Nitrogen dioxide effect in the reduction of nitric oxide by propane in oxidizing atmosphere

Zakaria Chajar [a], Michel Primet [a], Hélène Praliaud [a,1], Michèle Chevrier [b],
Catherine Gauthier [c] and Frédéric Mathis [d]

[a] *Laboratoire d'Application de la Chimie à l'Environnement, Unité Mixte*
CNRS–Université Claude Bernard, 43 Boulevard du 11 Novembre 1918,
69622 Villeurbanne Cedex, France
[b] *Renault Automobiles, Direction Etudes Matériaux,*
92109 Boulogne Billancourt Cedex, France
[c] *Renault Automobiles, Centre de Lardy, 1 allée Cornuel,*
92510 Lardy, France
[d] *Renault Automobiles, Direction de la Recherche, 9-11 Avenue du 18 Juin 1940,*
92500 Rueil Malmaison, France

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The role of nitrogen dioxide in the selective reduction of NO by propane over a Cu-MFI zeolite is investigated. NO_2 and NO reductions were carried out under similar conditions of reaction. In the presence of oxygen, the reduction of NO by C_3H_8 does not differ significantly from that of NO_2. In the absence of oxygen, the reduction of NO_2 by propane occurs with a partial decomposition of the nitric dioxide molecule. Such a decomposition leads to the formation of oxygen, which is responsible for the increase in catalytic activity by comparison with the same reaction performed with NO. NO_2 formed and released in the gas phase during the reduction of NO by propane in the presence of oxygen does not play a predominant role in the catalytic process.

Keywords: nitric oxide; nitrogen dioxide; selective reduction; zeolite; Cu-MFI catalysts

1. Introduction

The selective catalytic reduction of NO_x by hydrocarbons in oxygen-rich atmosphere was reported to occur on copper-ion exchanged ZSM-5 zeolites [1–5], proton-exchanged zeolites [6], alumina and silica–alumina [7], cerium-exchanged zeolite [8], gallium-ion exchanged ZSM-5 [9], metallosilicates [10]. The addition of oxygen to the NO_x–hydrocarbon reactants mixture was necessary to reach high conversion levels. For instance the reduction of nitric oxide by propane in the pres-

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[1] To whom correspondence should be addressed.

ence of copper-MFI catalysts was strongly improved by the introduction of oxygen. Controversy exists concerning the role of the hydrocarbon and oxygen in this selective reduction of NO [11]. The promoting effect of oxygen has been previously assigned to the formation of nitric dioxide in the gas feed, NO_2 being more easily reduced than NO by the hydrocarbon molecule [12–17]. It was also suggested that the partial oxidation of the hydrocarbon leads to the formation of intermediates active in the selective reduction of NO [18,19].

The present paper reports a study of the role of NO_2 in the selective reduction of NO by propane in the presence of a Cu-MFI zeolite catalyst. An experimental study of the oxidation of NO by oxygen into NO_2 in the lines of the apparatus with and without catalyst was conducted as a function of the oxygen and NO pressures and of the flow rate. With the catalyst, a comparison of the reductions of NO and NO_2 by propane in the presence and in the absence of O_2 was performed, i.e., the $NO–C_3H_8–O_2$, $NO_2–C_3H_8–O_2$, $NO–C_3H_8$ and $NO_2–C_3H_8$ systems were studied.

2. Experimental

The parent Na-ZSM-5 zeolite with a Si/Al ratio of 18.9 (unit cell composition $H_{1.1}Na_{3.7}Al_{4.8}Si_{91.2}O_{192}$) (1.5 wt% Na) was hydrothermally synthesized in an autoclave from sodium silicate, aluminum sulphate and tetrapropylammonium bromide as a template. The solid thus obtained was calcined in nitrogen and then oxygen, at 773 K.

The Cu-Na-ZSM-5 sample was prepared according to the method described by Iwamoto et al. [2], by precipitation of a cupric nitrate precursor with ammonia until pH 7.5. The solid was then filtered, washed, dried at 383 K and calcined in oxygen at 773 K. The solid thus obtained contained 3.8 wt% Cu and 0.12% Na.

The catalytic tests were carried out at atmospheric pressure with a fixed bed flow reactor. Streams of $NO–He–C_3H_8–O_2$ were generally mixed outside the reactor at room temperature, but, it was also possible to introduce oxygen near the catalyst bed, i.e. inside the furnace. The flow rates were adjusted using Brooks mass flow controller units. Reactants and products were analyzed every 10 min by gas chromatography using a dual CTR1 column from Alltech (Porapak and molecular sieves) with a thermal conductivity detector for O_2, N_2, CO, CO_2, N_2O and a Porapak column with a flame ionization detector for C_3H_8. NO and NO_2 were analyzed on-line continuously by means of Rosemount infrared analyzers. Helium was used as carrier gas as well as diluent gas.

The calcined solids (100 mg) were diluted with 400 mg of inactive α alumina. In a first step, they were contacted with a mixture C_3H_8 (2000 vpm)–NO (2000 vpm)–He, without oxygen, at increasing and decreasing temperatures between 298 and 773 K, with heating and cooling rates of 4 K min^{-1}. The total flow rate was 10 $dm^3\ h^{-1}$ corresponding to a gas hourly space velocity of 200 000 h^{-1} (density of ca. 2 g cm^{-3} for the zeolitic catalyst). In a second step, at a given temperature, generally 623 K, oxygen was then admitted, the oxygen content varying in the 0.2–10% volume range. Oxygen was introduced either at 298 K, out of the furnace, or at 623 K, near the catalyst bed. The catalytic activities were expressed in percent conversions of NO into nitrogen.

The reaction of NO and oxygen in the lines of the apparatus at room temperature was also studied in the absence of catalyst, as a function of oxygen and NO pressures, total flow rate and temperature of reaction.

3. Results

3.1. OXIDATION OF NO INTO NO_2 WITHOUT CATALYST

NO is known to react with oxygen in the homogeneous phase at room temperature in the pipes of the apparatus, before the reactor and in the exit lines from the reactor [20]. Furthermore, the walls may act as a third body. In our apparatus, at room temperature, NO oxidation was tested in blank experiments by flowing mixtures NO–O_2–He through the system in the absence of catalyst. Table 1 shows that substantial amounts of NO_2 were formed, these amounts increasing with the NO and oxygen contents and decreasing when the total flow rate increases. Furthermore, the oxidation of NO increased with the volume of the apparatus, for instance by increasing the volume of gas mixers, but it was not modified by heating the reactor (without catalyst) between 298 and 773 K.

From a thermodynamic point of view, NO_2 formation from NO and O_2 is unfa-

Table 1
NO conversion into NO_2 in the pipes of the apparatus, at room temperature, in the absence of catalyst, as a function of NO and oxygen contents and total flow rate (NO + O_2 + He mixtures)

O_2 content (vol%)	NO content (vpm)	Flow rate ($dm^3 h^{-1}$)	NO conversion into NO_2 (%)
2	2060	18	5
	2060	10	7
	2060	4	19
	1030	10	3.5
	515	10	2.5
6	2060	18	14
	2060	10	18
	2060	4	38
	1030	10	9
	515	10	5
10	2060	18	19
	2060	10	25
	2060	4	50
	1030	10	13
	515	10	8

vored by an increase in temperature [20]. Nevertheless, NO_2 formation is still possible at 773 K. The ΔG values are equal to −69.39, −8.69 and +6.52 kJ mol^{-1} at 298, 700 and 800 K respectively. Above 773 K, NO_2 formation is limited by thermodynamics, but below 773 K, NO_2 formation is kinetically controlled, the rate of the reaction being a third-order process $d[NO_2]/dt = k[NO]^2[O_2]$.

3.2. REDUCTION OF NO AND NO_2 BY PROPANE IN THE PRESENCE OF OXYGEN AND CATALYST

Fig. 1 shows the conversions of NO into N_2, at 623 K, as a function of the oxygen content up to 10 vol%. The conversion of NO into nitrogen was very low in the absence of oxygen (vide infra): 2% at 623 K, 4% at 673 K and 8% at 773 K. The activity was strongly enhanced by the introduction of oxygen (mixture NO–C_3H_8–O_2–He), reaching 20% for 0.07 vol% O_2 and 97% for 0.5 vol% O_2. For higher oxygen contents, the activity decreased but it was still much higher than in the absence of oxygen (51% for 10 vol% O_2). In addition, the conversion remained high at O_2/C_3H_8 ratios much higher than those corresponding to the stoichiometry required for total oxidation of propane.

The activity decrease (fig. 1) was not due to a catalyst deactivation, but to the decrease in the C_3H_8 partial pressure due to the oxidation by O_2. As a matter of fact, the NO conversion into nitrogen increased with the C_3H_8 concentration, for instance, at 623 K and with 10 vol% O_2, from 35 to 51 and then to 70% with 1000, 2000 and 4000 vpm C_3H_8 respectively.

The main products were N_2, NO_2 and CO_2. The N_2O formation was negligible and propane was completely oxidized into CO_2. The formation of CO_2 followed the

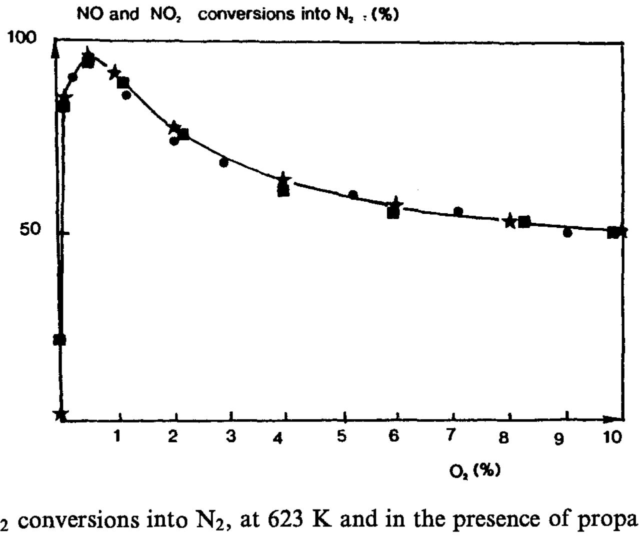

Fig. 1. NO and NO_2 conversions into N_2, at 623 K and in the presence of propane, as a function of the oxygen content, oxygen being introduced at 298 or 623 K. (★) NO conversion, oxygen introduced at 298 K, (●) NO conversion, oxygen introduced at 623 K, (■) NO_2 conversion, oxygen introduced at 298 K.

propane consumption and the NO_2 formation increased with the oxygen content (table 2). This NO_2 formation was lower than in the absence of catalyst (at 623 K, 40% lower in the presence of 10% O_2 and with a flow rate of 10 $dm^3\ h^{-1}$) (comparison of the tables 1 and 2) since the residual NO partial pressure, in the pipes at the exit of the reactor, was lowered by the NO reduction into nitrogen.

For a given oxygen content, the NO reduction into nitrogen reaches a maximum at 623 K (fig. 2). The oxidation of propane into CO_2 increased continuously with the temperature. In the presence of 10 vol% O_2, it began at around 523 K, i.e., at the same temperature as the NO reduction and reached 50% at 601 K and 99% at 623 K.

The conversions of NO and propane were similar whatever the temperature of oxygen introduction, i.e., at room temperature in the pipes of the apparatus well before the catalyst, or at 623 K near the catalyst (fig. 1).

Identical results, NO_x conversion into nitrogen and C_3H_8 conversion (when the O_2 content was equal or superior to 1 vol%), were obtained when NO_2 was substituted for NO (mixtures NO_2–C_3H_8–He) (fig. 1). NO and NO_2 were reduced to N_2 when the propane oxidation proceeded. Even with NO_2 in the feed stream the reduction into nitrogen was enhanced by oxygen introduction, increasing from 23% without oxygen to 96% for 0.5 vol% O_2. With an excess of oxygen (10 vol%) the reduction of NO_2 into nitrogen remained higher (51%) than without oxygen (23%).

3.3. REDUCTION OF NO AND NO_2 BY PROPANE IN THE ABSENCE OF OXYGEN AND WITH CATALYST

In the absence of oxygen, the reduction of NO by propane (mixture NO–C_3H_8–He) was limited: it began at around 573 K, reached 2.5% at 623 K, 11% at 723 K

Table 2
Conversions of NO and C_3H_8, at 623 K, as a function of the oxygen content, in the presence of the catalyst, oxygen being introduced at room temperature in the NO (2000 vpm)–C_3H_8 (2000 vpm)–He mixture

O_2 content (%)	NO conversion (%)		C_3H_8 conversion into CO_2
	into N_2	into NO_2	
0	2	0	4
0.07	20	0	16
0.2	85	0	34
0.5	97	0	64
1	93	0	88
2	77	2	98
4	65	4	99
6	59	6	99
8	55	9	99
10	51	15	99

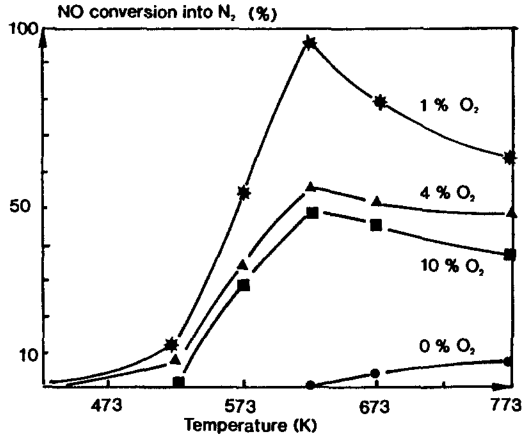

Fig. 2. NO conversion into N_2 by C_3H_8 as a function of the reaction temperature for various oxygen contents, oxygen being introduced at room temperature.

and 21% at 773 K. N_2 and CO_2 were the only products detected.

The reduction of NO_2 by propane (mixture NO_2–C_3H_8–He) was much more efficient than that of NO. It occurred at low temperature (fig. 3) and led to NO, N_2 and O_2 formation. At a temperature as low as 523 K, the overall NO_2 conversion reached 98% (73% into NO and 25% into N_2). At 623 K the conversions into NO and N_2 were 76 and 22% respectively which led to the formation of 1520 vpm NO and 760 vpm O_2. This oxygen formation was directly comparable to the amount of oxygen (0.07%) necessary for the reduction of 20% of NO into nitrogen by propane (fig. 1, table 2).

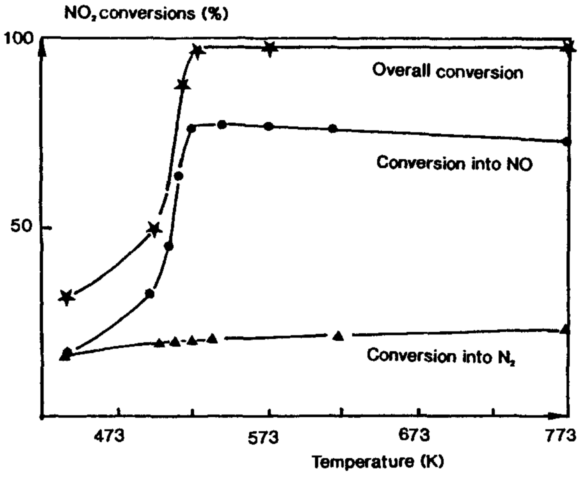

Fig. 3. NO_2 conversions by C_3H_8 as a function of the temperature in the absence of oxygen: overall conversion, conversion into nitric oxide, conversion into nitrogen.

In both cases the oxidation of C_3H_8 led to CO_2 and was more important with NO_2 than with NO: at 623 K the C_3H_8 conversion reached 12% with NO_2 and 4% with NO.

In the absence of oxygen, the reduction of NO_2 by propane is thus explained by the partial decomposition of NO_2 leading to the formation of oxygen which is responsible for the increase in activity.

4. Discussion and conclusion

The present work shows that, in the presence of oxygen, the reduction of NO on Cu-MFI by C_3H_8 does not differ from that of NO_2, in contrast with the study of Iwamoto and Mizuno [21], in which ethene was used as reducing agent. In the literature different behaviors have been reported according to the solid and to the reducing agent [11]. In the SCR process (selective catalytic reduction of NO_x by NH_3), the presence of NO_2 in the feed stream improved the catalytic activity for V_2O_5–TiO_2 and CuO–NiO–Al_2O_3 catalysts, but had a negative effect for Pt/Al_2O_3 solids [22]. The oxidation of NO to NO_2 would play an important role in the case of H-zeolites [15,23,24] but not over Cu-ZSM-5 and Pt/Al_2O_3 [23].

Under our experimental conditions, the reduction of NO_2 and NO is enhanced by the introduction of oxygen. In addition, the conversion is higher in the presence of a large excess of oxygen (10 vol%) than in the absence of oxygen. In this latter case the reduction of NO_2 by propane leads to a partial decomposition into NO and oxygen; oxygen so formed is thus responsible for the increase in activity. From these results it is concluded that the formation of NO_2 in the pipes of the apparatus at room temperature does not explain the promoting effect of oxygen in the reduction of NO by propane. Either NO or NO_2 are reduced when the oxidation of propane proceeds. The first step would be a partial oxidation of propane followed by reaction with NO or NO_2. The role of oxygen may be also to keep the catalyst clean [13,25] and (or) to prevent excessive reduction of Cu^{2+} [13]. Even if the formation of NO_2 in the gaseous phase does not play a predominant role, we cannot rule out mechanisms involving NO_2-containing species on the catalyst surface [17,26,27].

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