xylene, and trimethyl benzene) resulting from aromatization were also detected. At 673 K, minor products were completely oxidized.

We can consider that the three mechanisms quoted in the Introduction for the transformation of the hydrocar-

bons can occur. In order to define the most valid of the three, transient $DeNO_x$ activities of the catalyst have been examined.

Step-Change Experiments

These experiments were carried out in two stages: first there was a pretreatment of the catalyst and then there was the $NO + O_2$ reaction on the pretreated catalyst degassed in helium. Figure 4 shows the change in the gas phase composition during the pretreatment stage of Cu-MFI in $HC + NO$ or HC alone.

There is no definite difference between treatments with propene and with propane. Initially, there was a rapid NO uptake for the two hydrocarbons (2 min) while in the case of propene, HC uptake was longer (12 min) and the initial HC concentration was not recovered. This observation indicates that NO and hydrocarbon uptakes were almost instantaneous. The behavior of propene depended mainly on the zeolite: first there was adsorption, followed by acid catalysis (30% propene conversion at 673 K; see Fig. 5 for the detailed products of cracking and homologation in the $C_3H_6 + NO$ reaction). Very small amounts of cracking and homologation products were observed during treatments with propane (<1% of propane conversion). For

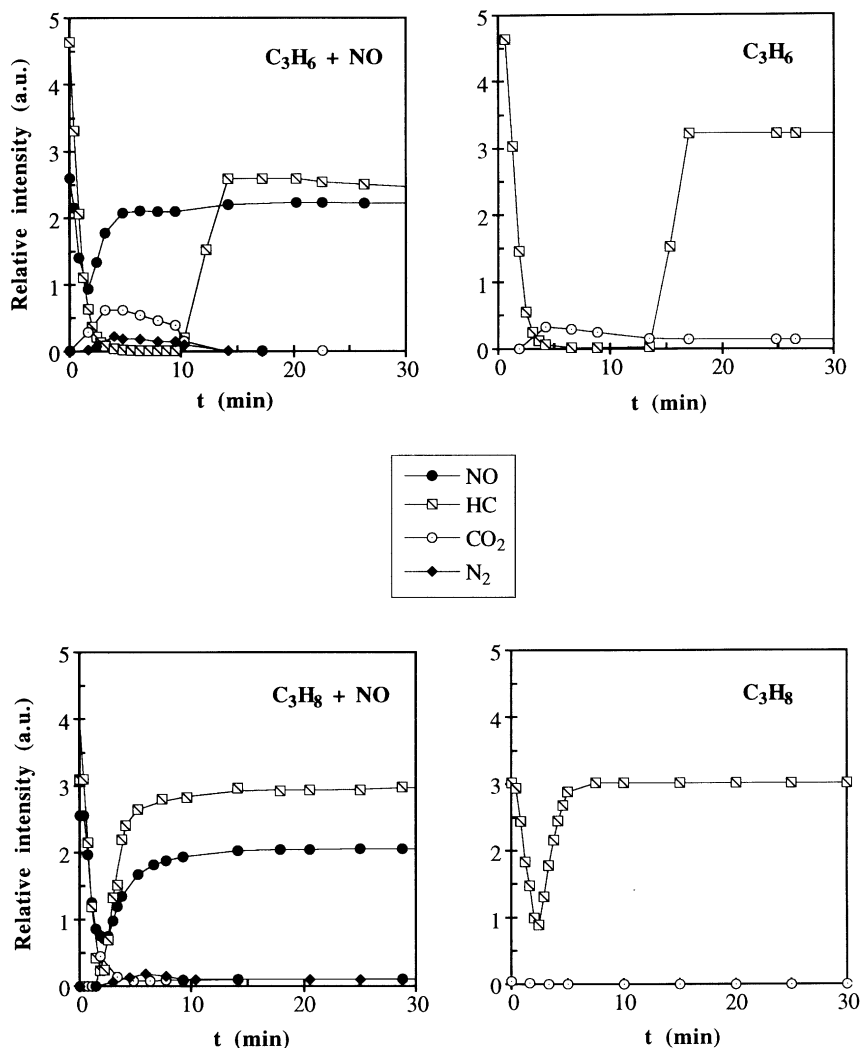


FIG. 4. Evolution of the gas phase composition during HC + NO and HC treatments at 673 K over Cu-MFI as a function of time. At $t=0$ min, the HC or HC + NO gas mixture in the bypass system was introduced to the catalyst which had been flushed with He (the reactor dead volume is subtracted).

both hydrocarbons, a weak activity in NO reduction was noticed during HC + NO treatment.

The effect of treatments by HC, HC + NO, and NO + O₂/HC (Fig. 1) on NO reduction at 673 K from a NO + O₂ reactant mixture is given in Tables 1 and 2 and in Figs. 6 and 7. The fresh oxidized catalyst is inactive in N₂ formation when no HC treatment is carried out (no response at 28 amu in Fig. 7), although we can observe an apparent NO consumption resulting from an immediate NO uptake on the catalyst before NO₂ is formed (Fig. 6). Conversion of NO into NO₂ is around 25%, which accounts for the plateau of NO consumption.

Pretreating the catalyst with either of the two hydrocarbons involves a positive effect on NO reduction in the presence of O₂: N₂ is formed accompanied by release of CO₂ (Fig. 7). With respect to NO consumption, the catalyst is ac-

tive for longer than the untreated catalyst (Fig. 6). This effect is particularly obvious for propene and less marked for propane. The parallelism between CO₂ and N₂ responses indicates that oxidation of the carbonaceous material resulting from the pretreatments is associated with NO reduction. After the transient N₂ and CO₂ formation, NO₂ is formed similarly as in the experiment without treatment with hydrocarbon.

Whatever the kind of treatment used, the order of hydrocarbon reactivity in NO conversion into N₂ in this transient method is C₃H₆ > C₃H₈ and it correlates with the amount of oxidized carbon formed during treatment (Tables 1 and 2). It is clear that carbon deposition is easier with alkenes (26).

Specific indication on the nature of these deposits can be obtained from the effects of the different treatments on NO reduction in the presence of O₂. HC treatments

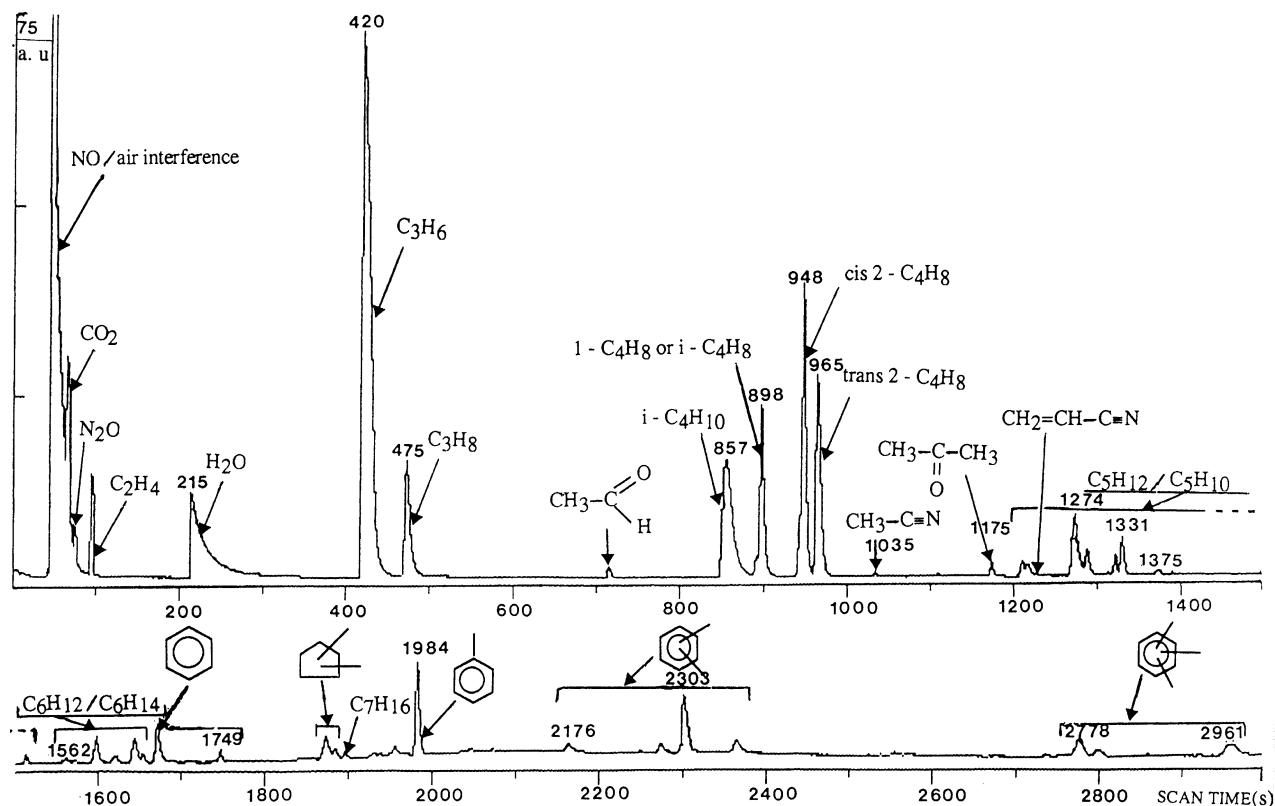


FIG. 5. GC-MS chromatogram of products in $C_3H_6 + NO$ reaction at 573 K. GHSV 10,000 h^{-1} ; 1000 ppm NO, 1700 ppm C_3H_6 , 5% O_2 .

as well as $NO + O_2/HC$ treatments (HC preceded by a sequence $NO + O_2$) give similar N_2 amounts. For both hydrocarbons, the $HC + NO$ treatment is the more favorable for NO reduction. This observation suggests that both gaseous NO and nitrogen-containing species can give N_2 after the $HC + NO$ treatment.

By further experiments we investigated in more detail what happens when the catalyst is treated with $C_3H_6 + NO$ at 673 K (Fig. 8 and Table 3). The presence of nitrogen-containing species is proved when O_2 is injected alone after $C_3H_6 + NO$ treatment, O_2 being the essential agent to acti-

vate these species on which NO alone cannot react (Fig. 8a). Nitrogen monoxide reduction with propene seems to require imperatively these species since the transient activity in the case of $NO(0.1\%) + O_2(5\%)$ introduction does not show a significant conversion of gaseous NO.

Apparently the carbonaceous deposits are poor NO reducers (Fig. 7); it was essential to show that they could play a role in the formation of nitrogen-containing species. When NO is in contact with a catalyst pretreated with C_3H_6 (Fig. 8b), it is not reduced (no N_2 formed) but adsorbs and probably reacts with carbonaceous deposits to form the

TABLE 1

Amounts of N_2 and CO_2 (Per Gram of Catalyst) Formed during Transient Activities of Treated Cu-MFI with C_3H_6 at 673 K

Treatment ^a	Reaction $NO + O_2^b$ formed products	
	N_2 ($\mu\text{mol g}^{-1}$)	CO_2 ($\mu\text{mol g}^{-1}$)
C_3H_6	0.48	4.2
$C_3H_6 + NO$	2.1	5.8
$NO + O_2/C_3H_6$	0.52	5.5

^a GHSV 10,000 h^{-1} ; 1000 ppm NO, 1700 ppm C_3H_6 , 5% O_2 ; treatment time, 45 min.

^b GHSV 10,000 h^{-1} ; 1000 ppm NO, 5% O_2 .

TABLE 2

Amounts of N_2 and CO_2 (per Gram of Catalyst) Formed during Transient Activities of Treated Cu-MFI with C_3H_8 at 673 K

Treatment ^a	Reaction $NO + O_2^b$ formed products	
	N_2 ($\mu\text{mol g}^{-1}$)	CO_2 ($\mu\text{mol g}^{-1}$)
C_3H_8	0.07	1.1
$C_3H_8 + NO$	0.4	0.9
$NO + O_2/C_3H_8$	0.01	1.7

^a GHSV 10,000 h^{-1} ; 1000 ppm NO, 1700 ppm C_3H_8 , 5% O_2 ; treatment time, 45 min.

^b GHSV 10,000 h^{-1} ; 1000 ppm NO, 5% O_2 .

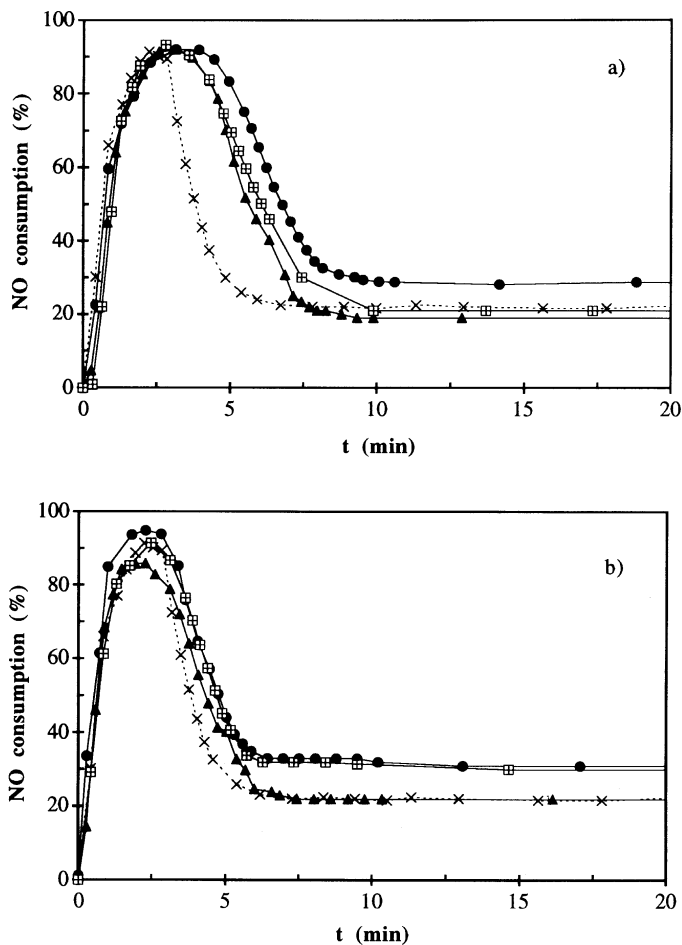


FIG. 6. Transient NO consumption following the introduction of NO + O₂ at 673 K as a function of time over Cu-MFI treated with (a) propene or (b) propane by (▲) HC, (●) HC + NO, (◻) NO + O₂/HC; comparison with the introduction of NO + O₂ at 673 K over the fresh catalyst (×). (The apparent NO consumption in experiment (×) corresponds to the reactor dead volume). Step change procedure as in Fig. 1. Reactant gases: 1000 ppm NO, 1700 ppm C₃H₆ or C₃H₈, 5% O₂, GHSV 10,000 h⁻¹.

same species as those occurring during the C₃H₆ + NO pre-treatment (Fig. 8a): O₂ can in each case decompose these nitrogen-containing species into N₂. After treating the catalyst first with C₃H₆ and with NO (Fig. 8b) the introduction of O₂(5%) leads to the formation of N₂ and CO₂. The same result is obtained after treating with a mixture C₃H₆ + NO (Fig. 8a) except that there is a greater amount of N₂ formed in this case. NO cannot adsorb at 673 K on the fresh catalyst. Therefore, if the treatment by NO precedes the one by C₃H₆ (Fig. 8c), there will be no formation of N₂.

Figure 9 gives a general summary of results obtained in the transient experiments.

DISCUSSION

Our results support the mechanistic hypothesis that the intermediate state of the reducer molecule can be a

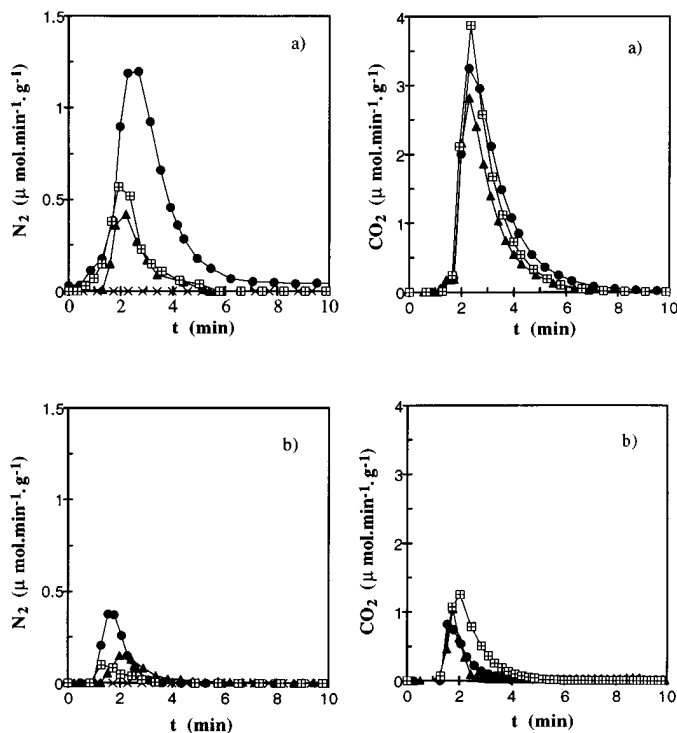


FIG. 7. Transient N₂ and CO₂ formation following the introduction of NO + O₂ at 673 K as a function of time over Cu-MFI treated with (a) propene or (b) propane by (▲) HC, (●) HC + NO, (◻) NO + O₂/HC; comparison with the introduction of NO + O₂ at 673 K over the fresh catalyst (×). Step change procedure as in Fig. 1. Reactant gases: 1000 ppm NO, 1700 ppm C₃H₆ or C₃H₈, 5% O₂, GHSV 10,000 h⁻¹.

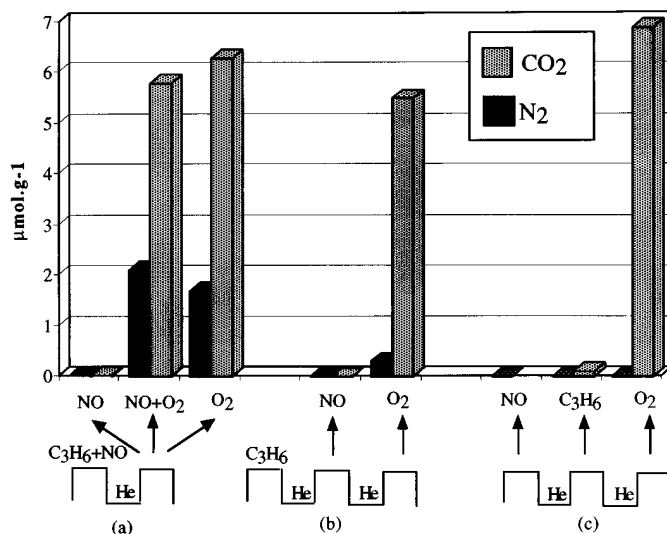


FIG. 8. Relative amounts of N₂ and CO₂ produced in step change experiments over Cu-MFI treated with C₃H₆ + NO and over Cu-MFI treated with C₃H₆ at 673 K. (a) Sequences following C₃H₆ + NO treatment: 1000 ppm NO or 1000 ppm NO + 5% O₂ or 5% O₂. (b) Sequences following C₃H₆ treatment: 1000 ppm NO and then 5% O₂. (c) Sequences following NO treatment: 1000 ppm C₃H₆ and then 5% O₂. Duration of each step was 45 min. Reactant gases: 1000 ppm NO, 1700 ppm C₃H₆, 5% O₂, GHSV 10,000 h⁻¹.

TABLE 3

Amounts of N₂ and CO₂ (per Gram of Catalyst) Formed in Step Change Experiments over Treated Cu-MFI with C₃H₆ + NO and over Treated Cu-MFI with C₃H₆ or NO at 673 K

Treatment ^a	Reaction ^b	Formed products	
		N ₂ (μmol g ⁻¹)	CO ₂ (μmol g ⁻¹)
C ₃ H ₆ + NO	NO	0	0
	or NO + O ₂	2.1	5.8
	or O ₂	1.7	6.3
C ₃ H ₆	NO	0	0
	then O ₂	0.3	5.5
NO	C ₃ H ₆	0	0
	then O ₂	0	6.9

^a GHSV 10,000 h⁻¹; 1000 ppm NO, 1700 ppm C₃H₆; treatment time, 45 min.

^b GHSV 10,000 h⁻¹; 1000 ppm NO, 5% O₂.

nitrogen-containing deposit. The role of carbonaceous material in NO reduction and its nature have been much discussed on the Cu-MFI catalyst. In the case of propene, nitration reaction is one where O₂ is supposed to activate NO to form Cu-NO₂ species (22) or nonadsorbed NO₂ (25) which decompose on carbonaceous material. Another proposition argues that the role of carbon deposits is very small and that the active reducer is propene itself which can be stored in the zeolite network (7). Analysis of deNO_x reaction with propene *in situ* on Cu-MFI by XANES has shown the presence of hydrocarbon species on copper, suggesting the formation of a possible Cu^I-CH_x complex (26). Addition of NO to copper-alkyl species could form *N*-nitroso-*N*-alkylhydroxylamate species (12).

Nitrogen-containing species are beginning to be proposed as possible reaction intermediates. Figure 4 shows that the reaction of NO with HC during the pretreatment stage is very fast so that the formation of CH_xN_y species can

be considered extremely rapid under reaction conditions. Activation of this deposit by O₂ results in the formation of N₂ and CO₂ with propene (Fig. 8) and has also been observed with propane. O₂ is needed to decompose stored nitrogen-containing species resulting from reaction of NO with propene. This has already been shown by Hayes *et al.* (14). Reactions involving nitrogen-containing species could explain the formation of NH₃ and HCN recently reported in the HC-SCR reaction (27, 28). The surface species resulting from the HC + NO sequence could be fulminate (-CNO)-, isocyanate (-NCO)-, and amine (-NH₂)-adsorbed species since such species have been observed by IR in the case of the C₃H₆ + NO reaction on our catalyst (24, 29). Isocyanates and nitriles have already been proposed as possible intermediates located on copper sites and reacting with NO to form N₂, CO₂, and CO (13). Cu(N_xO_y)_z species have been detected recently at the temperature of maximum NO reduction by propene (9).

Correlation between the formation of the surface species and the formation of nitro and nitrile products in the steady-state experiments can be made. The results given in Table 4 and Figs. 3 and 4 emphasize the following points. Nitrile compounds are detected in both C₃H₆ + NO and C₃H₆ + NO + O₂ reactions but their concentration is higher in the presence of O₂ (significant formation of C₂N₂). No adsorbed nitrile compounds have been mentioned. They could be the undesirable side-products from a partial oxidation of -NH₂ species (30) or precursors of active isonitrile species CuN=C (31). The source of oxygenated compounds is not obvious since at this stage of the study, acetaldehyde and acetone were detected as the principal products in both the reactions of C₃H₆ + NO and C₃H₆ + O₂. The concentration of oxygenated compounds was higher in the presence of O₂, indicating that it is unlikely that these latter have the role of intermediates in NO reduction. CH₃NO₂ found in the presence of O₂ is probably the product of C₃H₆ + NO₂ reaction in the gas phase (32).

From the above observations, some mechanisms which have been proposed in the literature can be excluded:

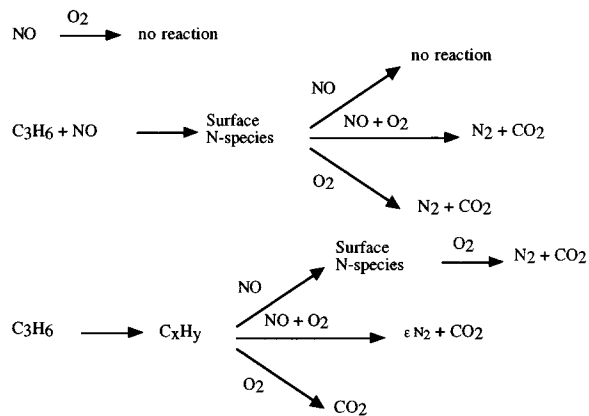


FIG. 9. Results of transient activity experiments of selective NO reduction by propene.

TABLE 4

Relative Intensities of Minor Oxygen- and Nitrogen-Containing Products at the Steady State of C₃H₆ + O₂, C₃H₆ + NO, and C₃H₆ + NO + O₂ Reactions^a at 573 K

	C ₃ H ₆ + O ₂	C ₃ H ₆ + NO	C ₃ H ₆ + NO + O ₂
CH _x O _y ^b	14	4	11
CH _x N _y ^c	0	2	30
CH _x N _y O _z ^d	0	0	1

^a GHSV 10,000 h⁻¹; 1000 ppm NO, 1700 ppm C₃H₆, 5% O₂.

^b GH_xO_y for mainly aldehydes and ketones.

^c CH_xN_y for nitriles.

^d CH_xN_yO_z for nitromethane.

(i) Surface reaction of NO with H₂: Dehydrogenation and coking of C₃H₈ and C₃H₆ on the Brønsted acid sites of the zeolite can produce small quantities of hydrogen. However, the partial pressure of H₂ is extremely low (33). Moreover, in excess of O₂, H₂ is not a good reducer with respect to hydrocarbons (34). Nitrogen oxide reduction by H₂ is most unlikely.

(ii) Surface reaction of NO with CH_x intermediates: As shown by the results of transient activities comparing the effects of HC and HC + NO treatments over the catalyst, the scheme of a direct reactive carbon material cannot be retained. It cannot be accepted in the case of propane whose carbon deposit is low (24). There is rather a surface reaction on NO with CH_x species which leads to the formation of nitrogen-containing intermediates.

(iii) Surface reaction of NO with CH_xO_y intermediates: Our results show that partially oxygenated products do not play a role in NO reduction since their formation depends only on oxygen partial concentration. Moreover, the hypothesis of their role as reaction intermediates is less accepted (7, 22).

Thus the scheme of N-containing species involving NO + hydrocarbon and activated by O₂ appears to be the most appropriate pathway. Among the possible reactive N-containing species, nitro species have been proposed in the recent literature. Nitromethane is known to yield N₂ easily on Cu-MFI (35), Pt/SiO₂ (36), and Ce/ZSM5 (37) in the presence of O₂. On Cu-MFI, the reactivity of nitro species is preferred to direct decomposition of NO₂ in the gaseous phase by hydrocarbon (38). However, the aforementioned adsorbed species (-CNO, -NCO, -NH₂), in which the oxidation state of nitrogen is -III, are most likely to be more reactive with O₂ than nitrogen surface species with a higher oxidation state of nitrogen (-N^{+I}O, -N^{+III}O₂, -N^{+V}O₃). Reactivity of nitro species could be rather due to a transformation to N₂ via an intermediate reacting with O₂: isocyanate species have been proposed as a possible intermediate (37).

The most valid mechanistic scheme in the selective NO reduction by C₃H₆ is summarized in Fig. 10.

The results obtained in steady-state experiments showed that propane was as good a reducer as propene in the reaction of HC + NO + O₂ (Fig. 2). The difference in activity between C₃H₆ and C₃H₈ cannot be explained by a blockage of the active sites by the deposit at low temperature since there is no hysteresis in the activity. Yet very little N₂ was obtained after activating the catalyst pretreated with C₃H₈ + NO with respect to the catalyst pretreated with C₃H₆ + NO (Fig. 7). The most likely hypothesis is that C₃H₈ produces less N-containing intermediates than C₃H₆ but that the intermediates from propane react very fast with O₂ over a large temperature range: complementary GC-MS analysis showed that the N-containing products in the gas phase at the steady-state were in smaller quantities in

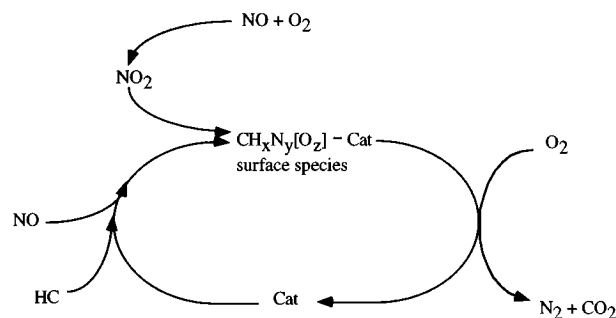


FIG. 10. Mechanistic scheme proposed for the selective NO reduction by C₃H₆.

the gas phase in propane reaction than in propene reaction. This point deserves further studies to elucidate the exact role of the N-intermediates species in selective NO_x reduction with propane.

CONCLUSION

Cu-MFI appears to be quite an effective catalyst for NO_x reduction by propene and propane under oxidizing conditions at about 623 K. With propene, cracking and adsorption reactions occur at low temperatures before NO reduction starts; Cu-MFI is deactivated at high temperatures by coke. Propane is a good reducer even though it does not crack and does not produce carbonaceous deposits.

Investigation of the mechanism by transient HC-SCR activities has shown that a deposition of carbon in the absence of O₂ occurs on Cu-MFI, more abundantly with propene than with propane. This carbon has a definite positive effect on NO reduction only when it is deposited in the presence of NO. Nitrogen-containing surface species are formed between carbon and NO. Oxygen is necessary to decompose these species into N₂ and CO₂; there is no direct reduction of NO with carbon deposits and NO alone is unable to decompose CH_xN_y (or CH_xN_yO_z) species.

ACKNOWLEDGMENTS

This work was carried out under the auspices of the European Community (Contract BRE2-CT 92-0192). C.G. thanks the EC for a grant. We thank C. Canaff for her kind help in GC-MS experiments.

REFERENCES

1. Iwamoto, M., Mizuno, N., and Yahiro, H., *Sekiyu Gakkaishi* **34**, 375 (1991).
2. Truex, T. J., Searles, R. S. A., and Sun, D. C., *Platinum Metals Rev.* **36**, 2 (1992).
3. Konno, M., Chikahisa, T., Murayama, T., and Iwamoto, M., *SAE Techn. Pap. Ser.* 920091 (1992).
4. Iwamoto, M., and Hamada, H., *Catal. Today* **10**, 57 (1991).
5. Held, W., König, A., Richter, T., and Puppe, L., *SAE Techn. Pap. Ser.* 900496 (1990).
6. Li, Y., and Hall, W. K., *J. Phys. Chem.* **94**, 6145 (1990).

7. Burch, R., and Millington, P. J., *Appl. Catal. B* **2**, 101 (1993).
8. Cho, B. J., *J. Catal.* **142**, 418 (1993).
9. Bell, V. A., Feeley, J. S., Deeba, M., and Farrauto, R. J., *Catal. Lett.* **29**, 15 (1994).
10. Beutel, T., Adelman, B. J., Lei, G. D., and Sachtler, W. M. H., *Catal. Lett.* **32**, 83 (1995).
11. Bethke, K. A., Li, C., Kung, M. C., Yang, B., and Kung, H. H., *Catal. Lett.* **31**, 287 (1995).
12. Kharas, K. C. C., *Appl. Catal. B* **2**, 207 (1993).
13. Usiku, Y., Sato, S., Abe, A., and Yoshida, K., *Appl. Catal. B* **2**, 147 (1993).
14. Hayes, N. W., Grünert, W., Hutchings, G. J., Joyner, R. W., and Shpiro, E. S., *J. Chem. Soc. Chem. Commun.* 531 (1994).
15. Radtke, F., Koeppel, R. A., and Baiker, A., *J. Chem. Soc. Chem. Commun.* 427 (1995).
16. Sasaki, M., Hamada, M., Kintaishi, Y., and Ito, T., *Catal. Lett.* **15**, 297 (1992).
17. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **2**, L 17 (1993).
18. Montreuil, C. N., and Shelef, M., *Appl. Catal. B* **1**, L 1 (1992).
19. Bennett, C. J., Bennett, P. S., Golunski, S. E., Hayes, J. W., and Walker, A. P., *Appl. Catal. A* **86**, L 1 (1992).
20. Inui, T., Iwamoto, S., Kojo S., and Yoshida, T., *Catal. Lett.* **13**, 87 (1992).
21. Petunchi, J. O., Sill, G., and Hall, W. K., *Appl. Catal. B* **2**, 303 (1993).
22. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P., *Appl. Catal. B* **2**, 81 (1993).
23. Ensuque, E., Tachon, D., Coq, B., and Figueras, F., private communication.
24. Itri, J. L., and Sachtler, W. M. H., *Appl. Catal. B* **2**, L 7 (1993).
25. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **3**, 239 (1994).
26. Jen, H. W., Otto, K., *Catal. Lett.* **26**, 217 (1994).
26. Liu, D. J., and Robota, H. J., *Appl. Catal. B* **4**, 155 (1994).
27. Poignant, F., Saussey, J., Lavalley, J. C., and Mabilon, G., *J. Chem. Soc. Chem. Commun.*, 89 (1995).
28. Radtke, F., Koeppel, R. A., and Baiker, A., *Catal. Lett.* **28**, 131 (1994).
29. Pieplu, T., Poignant, F., Vallet, A., Saussey, J., Lavalley, J. C., and Mabilon, G., Preprints, 3rd International Congress on Catalysis and Automotive Pollution Control (Brussels, 1994), Vol. 2, p. 387 (U.L.B. Eds.). Brussels, 1994.
30. March, J., in "Advanced Organic Chemistry," 4th rev. ed., p. 1172. Wiley Interscience, New York, 1992.
31. Poignant, F., Saussey, J., Lavalley, J. C., and Mabilon, G., Preprints, 2nd Japan-EC Joint Workshop on the Frontiers of Catalytic Science and Technology for Energy, Environment and Risks Prevention, Lyon-Villeurbanne, Vol. 2, p. 67 (*JECAT Eds.*). 1995.
32. Levy, N., and Scaige, C. W., *J. Chem. Soc.* 1093 (1946).
33. Buckles, G. J., and Hutchings, G. J., *J. Catal.* **151**, 33 (1995).
34. Yamashita, H., Hamada, H., and Tomita, A., *Appl. Catal.* **78**, L1 (1991).
35. Takeda, H., and Iwamoto, M., Preprints, 1st International Congress on Environmental Catalysis, Pisa, p. 49 (G. Centi *et al.*, Eds.). Rome, 1995.
36. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal. B* **4**, L1 (1994).
37. Yasuda, H., Miyamoto, T., and Misono, M., Preprints, 207th A.C.S. Meeting, Div. Petrol. Chem., San Diego, CA, p. 99, (A.C.S., Eds.). Washington D. C, 1994.
38. Chajar, Z., Primet, M., Praliald, H., Chevrier, M., Gauthier, C., and Mathis, F., *Catal. Lett.* **28**, 33 (1994).