

Research Note

# On the role of external Co sites in NO oxidation and reduction by methane over Co–H-MFI catalysts

G. Bagnasco,<sup>a</sup> M. Turco,<sup>a</sup> C. Resini,<sup>b</sup> T. Montanari,<sup>c</sup> M. Bevilacqua,<sup>c</sup> and G. Busca<sup>c,\*</sup>

<sup>a</sup> Dipartimento di Ingegneria Chimica, Università “Federico II” di Napoli, p.le V. Tecchio, 80, I-80125, Napoli, Italy

<sup>b</sup> Centro di ricerca Interuniversitario in Monitoraggio Ambientale, Università degli Studi di Genova, via Cadorna, 7, I-17100, Savona, Italy

<sup>c</sup> Dipartimento di Ingegneria Chimica e di Processo, Università degli Studi di Genova p.le J. F. Kennedy, 1, I-16129, Genova, Italy

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## Abstract

Co–H-MFI and Co–silica–alumina catalysts were comparatively characterized and their activities in CH<sub>4</sub>-SCR and NO oxidation were compared. IR measurements evidence that Co sites distribute between internal cavities and external surface of Co–H-MFI; a large fraction of protonic sites are retained. Co–silica–alumina, unlike Co–H-MFI, is inactive in CH<sub>4</sub>-SCR and catalyzes only NO oxidation and methane combustion. The CH<sub>4</sub>-SCR activity is related to Co sites located in the zeolitic cavities. The role of NO<sub>2</sub> gas as intermediate in the CH<sub>4</sub>-SCR reaction appears unlikely. The activity of zeolitic protons in NO oxidation seems negligible in the presence of cobalt.  
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## 1. Introduction

NO reduction from flue gases of power stations could be performed using methane as reductant (CH<sub>4</sub>-SCR), according to the following reaction:



Co-containing zeolites, such as Co-MFI and Co-FER, were found by Armor [1] to be active under conditions that allow application in high-dust configurations.

Several questions are still open about the active sites of these catalysts for whose characterization the use of UV-vis spectroscopy has been much emphasized [2–4]. The reaction mechanism for these catalysts was also investigated [5,6], but a substantial disagreement still exists about the role of NO<sub>2</sub> as a possible intermediate in the reaction. According to Yan et al. [7] Co cations act in the oxidation of NO to NO<sub>2</sub> whereas Brønsted acid sites act in the actual reduction by methane. On the contrary, Kauchy et al. [5] suggest that

Brønsted sites enhance the activity in oxidizing NO to NO<sub>2</sub>. According to our recent work [8], the oxidation of NO to NO<sub>2</sub> is not beneficial as NO oxidation seems to be competitive with respect to the overall CH<sub>4</sub>-SCR process; i.e., NO<sub>2</sub> appears not to be an intermediate of the CH<sub>4</sub>-SCR process.

In the present work we will compare the activity of Co-MFI zeolite and of Co–silica–alumina in the conversion of NO in excess oxygen, both in the presence and in the absence of methane to gain information on the reactivities of internal channel ions and external surface ions. The role of NO<sub>2</sub> in NO reduction is also discussed.

## 2. Experimental

### 2.1. Preparation procedures

The preparation of Co–H-MFI (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50) has been previously reported [8]. A similar procedure has been applied to the production of Co–silica–alumina (Co–SA) starting from silica alumina from STREM Chemicals (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 11.6). The resulting Co loadings are 1.7% for Co–H-MFI and 11.4% (w/w) for Co–SA. The Co/Al atomic ratios are 0.76 for Co–SA and 0.55 for Co–H-MFI.

\* Corresponding author. Dipartimento di Ingegneria Chimica e di Processo, Università degli Studi di Genova, p.le J. F. Kennedy, 1, pad. D, I-16129 Genova, Italy. Fax: +39 010 353 6028.

E-mail address: [Guido.Busca@unige.it](mailto:Guido.Busca@unige.it) (G. Busca).

## 2.2. Characterization techniques

Diffuse reflectance spectra (DR-UV-vis-NIR) have been recorded by use of a Jasco V-570. The IR spectra were recorded on a Nicolet Protégé 460 spectrophotometer Fourier transform instrument. The nitriles used for in situ adsorption were from Aldrich. Temperature-programmed reduction (TPR) tests were carried out by a Micromeritics TPD/TPR 2900 instrument equipped with a TCD detector. The analytical procedures are reported elsewhere [9].

## 2.3. Catalytic activity measurements

Catalytic tests were performed in a flow laboratory plant equipped with a fixed-bed reactor operating at atmospheric pressure. The operation conditions were reacting mixture composition: NO = 1500 ppm, CH<sub>4</sub> = 1500 or zero ppm, O<sub>2</sub> = 25,000 ppm, He balance; *T* = 523–773 K; GHSV = 30,000–60,000 h<sup>-1</sup>. The analyses of NO, NO<sub>2</sub>, and N<sub>2</sub>O were performed by a continuous spectrophotometer analyzer ABB URAS 14 equipped with a NO<sub>2</sub> converter. CH<sub>4</sub>, N<sub>2</sub>, CO, and CO<sub>2</sub> were detected by a HP 5890 gas chromatograph equipped with a TCD detector and a 5A-Porapak Q molecular sieves double-packed column.

## 3. Results and discussion

### 3.1. Catalysts characterization

In Fig. 1 the UV-vis spectra of Co–H-MFI and of Co–SA are reported, both obtained after evacuation at 773 K for 5 h. In both cases, absorptions are found that can be interpreted as a triplet near 19,000 cm<sup>-1</sup>, near 17,000 cm<sup>-1</sup> and

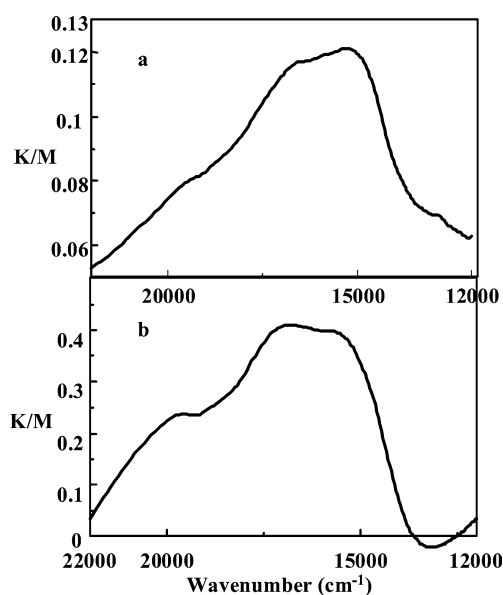


Fig. 1. DR-UV-vis spectra of samples Co–H-MFI (a), Co–SA (b), both out-gassed for 5 h at 773 K.

near 15,000 cm<sup>-1</sup>. No other absorption occurs in the range 40,000–22,000 cm<sup>-1</sup>. The spectra we observe are similar to those reported and deeply discussed by Dedecek et al. [3] and by Drozdova et al. [4], for Co–MFI and other Co–H zeolites. The absolute intensity ratio of these absorptions roughly agrees with the Co amount ratio (Co–SA:Co–H-MFI ≈ 7). These bands are not present in the spectra of Co-free H-MFI and SA. The spectra of Co–H-MFI and Co–SA are very similar qualitatively and can be both assigned to low-coordination Co<sup>2+</sup> species [4]. As discussed elsewhere [9], these spectra are similar to those observed when Co ions are dispersed on different oxide supports, like out-gassed Co–alumina [10]. This suggests that the nature of cobalt sites in both samples is similar and that this technique does not allow differentiation of Co sites in zeolite cavities from those located on the open surfaces of different oxides.

In Fig. 2 the IR spectra of Co–H-MFI after outgassing at 773 K, and after subsequent contact at RT with pivalonitrile vapors, are reported. It has been shown [11,12] that this molecule, because of its steric hindrance, cannot enter the cavities of MFI zeolites at RT and low pressure. On the other hand, it is possible to detect its interaction with external silanol groups and with two types of Al<sup>3+</sup> Lewis sites of H-MFI, also located at the external zeolitic surface. On Co–H-MFI (Fig. 2) it is evident again that PN does not enter the zeolite cavities. In fact, the band of bridging OH groups at 3620 cm<sup>-1</sup> is essentially unperturbed. Interaction with external silanols is evident with their shift from 3747 cm<sup>-1</sup> to near 3440 cm<sup>-1</sup>. The corresponding CN-stretching band of H-bonded PN is split at 2235 and 2250 cm<sup>-1</sup>. These features disappear by outgassing. Additionally, a quite strong band is formed at 2280 cm<sup>-1</sup>, with a sharp weaker peak at 2319 cm<sup>-1</sup>, that even increase after outgassing. The main band at 2280 cm<sup>-1</sup> is much more intense and defined than for H-MFI and is assigned to PN interacting with cobalt sites. This indicates that part of cobalt sites are located at the external surface of the zeolite where they can interact with PN. The spectra of hindered nitriles adsorbed on Co sites at the external surface of Co–H-MFI are similar to those of the same complexes on Co–SA.

The results of TPR measurements obtained with Co–H-MFI and Co–SA are reported in Fig. 3 and in Table 1. The data referring to Co–H-MFI have been reported in Ref. [8]. Neither H-MFI nor SA undergo significant reduction. H<sub>2</sub> consumption is due only to the reduction of cobalt species. The TPR signals of Co–H-MFI are much smaller than those of Co–SA, according to the lower Co content. The three components that appear in the curve of Co–H-MFI are attributed to two different quite easily reducible species (possibly polynuclear and/or nanosized Co oxide particles) and to hardly reducible zeolitic Co<sup>2+</sup> ions [8,13]. The curve of Co–SA shows two components only, with maxima at 648 and 1043 K. The amount of consumed H<sub>2</sub> per mole of Co is close to that corresponding to the reduction Co<sup>2+</sup> → Co<sup>0</sup> (Table 1). The high temperature signal represents the reduction of 77% of the overall Co ions and can be reasonably

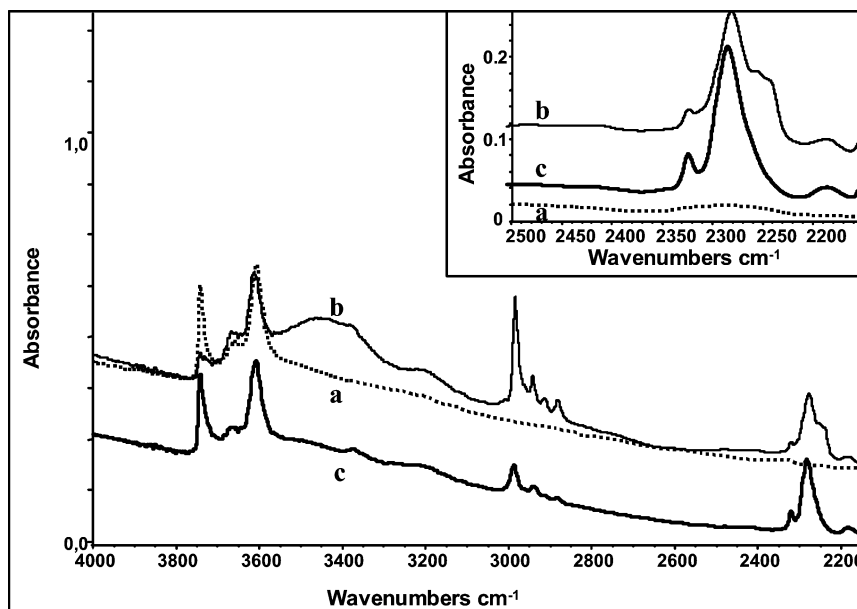


Fig. 2. FT-IR spectra of Co-H-MFI after activation at 773 K (a), in contact with pivalonitrile 10 Torr (b), after successive outgassing at 573 K for 10 min (c).

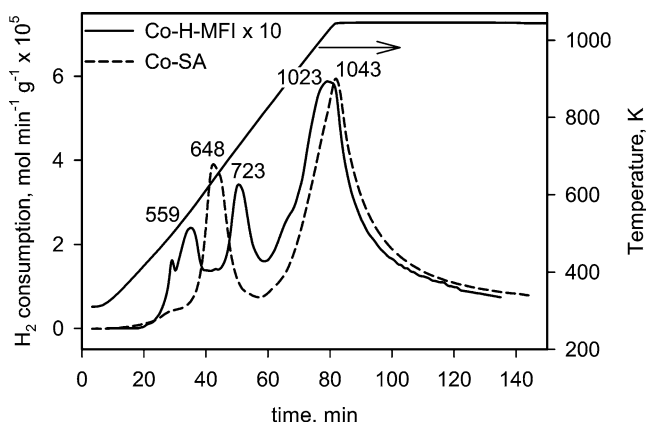


Fig. 3. TPR curves of Co-H-MFI and Co-SA. Note that the pattern of Co-H-MFI sample is reported increased 1 order of magnitude.

Table 1

TPR results: peak temperatures, consumed H<sub>2</sub> amounts and molar ratio H<sub>2</sub>/Co

Sample	$T_{\text{peak}}$ (K)	$n_{\text{H}_2}$ (mmol g <sup>-1</sup> )	H <sub>2</sub> /Co (mol mol <sup>-1</sup> )
Co-H-MFI	559	0.03	0.10
	723	0.05	0.17
	1023	0.23	0.80
		0.31	1.07
Co-SA	648	0.39	0.21
	1043	1.31	0.69
		1.70	0.90

attributed to the reduction of nearly isolated Co<sup>2+</sup> ions. This reduction occurs with great difficulty, as observed for Co-H-MFI [8,13], possibly because it needs aggregation of Co atoms to form Co-Co bonds as a preliminary step. The TPR

signal at 648 K must be representative of some aggregated Co oxide species, that undergo reduction more easily than isolated Co<sup>2+</sup> ions. The corresponding amount of H<sub>2</sub> (Table 1) shows that in Co-SA less than one-fourth of Co ions is present in oxide-like form. Co<sub>3</sub>O<sub>4</sub> is the most stable Co oxide phase under the conditions applied in the catalyst preparation process but the TPR peak temperature is somewhat lower than that measured for the reduction of a Co<sub>3</sub>O<sub>4</sub> phase under the same conditions [8]. Moreover, on the basis of the low total H<sub>2</sub> consumption per mole of Co (Table 1) and of the absence of any spectroscopic evidence, it seems unlikely that a segregated Co<sub>3</sub>O<sub>4</sub> phase is present on the SA surface. The TPR signal at 648 K is more likely due to the presence of polynuclear Co<sup>2+</sup> oxo-ions, that are reduced to Co<sup>0</sup> nano-clusters by H<sub>2</sub>, similar to one of the two species observed for Co-MFI samples [13].

These data show that most cobalt species (those reduced at the highest temperature) are isolated Co<sup>2+</sup> with a similar redox behavior in the two catalysts. In the case of Co-H-MFI we showed previously [9] that the exchange of the internal bridging OH groups is far from total; from the intensity of the IR band of the residual internal OHs we can deduce that no more than 50% protons have been actually exchanged. From this datum and from Al and Co contents of the catalyst (Co/Al = 0.55 a.r.), we can deduce that only 45% Co species are in internal substitution position. Although this evaluation is very rough, it seems evident that the TPR peak at 1023 K is due not only to the reduction of internal Co ions in substitutional position, but also to additional cobalt in other positions either internal or external. These ions have very similar redox behavior and UV-vis spectrum with respect to those located on the open surface of Co-SA. More easily reducible centers are also observed for both samples

and part of them is even more easily reducible on Co-MFI than on Co-SA.

### 3.2. Catalytic activity measurements

Catalytic activity of Co-H-MFI, of H-MFI, and of Co-SA was studied for CH<sub>4</sub>-SCR and NO oxidation reactions. NO oxidation tests were carried out by feeding the same NO and O<sub>2</sub> concentrations as in CH<sub>4</sub>-SCR tests, and no CH<sub>4</sub>. Preliminary tests ascertained that no reaction occurred without catalysts, under our experimental conditions. H-MFI shows very weak activity in both reactions. In CH<sub>4</sub>-SCR tests over Co-H-MFI the reaction products are N<sub>2</sub>, NO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O whereas N<sub>2</sub>O and CO were not produced. In NO oxidation tests only NO<sub>2</sub> was formed. The results are shown in Fig. 4 where total NO conversion and NO<sub>2</sub> yield for the samples Co-H-MFI and Co-SA, respectively, are reported. N<sub>2</sub> is the only other N-containing product. The N<sub>2</sub> yield is not plotted in the figures because it is equal to the difference between total NO conversion and NO<sub>2</sub> yield, in the precision of N balance (see Section 2). The conversions are compared with the equilibrium values of NO oxidation to NO<sub>2</sub>. The behavior of Co-H-MFI in the CH<sub>4</sub>-SCR tests (Fig. 4, top) was previously studied [8]. NO conversion shows a maximum value of about 30% at 673 K and slightly decreases with temperature. NO<sub>2</sub> is the main product at temperatures lower than 773 K and reaches a maximum value at

673 K. The selectivity to N<sub>2</sub> increases with temperature from 20% at 623 K to 70% at 823 K. In the NO oxidation tests NO conversion is very close to that observed in SCR tests at  $T \leq 723$  K, whereas it is lower at higher temperature. It is close to the equilibrium conversion values at  $T \geq 673$  K. These data show that under CH<sub>4</sub>-SCR conditions,



besides the reduction Reaction (1) also NO oxidation (2) occurs. Reaction (1) prevails at temperatures higher than 723 K, when NO oxidation (2) becomes thermodynamically limited. On the other hand, the analysis of the conversion of methane, that increases with temperature from 15% at 623 K to 65% at 823 K, provides evidence for the additional occurrence of the oxidation of methane to CO<sub>2</sub>:



At 620 K Reaction (1) does not occur at all, nitrogen not being detected among the products. This means that, at this stage, both Reactions (2) and (3) are faster than Reaction (1). By increasing the temperature, Reaction (1) starts to occur while the selectivity to NO<sub>2</sub> decreases and methane conversion steadily increases. It is evident that at  $T = 670$ – $770$  K without methane the NO<sub>2</sub> yield corresponds to that forecast by thermodynamics, indicating that the equilibrium is reached. In the presence of methane the conversion of NO is higher by an amount corresponding to the fraction of NO that is reduced by methane to N<sub>2</sub>. Below 670 K the equilibrium of Reaction (2) is not reached and conversion increases with temperature because of the increase of reaction rate. This shows that Co-H-MFI acts as an efficient catalyst for Reaction (2) and, at the same time, catalyses Reactions (1) and (3). At high temperature, when Reaction (2) is no more favored, Reaction (3) becomes progressively faster and faster. This means that Reactions (2) and (3) compete with Reaction (1).

The behavior of Co-SA (Fig. 4, bottom) in the CH<sub>4</sub>-SCR reaction is quite different. NO conversion and NO<sub>2</sub> yield are practically the same, evidencing that Co-SA catalyzes the oxidation of NO to NO<sub>2</sub>, whereas it does not catalyze at all the CH<sub>4</sub>-SCR reaction, no nitrogen being observed among the reaction products. On the other hand, CH<sub>4</sub> conversion and formation of CO<sub>2</sub> are noticeable, indicating the occurrence of Reaction (3). The behavior of this catalyst in NO oxidation is similar to that of Co-H-MFI, showing a maximum in NO conversion at about 670 K and values close to the equilibrium at temperatures higher than 673 K. The NO conversion obtained in these conditions is markedly higher than that obtained in SCR tests, indicating that the NO oxidation activity of this catalyst is partly inhibited by the presence of CH<sub>4</sub>. This effect can be due to H<sub>2</sub>O (produced from CH<sub>4</sub> oxidation) that can compete with NO for adsorption on the active sites, thus partially inhibiting NO oxidation. The similar activity of the two catalysts in NO oxidation at low temperature, despite the much higher cobalt content in Co-SA, can be related to the easier reducibility of part of cobalt

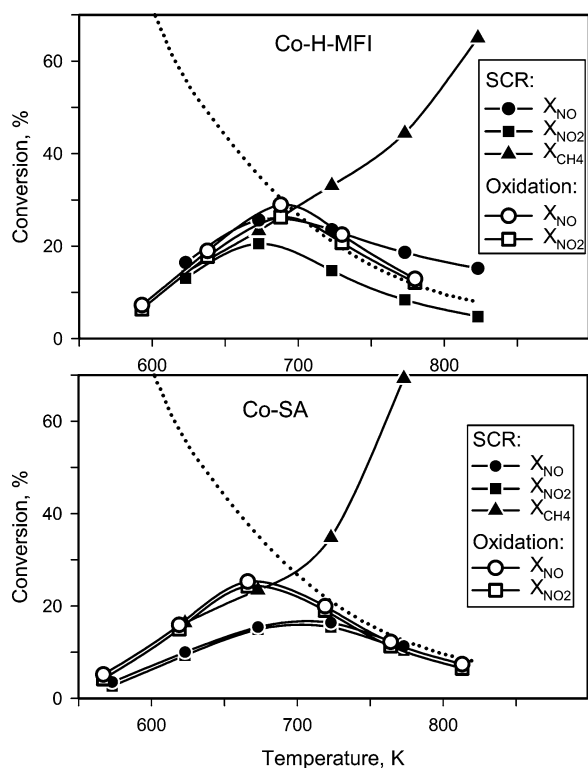


Fig. 4. NO and CH<sub>4</sub> conversions and NO<sub>2</sub> yield as a function of temperature in tests of CH<sub>4</sub>-SCR and NO oxidation on Co-H-MFI (top) and Co-SA (bottom). The dotted lines represent NO conversion in equilibrium conditions.



sites in Co–H-MFI than in Co–SA. The above reported data show that Co–H-MFI catalyst is active both in CH<sub>4</sub>-SCR reaction and in NO oxidation to NO<sub>2</sub> and that these reactions are competing. Actually, CH<sub>4</sub>-SCR activity appears mostly above 673 K, i.e., when the oxidation of NO to NO<sub>2</sub> becomes less thermodynamically favored. The Co–SA catalyst, on the contrary, seems to be inactive in CH<sub>4</sub>-SCR, but active in NO oxidation to NO<sub>2</sub>, as well as in the oxidation of methane to CO<sub>2</sub>. Over both catalysts the equilibrium of NO oxidation to NO<sub>2</sub> is reached above 673 K. In the region where equilibrium is not reached, the activity of Co–H-MFI is a little higher than that of Co–SA. The characterization data show that part of the Co centers are located at the exterior of Co–H-MFI. These external sites look similar to those observed on the open surface of Co–SA. This suggests that Co ions located at open external surfaces of zeolites are likely not (or very poorly) active in CH<sub>4</sub>-SCR, although being likely active in NO oxidation to NO<sub>2</sub>. The active sites for SCR of NO by methane and other hydrocarbons are likely those located in the interior of the zeolite cavities, in agreement with the data reported by Satsuma et al. [14], who showed that hydrocarbons not accessing the zeolite cavities do not reduce NO over Co zeolites, or give very slow reaction. The cavity sites are apparently also more active in NO oxidation than those on the open surface. The data reported here show that the activity in NO oxidation to NO<sub>2</sub> does not necessarily imply CH<sub>4</sub>-SCR activity. The less NO oxidation is favored, the more CH<sub>4</sub>-SCR on Co–H-MFI occurs and the lack of any correlation between the activity in NO oxidation to NO<sub>2</sub> and CH<sub>4</sub>-SCR suggests that the two reactions are more likely competitive than successive. Oxidation of NO can actually occur at the catalyst surface, although NO<sub>2</sub> is not produced in the gas. Formation of oxidized surface species like nitrates by NO oxidative adsorption, followed by decomposition back to NO, has been frequently observed [15]. According to previous work [16], it is likely that the reaction mechanism involves the preliminary adsorption of NO that is oxidized by O<sub>2</sub> forming an adsorbed NO<sub>y</sub><sup>x-</sup> species (y = 2, 3) bound to a Co<sup>2+</sup> center. This species could acti-

vate the CH<sub>4</sub> molecule by subtracting a hydrogen atom and then forming a nitro- or nitroso-methane intermediate. The desorption of NO<sub>2</sub> from this intermediate can only occur when NO<sub>2</sub> is thermodynamically stable, but it can, in any case, be considered as a side reaction occurring through a parallel pathway. The active intermediate for CH<sub>4</sub>-SCR is probably formed in the zeolite cavities. In fact, if formed on the open surface of Co–SA it is not reduced by methane. The far higher catalytic activity of Co–H-MFI with respect to H-MFI in NO oxidation to NO<sub>2</sub> allows us to rule out a relevant effect of protonic sites of zeolites in favoring CH<sub>4</sub>-SCR due to NO oxidation. Residual protonic sites in the zeolite cavities could more probably be involved in the formation of the active intermediate or in the adsorption of the reducing hydrocarbon.

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