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Catalysis Today 137 (2008) 157–161

CATALYSIS TODAY

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Methanol interaction with NO_2: An attempt to identify intermediate compounds in CH_4-SCR of NO with Co/Pd-HFER catalyst

S. Capela [a,b], R. Catalão [a], M.F. Ribeiro [a], P. Da Costa [b], G. Djéga-Mariadassou [b], F. Ramôa Ribeiro [a], C. Henriques [a,*]

[a] IBB-Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Avenida Rovisco Pais 1, 1049-001 Lisboa, Portugal

[b] Université Pierre et Marie Curie, Laboratoire de Réactivité de Surface, CNRS UMR 7609, 4, Place Jussieu, Case 178, 75252 Paris, France

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Abstract

The objective of this work is the study of fundamental common aspects of NO_x catalytic reduction over a Co/Pd-HFER zeolite catalyst, using methanol or methane as reducing agent. Temperature Programmed Surface Reaction (TPSR) studies were performed with reactant mixtures comprising NO_2 and one of the reducing agents.

The formation of formaldehyde was detected in both studied reactions (NO_2–CH_4 and NO_2–CH_3OH) in the temperature range between 100 and 220 °C. At higher temperature, when the NO_x reduction process effectively begins, formaldehyde starts to be consumed.

Using methanol as reducing agent, nitromethane and nitrosomethane, are detected. At 300 °C these species are consumed and cyanides and isocyanides formation occurs. On the contrary, with methane, these last species were not detected; however, there are strong evidences for CH_3NO and CH_3NO_2 formation.

Thus, using methanol or methane, similar phenomena were detected. In both cases, common intermediary species seem to play an important role in the NO_x reduction process to N_2.

These results suggest that methanol can be considered as a reaction intermediate species in the mechanism of the reduction of NO_2 with methane, over cobalt/palladium-based ferrierite catalysts.

Keywords: NO_x; Methane; Methanol; CH_4-SCR mechanism

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1. Introduction

The use of oxygenated compounds as reducing agent (e.g. methanol) for the selective catalytic reduction of NO_x has both practical and academic importance: (i) methanol has been deeply studied as a transportation fuel because it is readily available from the conversion of coal and natural gas; (ii) studying the fundamental aspects of the NO_x reduction with methanol, can provide information for the understanding of the mechanism CH_4-SCR of NO_x.

Activation of methane represents an intensely challenging problem due to its refractory nature [1]. Selective oxidation of methane with O_2 and NO_2 has been shown to give a variety of oxygenated (mainly methanol and formaldehyde) products [2]. Studies performed by Tabata et al. [2] and Otsuka et al. [3] showed that the yield of oxygenated compounds detected during methane oxidation by NO_2 is very low. So, even if methanol is much more reactive than methane and parallel reactions can occur, an attempt can be made to try to identify ‘‘common’’ species, resulting from the reaction between NO_2 and the reducing agent, in the SCR of NO that will further decompose, leading to N_2 formation.

Metal-exchanged zeolite catalysts are known to be active in the SCR of NO_x by hydrocarbons [4–10].

NO_2 is widely accepted as the nitrogen oxygenated compound that really interacts with hydrocarbons in HC-SCR suggested mechanisms [11–13].

Literature reports different mechanistic hypotheses concerning NO_x-SCR, involving several types of intermediates that can result from the decomposition of reactive adsorbed species.

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* Corresponding author. Tel.: +351 218417325; fax: +351 218419198.
E-mail address: carlos.henriques@ist.utl.pt (C. Henriques).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.11.048

According to several authors [3,11,14,15], *R-NOx* species, are the first intermediates originated from the interaction between NO_2 and the reducing agent that decompose into mild oxygenated compounds and NO. This NO will be further reduced into N_2. The oxygen left on the surface is removed by reacting with the oxygenated species previously formed [11,14,15]. On the contrary, other authors defend that isocyanates (–NCO) and cyanates (–CN) are the main products resulting from the organo-nitro compounds decomposition [16]. Several studies conclude that the decomposition of these intermediates also leads to N_2 formation [16,17].

The tests performed in this work, using Co/Pd-HFER catalyst, are assembled in two different sets: the first one corresponds to the reduction of NO_2 in the presence of MeOH, performed under TPSR conditions (3000 ppm NO_2 and 3000 ppm CH_3OH in He). The second one corresponds to the TPSR run performed with CH_4 as reducing agent (3000 ppm NO_2 and 3000 ppm CH_4 in He). Methanol was chosen as reducing agent, in order to clarify the role of oxygenated compounds, formed by the interaction NO_2–CH_4, as intermediates in the mechanism of NO_x reduction to N_2, over Co/Pd-HFER catalysts.

2. Experimental

2.1. Catalysts preparation

The NH_4-FER form was prepared by ion-exchanging NaK-FER (obtained from TOSOH Co., Japan; Si/Al = 9) at 80 °C for 3 h, 3 times, with a 4.0 M NH_4NO_3 solution, under strong agitation. After the exchange, the catalyst was washed with deionised water and dried at 100 °C for 12 h. Co-HFER was obtained the by ion-exchanging the NH_4-FER form with a 0.05 M $Co(CH_3COO)_2$ (Fluka) solution in order to obtain 3% (wt.%) Co. The ratio between the volume of solution and the catalyst weight (v/w) was equal to 50. The ion-exchange occurred at 80 °C during 24 h, under a strong agitation. The catalyst was then washed with distilled water and dried at 100 °C for 12 h. This procedure was followed by calcination at 500 °C (3 h) under air flow (4 L h^{-1} g^{-1}) with a heating rate of 5 °C min^{-1}. Co/Pd-HFER catalyst was then, prepared by ion-exchanging the Co-HFER catalyst with the required amount of a solution of $Pd(NH_3)_4(NO_3)_2$ (Aldrich) in order to obtain a value of 0.3 (wt.%) Pd. The exchange occurred at RT during 2 h under a strong agitation. The catalyst was washed with distilled water and dried at 100 °C for 12 h. Then it was calcined at 450 °C (8 h) under air flow (4 L h^{-1} g^{-1}) with a heating rate of 1 °C min^{-1}.

2.2. Catalytic tests

Catalytic runs were carried out in a U-type quartz reactor, under Temperature Programmed Surface Reaction conditions (TPSR). The sample (170 mg) was held between plugs of quartz wool and the temperature was monitored through a Eurotherm temperature controller using a K-type thermocouple. The total flow rate was 250 mL min^{-1} corresponding to a space velocity (GHSV) of 45,000 h^{-1}. The sample was pre-treated in flowing argon from room temperature (RT) to 500 °C (5 °C min^{-1}) and kept at 500 °C for 1 h. After catalysts reach room temperature, they were submitted to different gas mixtures with $[NO_2] = [CH_3OH]$ or $[NO_2] = [CH_4] = 3000$ ppm in flowing He. These TPSR experiments were performed with a heating rate of 5 °C min^{-1}. The reactor outflow was continuously analysed using a combination of four different detectors. A Thermo 42C high level chemiluminescence NO_x analyser allowed the simultaneous detection of NO, NO_2 and NO_x. An Ultramat 23 IR analyser was used to monitor CO and CO_2. A Pfeiffer Omnistar mass spectrometer was used to follow the *m*/*z* signals sensible to the system perturbation: CH_4 ($m/z = 16$), H_2O ($m/z = 18$), HCN ($m/z = 27$), N_2/CO ($m/z = 28$), HCHO ($m/z = 29$), CH_3OH ($m/z = 31$) –NCO ($m/z = 42$), CH_3NO ($m/z = 45$), CH_3NO_2 ($m/z = 61$).

3. Results and discussion

3.1. NO_2 catalytic reduction with methanol

In Fig. 1a it is possible to verify that, when the mixture containing NO_2 and methanol contacts the catalyst, both compounds adsorb from RT until 70 °C. At 100 °C, NO_2 reaches the desorption maximum and NO formation is also verified. At about 220–240 °C a second maximum of NO formation and the second peak of NO_2 desorption are reached simultaneously. It must be pointed out that from about 130 °C until the end of the run, NO_x concentration is always below 3000 ppm; a minimum in the NO_x curve is attained at 160 °C. Almost simultaneously with this NO_x consumption, CO formation peak occurs (Fig. 1b).

N_2 formation was checked by following the $m/z = 28$, by mass spectroscopy; this fragment also corresponds to CO: thus, the identification of N_2 in this run is substantially made difficult by the presence of CO in the MS analysed gas mixture. Following $m/z = 28$ (Fig. 1c), it is possible to detect three peaks that correspond exactly to the peaks of CO formation (detected by an IR detector). However, the evolution of CO (Fig. 1b) and $m/z = 28$ (Fig. 1c) curves with the temperature are quite different between 190 and 300 °C: CO formation decreases until 280 °C (Fig. 1b) and, by the contrary, $m/z = 28$ constantly increases (Fig. 1c).

The CO formation can result from the reaction between NO_2 and methanol as described by the following global process:

$$2CH_3OH + 2NO_2 \leftrightharpoons N_2 + 2CO + 4H_2O \tag{1}$$

At higher temperatures ($T > 190$ °C), besides CO, also CO_2 formation takes place and NO_x is totally consumed (Fig. 1b) accordingly to a second global reaction:

$$CH_3OH + 3NO \leftrightharpoons CO_2 + 3/2N_2 + 2H_2O \tag{2}$$

Thus, we consider that there is strong evidence that, in this temperature range, the methanol assisted NO_x reduction, leading to N_2 formation, predominates.

At 340 °C, no NO_x is detected (Fig. 1a). Simultaneously, a maximum of CO_2 is observed. In this temperature range,

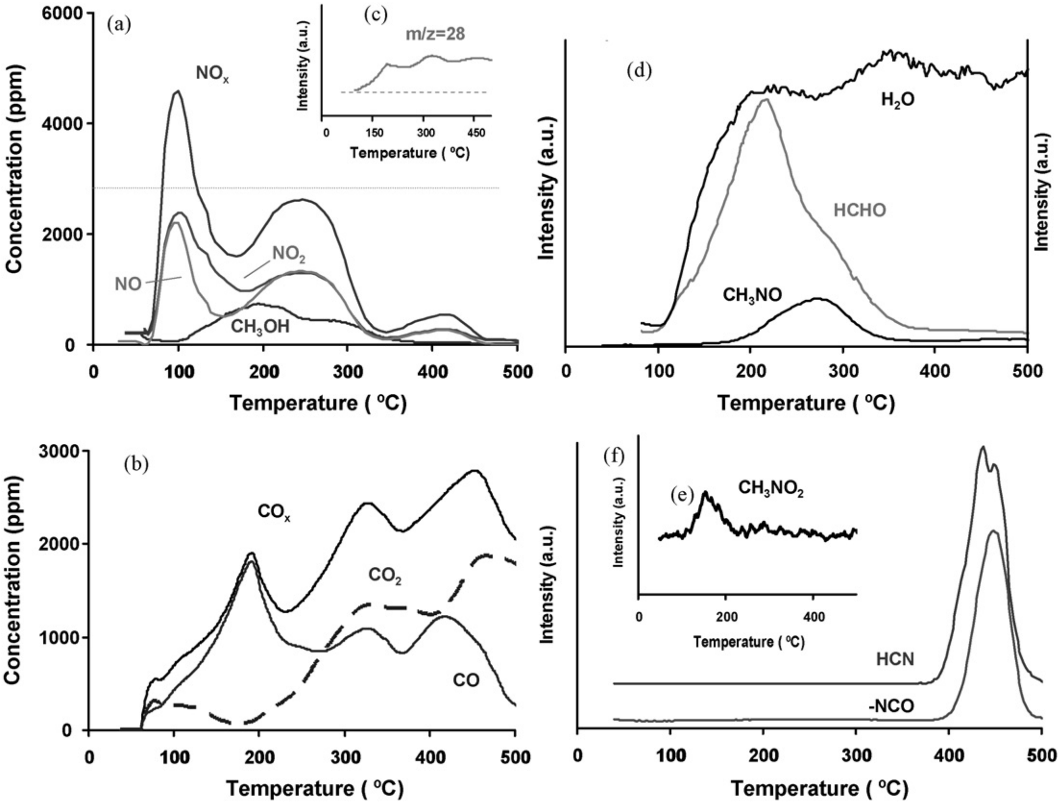


Fig. 1. TPSR profiles with 3000 ppm NO_2 and 3000 ppm CH_3OH in He; total flow of 250 mL min^{-1}; GHSV = 45,000 h^{-1}: (a) NO_x, NO, NO_2 and CH_3OH; (b) CO_x, CO_2 and CO; (c) N_2 (m/z = 28); (d) HCHO, H_2O and CH_3NO; (e) CH_3NO_2; (f) HCN and –NCO fragment evolution profiles.

besides reaction (1), the interaction between NO (present in the reaction mixture – Fig. 1a) and CH_3OH can also occurs. This fact is in accordance with the results obtained with a TPSR performed with NO and CH_3OH (figure not shown), where NO consumption due to the presence of this oxygenated is already possible at 340 °C. The amount of CO and CO_2 produced at 340 °C (CO_x = 2600 ppm), corresponds to the exact quantity of NO_x converted. Moreover, it is possible to verify that from

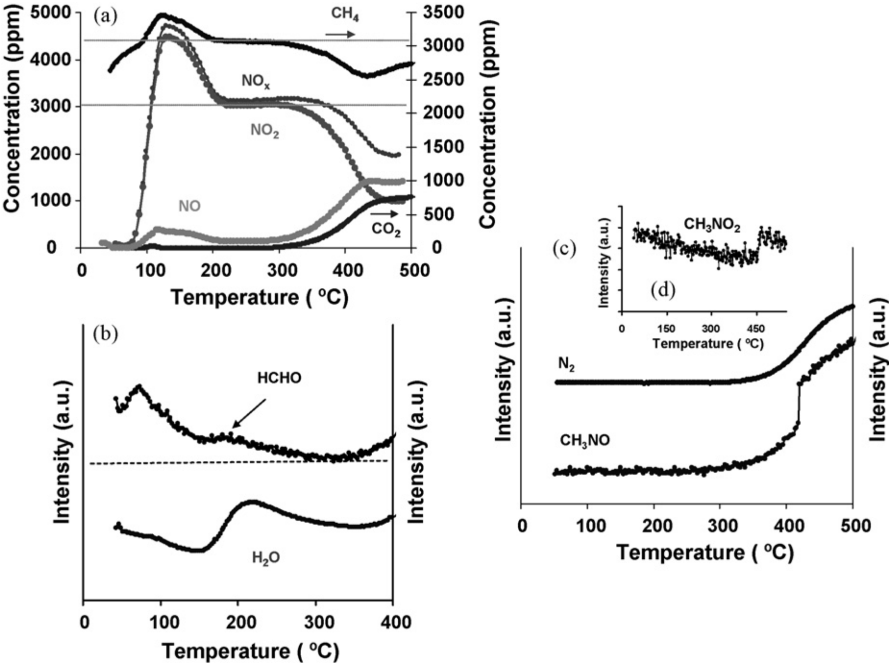


Fig. 2. TPSR profiles with 3000 ppm NO_2 and 3000 ppm CH_4 in He; total flow of 250 mL min^{-1}; GHSV = 45,000 h^{-1}: (a) NO_x, NO, NO_2, CH_4 and CO_2; (b) HCHO and H_2O; (c) CH_3NO and N_2; (d) CH_3NO_2 evolution profiles.

190 °C, CO formation increases and CO_2 formation also takes place. This means that both global reactions mentioned before occur simultaneously. Nevertheless, it is clear that, from 280 °C, the second global reaction (2) takes advantages toward the first one (1). This can be explained, both by a greater activation energy of reaction (2) and by the increasing concentration in NO, as the temperature increases.

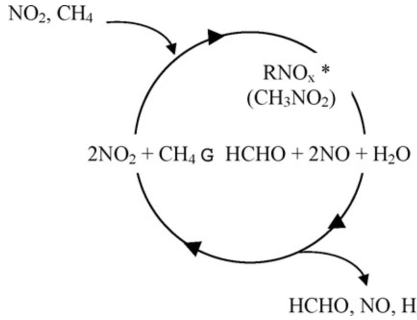
By mass spectroscopy (Fig. 1d) it was possible to detect HCHO and H_2O formation from 100 °C. Formaldehyde reaches its maximum at 220 °C, being further totally consumed. Comparing the results presented in Fig. 1a and d, it is possible to verify that NO (after the second maximum) and HCHO are simultaneously consumed. At 340 °C, a total NO_x consumption occurs and no more formaldehyde is detected in the mixture leaving the reactor. The detected formaldehyde can be formed by the partial oxidation of methanol by NO_2 described by the following reaction:

$$CH_3OH + NO_2 \leftrightarrows NO + HCHO + H_2O \qquad (3)$$

However, NO and HCHO evolution does not present the same behaviour:

1. NO release is observed from RT and HCHO detection only occurs from 100 °C: this can be explained by the fact that HCHO, at low temperatures, can remain adsorbed on the catalyst, as it was verified in IR tests (figure not shown); the formation of NO in this low temperature range can be associated with the dissociative adsorption of NO_2 on metal sites with the formation of $O_{(ads)}$ species or by interaction of NO_x with the zeolite structure;
2. above 100 °C, NO_2 consumption increases with simultaneous CO formation that reaches its maximum at 190 °C. At this temperature, the amount of CO formed (2000 ppm) exactly corresponds to the amount of NO_2 consumed (Fig. 1a), accordingly to global Eq. (1). Moreover, formation of HCOH increases and reaches a maximum at 220 °C;
3. between 220 and 340 °C, NO and HCHO consumption occurs (Fig. 1a and d) and, simultaneously, the formation of N_2 can be detected (Fig. 1c). This result can be interpreted assuming that formaldehyde can act as an intermediate in N_2 formation, by regenerating the active sites involved in NO dissociation process.

In this catalytic run, it was possible to verify the formation of different nitrogen containing organic compounds. Fig. 1e shows that, until 200 °C, there are evidences for CH_3NO_2 formation that probably further react to give CH_3NO (Fig. 1d), who is maximum of formation is observed at 275 °C. This transformation of CH_3NO_2 into CH_3NO has been also suggested by other authors [18]. From 400 °C, there are also evidences of HCN and –NCO fragments (probably HNCO) formation (Fig. 1f). From 450 °C, total NO_x conversion occurs.



Scheme 1. Intermediate products resulted from NO_2–CH_4 interaction [11,19].

3.2. Reduction of NO_2 with CH_4

Keeping constant the ratio NO_2/reducing agent = 1, a TPSR with 3000 ppm of NO_2 and 3000 ppm of CH_4 was performed, in an attempt to further compare with the catalytic runs performed in the presence of CH_3OH.

Observing Fig. 2a, NO_2 adsorbs from RT until 80 °C, reaching a desorption maximum at 130 °C. Observing methane evolution, from room temperature until 130 °C, an adsorption/desorption can be detected at low temperature, which involves the interaction NO_2–CH_4 (methane alone does not adsorbs on the catalyst surface). NO_2 reaches the maximum of desorption at 130 °C, when methane starts being consumed by reacting with NO_2. From this interaction results NO, formaldehyde and H_2O as it was detected by mass spectroscopy at 120 °C (Fig. 2b). This phenomenon was already observed in our previous work [19] and described according to Scheme 1. However, HCOH formation is much less evident than in methanol runs. In contrast to methanol, methane is very difficult to activate. At 120 °C, the amount of methane that reacts with NO_2 is very low, limiting the HCHO production, which can explain its weak formation. From 300 °C the NO reduction process already takes place (NO_x curve above 3000 ppm line) and formaldehyde presumably totally reacts following the N_2 formation mechanism [11]. At 300 °C the formation of CO_2 and N_2 occurs simultaneously (Fig. 2a and d). At 480 °C there is about 30% of NO_x conversion, which is inferior to that obtained with methanol.

Fig. 2c and d also evidence that from 450 °C, the NO_x consumption is accompanied by CH_3NO and CH_3NO_2 (small

Table 1
Resume of catalytic performance of Co/Pd-HFER during TPSR conditions using CH_3OH and CH_4 as reducing agents

Reducing agent	Minimum temperature of NO_x conversion (°C)	NO_x conversion 500 °C (%)	N_2 select. 500 °C (%)[a]	HCHO formation (°C)	HCN and –NCO formation (°C)
CH_3OH	130	100	45	220–340	400
CH_4	300	30	100	120–290	–

[a] N_2 selectivity $= \frac{N_2\ \text{formed}}{2NO_2\ \text{reacted}}$.

amount) formation, but no iso-cyanate or cyanide species were detected.

4. Conclusion

Co/Pd based zeolites are known to be very effective catalysts for the CH_4-SCR of NO_x. However, in the literature, very few information concerning the catalytic performance of the studied system is available, when methane is replaced by methanol. According to the present results, Co/Pd-HFER catalyst is very active for SCR of NO_x with methanol (Table 1). Steady-state tests performed with both reductants indicate that, under the studied reaction mixtures, catalyst behaviour is constant even at high temperature. Furthermore, it was found that both reducing agents lead to the formation of common intermediate species.

In the low temperature range, HCHO formation is detected and its participation in the NO reduction process was demonstrated. This species results from the interaction: NO_2–CH_3OH and NO_2–CH_4. From this interaction, and besides HCHO, there is also NO formation. Using methanol, it was possible to detect several R–NO_x compounds that can lead, in several steps, to N_2 formation. With methane, CH_3NO_2 was also identified in the high temperature range.

This study allowed confirming the existence of several common aspects in the reaction of NO_2 with methane and methanol. However, other complementary techniques are needed for a deep understanding of the studied mechanisms. An *operando* IR study is under progress, in order to get further information concerning the identification and role of the intermediate species.

Acknowledgements

The authors wish to thanks to Fundação para a Ciência e Tecnologia (FCT) for financial support (FRH/BD/18315/2004 and POCI/EQU/55678/2004).

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