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Positive effect of NO_x on the performances of VO_x/TiO_2-based catalysts in the total oxidation abatement of chlorobenzene

F. Bertinchamps, M. Treinen, N. Blangenois, E. Mariage, E.M. Gaigneaux [*]

Université catholique de Louvain, Unité de catalyse et chimie des matériaux divisés, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

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Abstract

The influence of NO on the performances of VO_x/TiO_2, VO_x–WO_x/TiO_2, and VO_x–MoO_x/TiO_2 catalysts is investigated in the combustion of chlorobenzene. NO proves to induce an increase in the chlorobenzene conversion. However, this happens only if O_2 is present and is maximized when the catalyst contains W or Mo. The suggested mechanism for the effect is: 1) NO is oxidized to NO_2 mainly on WO_x and MoO_x; 2) afterward, NO_2 assists O_2 in the reoxidation step (as described by Mars–van Krevelen) of the VO_x phase, thus speeding up the oxidation cycle, which macroscopically corresponds to the increase in chlorobenzene conversion.

Keywords: Catalytic oxidation; PCDDs/PCDFs; Chlorinated VOC; Dioxins; Chlorobenzene; Vanadia/titania; V/W/Ti; V/Mo/Ti; NO/NO_2; NO_x

1. Introduction

In recent years, environmental legislation has imposed stringent limits on atmospheric emission levels. In particular, the release of volatile organic compounds (VOCs) has received much attention. Among these compounds, chlorinated VOCs are among the most polluting. Polychlorinated dibenzo-dioxins and dibenzo-furans (PCDDs and PCDFs, also named dioxins) are very toxic, carcinogenic, and environmentally persistent organic pollutants [1–3]. Dioxins are formed systematically in all of the incineration processes in the presence of chlorinated compounds, as in municipal waste or medical waste incinerators or in biomass-fed cogeneration units.

Among the methods applied to destroy chlorinated VOCs (typically high-temperature incineration, hydrodechlorination, biological processes, steam reforming, photocatalytic degradation, etc.), catalytic oxidation to HCl, Cl_2, H_2O, and CO_x is the most viable and economical approach. Indeed, it operates at a relatively low destruction temperature, works for a wide range of pollutant concentration, and exhibits an excellent selectivity for the formation of harmless products [4].

Catalysts like VO_x/TiO_2, eventually “upgraded” to VO_x–MoO_x/TiO_2 and VO_x–WO_x/TiO_2, are reported to be very efficient in the total oxidation abatement of chlorobenzenes (taken as model molecules for dioxins) from combustion exhaust gases. In particular, they have proved to be highly resistant against deactivation, which proceeds on elements other than V through chlorination of these active phases [5]. However, although exhaust gases inevitably contain CO and NO_x, the efficiency of these catalysts was attested to in the literature only for flows containing chlorinated aromatics as a single pollutant. It is now crucial to assess whether VO_x/TiO_2-based catalysts still succeed in oxidizing chlorobenzene efficiently in the presence of co-pollutants or whether the latter induce some kind of deactivation. This research therefore was aimed at investigating the effect brought on by NO as a co-pollutant on the performances of VO_x, VO_x–WO_x, and VO_x–MoO_x supported on TiO_2 in the oxidation of chlorobenzene. To evaluate the catalyst activity under more realistic conditions, 1000 ppm of NO was thus introduced into the gaseous stream. Moreover, to have

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[*] Corresponding author. Fax: +32-10-473649.
E-mail address: gaigneaux@cata.ucl.ac.be (E.M. Gaigneaux).

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a better understanding of the interaction of NO with the catalyst, we changed the concentrations of NO and O_2 in the stream. In particular, some tests with NO but without O_2 were carried out. Finally, we addressed the reversibility of the eventual effect brought about by NO by cycling, at different temperatures, the concentration of NO incorporated into the gas feed.

2. Experimental

2.1. Preparation of the catalysts

Catalysts were supported on a 100% anatase titania (Millenium PC100, denoted hereafter as Ts). The active phase was VO_x (catalysts denoted by V) or a combination of VO_x with MoO_x (catalysts denoted by VM) or with WO_x (catalysts noted VW). The support was impregnated with solutions of, respectively, 9.3×10^{-3}, 6.6×10^{-3}, and 7.5×10^{-3} M in distilled water of salts $(NH_4)VO_3$, $(NH_4)_2WO_4$, or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Aldrich, 99.99%) complexed with oxalic acid (Aldrich; 99.99%). In the case of VM and VW, the impregnation was made at once from solutions containing simultaneously V and Mo, or V and W salts. A classical wet impregnation method was used to obtain a 0.75 theoretical monolayer of each transition metal oxide. Therefore the suspension of TiO_2 in the impregnation solution was stirred for 2 h at room temperature before the solvent was evaporated under a reduced atmosphere in a rotavapor at 45 °C. The solid obtained was dried overnight in an oven at 110 °C. Finally, the catalyst was calcined, in a muffle furnace, for 24 h at 400 °C under air, at atmospheric pressure.

2.2. Catalytic tests

2.2.1. Conventional test

Catalytic tests were performed in a metallic fixed-bed microreactor (PID Eng&Tech S.L) operated at atmospheric pressure and fully monitored by computer. The reactor was made of inconel with an internal diameter of 8 mm and a height of 300 mm, in which the temperature is checked with an inconel covered thermocouple. The catalytic bed was composed of a layer of inert glass wool surmounted by 200 mg of catalyst powder selected within the granulometric fraction of 200–315 µm and diluted in 800 mg of inactive glass spheres with diameters in the range of 315–500 µm. Four kinds of tests were performed. For all of them, He was used as a diluting gas to obtain a total stream of 200 ml min^{-1}. All gases were from Indugas and had a purity of 99.995%. The reference tests were made with a gaseous stream composed of 100 ppm of chlorobenzene and 20% O_2 (Table 1, conditions (1)). Under catalytic conditions (2) and (3), respectively, 100 and 1000 ppm of NO were added to the reference gaseous stream to investigate the influence of the NO concentration on the performance of the catalyst used in the presence of oxygen. To investigate the influence of the oxygen concentration, performances of the catalysts were compared under conditions (3) and (4), that is, in the presence of 1000 ppm of NO. Under condition (4), the catalytic test was operated without oxygen. The reaction was run at 200 and 250 °C for 150 min at each temperature. Reactants and products were continuously analyzed by on-line gas chromatography (GC) and with a commercial gas analyzer (Horiba PG250). The gas chromatograph, equipped with four columns, one methanizer, two FID, and one TCD, made it possible to quantify chlorobenzene, O_2, CO, CO_2, and N_2 and to detect other hydrocarbons and chlorinated hydrocarbons. The gas analyzer made it possible to quantify O_2, CO_2, CO, NO, and total NO_x. To calculate the conversions and the selectivities as listed in Table 1, only the concentrations of reactants and products measured after stabilization and averaged for the period of time from 100 to 150 min were taken into account. The measured performances were accurate within a range of about 1% (in relative) for the conversions of both chlorobenzene and NO.

2.2.2. Reversibility test

Additional tests were specifically adapted to probe the reversibility of the effect of NO. Therefore, tests during which the concentration of NO was cycled were performed at 200 and 250 °C. At each temperature, the catalysts were submitted to three 150-min periods with different gaseous conditions (see Table 1): first the reference conditions (1), 100 ppm of chlorobenzene and 20% O_2 diluted in He, were applied, then we applied conditions (3) by suddenly incorporating 1000 ppm of NO in the reference gas. Finally, we applied conditions (1) again by suddenly stopping the addition of NO in the feed.

3. Results

3.1. References tests

Column (1) of Table 1 gives the results of the reference tests at 200 and 250 °C. The catalyst V (containing VO_x as the only active phase) converted 43.0 and 88.0% of the chlorobenzene at 200 and 250 °C, respectively. The addition of the second phases, WO_x or MoO_x, to the VO_x active phase induced an enhancement of the activity at 200 °C from 43.0 to 45.5% (VW) and to 49.6% (VM), respectively. This improvement in activity was also observed at 250 °C as the chlorobenzene conversion increased from 88.0 to 91.7% (catalyst VW) and to 95.4% (catalyst VM). The beneficial effect of adding MoO_x or WO_x in VO_x/TiO_2 catalysts has already been reported and discussed in [6–9].

3.2. Effect of NO in the presence of oxygen

Columns (1), (2), and (3) of Table 1 give the catalytic performances for the test realized in the absence of NO and

Table 1
Catalytic conditions and results for VO_x/TiO_2, VO_x–WO_x/TiO_2 and VO_x–MoO_x/TiO_2 catalysts

Catalyst	Temperature	Chlorobenzene conversion (%)			
		(1) [NO] = 0 ppm $[O_2]$ = 20%	(2) [NO] = 100 ppm $[O_2]$ = 20%	(3) [NO] = 1000 ppm $[O_2]$ = 20%	(4) [NO] = 1000 ppm $[O_2]$ = 0%
VO_x/TiO_2 (V)	200 °C	43.0	44.2 (+1.2)	45.9 (+2.9)	0.2
	250 °C	88.0	88.4 (+0.4)	87.7 (−0.3)	0.5
VO_x–WO_x/TiO_2 (VW)	200 °C	45.5	69.5 (+24.0)	76.6 (+31.1)	0.3
	250 °C	91.7	98.5 (+6.8)	99.3 (+7.6)	0.4
VO_x–MoO_x/TiO_2 (VM)	200 °C	49.6	73.0 (+23.4)	90.8 (+41.2)	0.7
	250 °C	95.4	98.7 (+3.3)	99.8 (+4.4)	0.9

for the tests realized with the addition of, respectively, 100 and 1000 ppm of NO in the reference gas.

At 200 °C, in the case of the VO_x-supported phases, the introduction of 100 and 1000 ppm of NO into the gaseous stream induced only a slight increase in the activity, +1.2% and +2.9%, respectively. But the presence of NO induced a dramatic increase in activity when WO_x or MoO_x was present. For the catalyst VW, the chlorobenzene conversion increased from 45.5 to 69.5% (+24.0%) when 100 ppm of NO was added to the stream and to 76.6% (+31.1%) when 1000 ppm of NO was added. The highest effect of the addition of NO to the gaseous flow was observed for the catalyst containing VO_x and MoO_x simultaneously. For this catalyst, adding 100 or 1000 ppm of NO induced an increase in the catalyst activity of 23.4 and 41.2%, respectively, and the conversion of chlorobenzene increased from 49.6% in the absence of NO to 73.0 and 90.8% in the presence of 100 and 1000 ppm of NO, respectively. To summarize these results: the positive effect of NO is progressive with the NO concentration and is stronger on the VO_x–MoO_x and VO_x–WO_x catalysts than on the single VO_x active phase.

At 250 °C, identical tendencies, although they were attenuated, were observed. The addition of NO did not induce any significant modification of the chlorobenzene conversion (+0.4% and −0.3%) in the case of catalyst V. For catalysts VW and VM, the introduction of NO into the stream was followed by a slight increase in the activity: respectively, +6.8% and +3.3% of conversion in the presence of 100 ppm and +7.6% and +4.4% in the presence of 1000 ppm.

Under all tested conditions (100 or 1000 ppm of NO, 200 or 250 °C) and for all catalysts, NO was recovered at the reactor outlet at a concentration of exactly 100 or 1000 ppm. This shows that no global consumption of NO occurs during any experiment.

3.3. *Influence of the oxygen concentration on the effect of NO*

Column (4) of Table 1 gives the activity in terms of chlorobenzene conversion for the three catalysts in the presence of 1000 ppm of NO, but in the absolute absence of oxygen in the feed. Under these conditions, the conversion of chlorobenzene always remained below 1% at both 200 and 250 °C. It must be mentioned that for the three catalysts, during the first 5 min of reaction, the chlorobenzene was almost totally converted to CO_2 and CO. But after this short period of time, the conversion decreased rapidly to about 0.5%.

These behaviors and performances are obviously different from those observed in the presence of both O_2 and NO in the feed. As a reminder (Table 1, column (3)), the catalyst VM gave 99.8% of conversion at 250 °C. Thus it is clear that NO is able to induce a huge positive effect on the ability of VO_x/TiO_2, VO_x–MoO_x/TiO_2, and VO_x–WO_x/TiO_2 catalysts to oxidize chlorobenzene. This effect is possible *only* when oxygen is present in the gaseous stream.

3.4. *Reversibility tests*

For catalyst V, containing VO_x as the only active phase, the introduction of 1000 ppm of NO into the gaseous stream induced an increase of activity in the same range as that observed between the performances in the reference test and the performances in the test with 1000 ppm (see Table 1). After 150 min under conditions (3), shutdown of the NO input induced a decrease in the chlorobenzene conversion to the level of activity observed during the first stage of the cycle (conditions (1)). Fig. 1 shows the corresponding result obtained by cycling of the concentration of NO during the test with the catalyst VW. A similar behavior was observed for catalyst VM. The activity increased rapidly when the gaseous composition was switched from the reference conditions to conditions (3) corresponding to the addition of 1000 ppm of NO. This enhancement of conversion was in the same range as the difference between the performances observed in the reference tests and those obtained by the application of conditions (3) from the very beginning of the experiment (see Table 1, Fig. 1). After the sudden removal of NO from the stream, the activity of the catalyst almost immediately went back to a level of conversion obtained under the reference conditions (Fig. 1). Similar effects were obtained at 250 °C.

The effect of NO on the performances of VO_x/TiO_2, VO_x–MoO_x/TiO_2, and VO_x–WO_x/TiO_2 catalysts in the oxidation of chlorobenzene is thus clearly reversible.

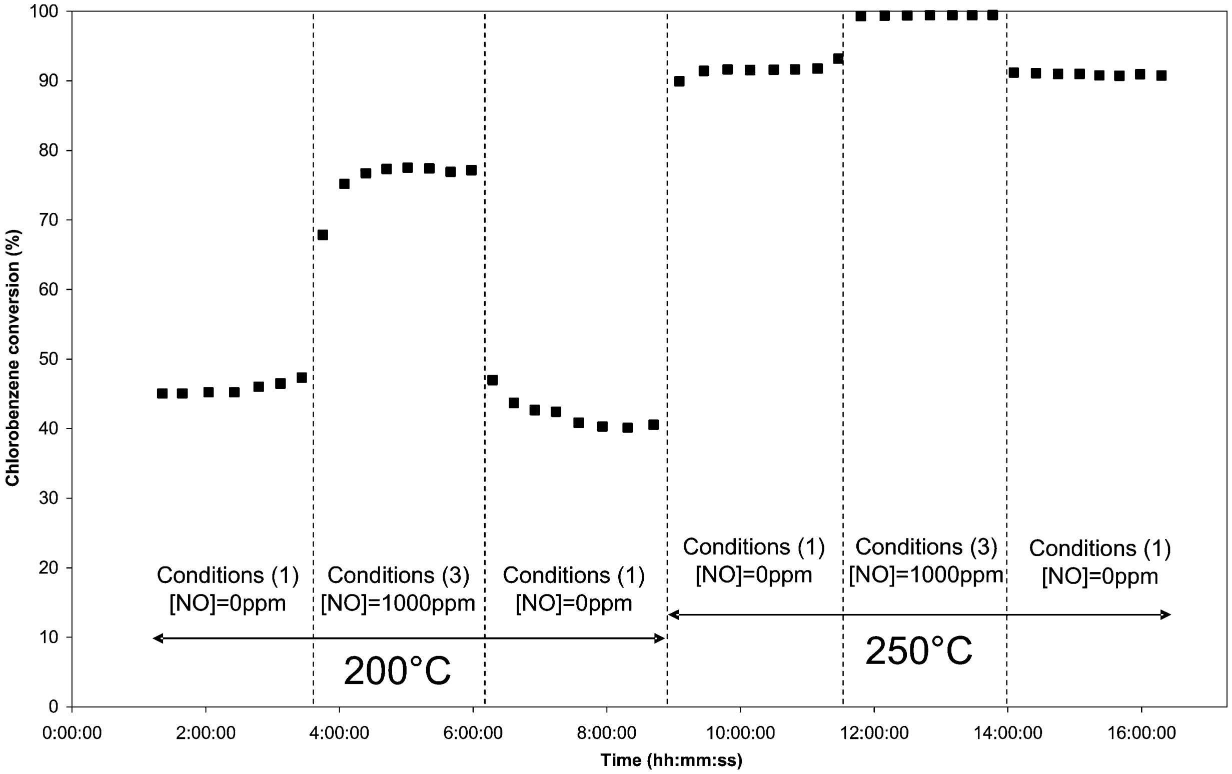

Fig. 1. Chlorobenzene conversion during the cyclic test on Ts(VW).

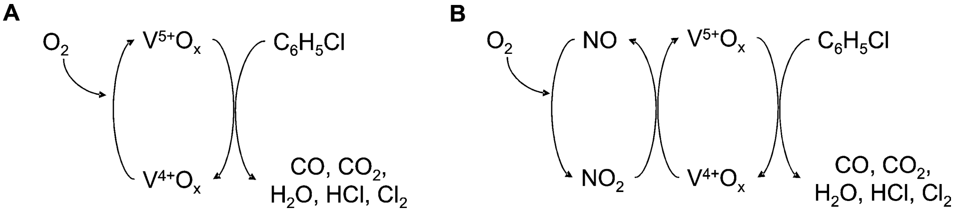

Fig. 2. Scheme of the chlorobenzene oxidation in the absence (A) or presence (B) of NO.

4. Discussion

For the three catalysts, adding NO in the gaseous stream is clearly beneficial for the conversion of chlorobenzene. Within the range investigated, this enhancement of activity increases with increasing NO concentration. Moreover, this beneficial effect of the presence of NO is much more important when WO_x or MoO_x is associated with the VO_x active phase. However, this beneficial effect is possible only if some oxygen is present in the stream. In the absence of oxygen, the activity decreases very rapidly to less than 1% of chlorobenzene conversion. Moreover, the enhancement of activity brought on by the presence of NO disappears very quickly when NO is suddenly removed from the stream. Finally, all of this occurs without any global consumption of NO during any catalytic test.

To account for all of these observations, a reaction mechanism in two or three steps is suggested, depending on the gaseous composition. In the reference tests, namely without NO, the conversion of chlorobenzene occurs in two steps (Fig. 2A), as classically described by the Mars and van Krevelen mechanism [10]. In the first step, the $V^{5+}O_x$ phase gives some of its lattice oxygen atoms to oxidize chlorobenzene, which leaves behind reduced $V^{4+}O_x$ species. In the second step, these $V^{4+}O_x$ species are reoxidized by O_2 from the gaseous stream. Our hypothesis for the effect of NO on the behavior of VO_x/TiO_2-based catalysts is based on a mechanism of chlorobenzene oxidation in three steps. Compared with the mechanism proposed for the reference conditions, the additional step is that NO would react with oxygen (when it is present) at the surface of the catalyst to produce NO_2 (Fig. 2B). The NO_2 thus formed would then assist (or replace, at least partially) O_2 to reoxidize the reduced $V^{4+}O_x$ as in the second step of the Mars and van Krevelen mechanism. The participation of NO_2—a stronger oxidant than O_2, as shown by Koebel et al. [11]—in the reoxidation step of the $V^{4+}O_x$ sites would thus speed up this reaction step and would thus macroscopically correspond to the observed increase in the chlorobenzene conversion.

This three-step mechanism proposed for the oxidation of chlorobenzene on VO_x-based catalysts in the presence of oxygen and NO accounts not only for the activation of the catalyst by NO, but also for several other of our catalytic observations. It is also supported by several reports from the literature.

1. The observed increase in the conversion of chlorobenzene is well explained by the three-step mechanism that involves NO_2 as a powerful oxidant for the regeneration of the $V^{4+}O_x$ reduced sites. The enhancement of the activity due to the speeding up of the reoxidation step of the Mars and van Krevelen mechanism in the presence of the in situ produced NO_2 is strengthened by the observations of Koebel et al. [11]. They showed the faster oxidation of the vanadia-reduced sites by NO_2 than by O_2 at temperatures below 300 °C in the case of VO_x–WO_x/TiO_2 catalysts. The higher oxidizing power of NO_2 than of O_2 explains the increase in activity in the case of the addition of NO to the gaseous stream.
2. The proposed mechanism elucidates the occurrence of an activity enhancement brought about by NO, although no NO consumption was observed during any catalytic tests. Our mechanism indeed proposes that first, NO is oxidized to NO_2 on the surface of the catalyst, thanks to the presence of oxygen in the stream. Then NO_2 gives one of its oxygen atoms to oxidize $V^{4+}O_x$ species while giving back NO. Such a “cycle of NO” indeed fits quite well with the absence of NO consumption.
3. The absence of conversion when the gaseous stream contains only NO and no O_2 could be explained by the proposed three-step mechanism. In the presence of NO and the absence of O_2, over a very short period of time (about 5 min), the VO_x phase gives some of its lattice oxygen atoms, inducing a limited conversion of chlorobenzene and leading to the formation of reduced $V^{4+}O_x$ sites. The next step of the mechanism, which is the reoxidation of the thus formed reduced $V^{4+}O_x$ sites, requires the presence of oxidizing species. The presence of NO alone, which is not able to play the role of oxidant by itself, induces the end of the chlorobenzene conversion. NO, following the proposed three-step mechanism, must be oxidized in situ to NO_2, by O_2, to induce the “cycle of NO” and to further induce the reoxidation of the $V^{4+}O_x$ sites by NO_2. The three-step mechanism involving the oxidation of NO to NO_2 by O_2 to induce the reoxidation of the $V^{4+}O_x$ sites explains well the absence of sustainable conversion in the presence of NO without O_2. With the purpose of strengthening the hypothesis of activation through the production of NO_2 in situ, we investigated the influence of NO_2 in the total absence of O_2. These tests indeed showed that NO_2 is able to induce by itself a sustainable oxidation of chlorobenzene during the entire catalytic test [12].
4. Another of our observations is that the enhancement of activity brought about by NO is much greater for the catalysts containing WO_x and MoO_x than for those containing only VO_x. This observation could be explained by our hypothesis that the oxidation of NO to NO_2 occurs mainly on the surface of the WO_x and MoO_x phases. This hypothesis is strongly supported by the observations of Dawody et al. [13], who showed that 400 ppm of NO could be oxidized to NO_2 in the presence of 8% O_2 at a temperature as low as, roughly, 140 °C on WO_x- and MoO_x-containing catalysts. The VO_x phase is also shown to be able to oxidize NO to NO_2, but at a higher temperature (170 °C) and to a lower extent. Moreover, additional tests have been performed to investigate further the NO oxidation step of the mechanism. The oxidation of 1000 ppm of NO in the presence of 20% O_2 has been probed on the three catalysts. The WO_x- and MoO_x-containing catalysts oxidize roughly 20% of the NO, whereas the VO_x catalyst oxidizes only 4% of it. In both cases the NO is converted to NO_2. The preferential oxidation of NO to NO_2 on the surface of WO_x and MoO_x explains very well the greater effect of NO on the conversion of chlorobenzene in the case of the VO_x–MoO_x/TiO_2 and VO_x–WO_x/TiO_2 catalysts than in the case of VO_x/TiO_2 catalysts.
5. The dependence of the thermodynamic equilibrium between NO and the produced NO_2 (mainly on the surface of the WO_x and MoO_x phases) on temperature explains the lower influence of NO at 250 °C than at 200 °C. Dawody et al. showed that above 220 °C, the oxidation of NO decreases in the case of the WO_x and MoO_x phases because of the thermodynamic equilibrium concentration. The decrease in the NO_2 production above 220 °C could be a key factor in understanding the lower *doping* effect of NO at 250 °C than at 200 °C.

5. Conclusion

In the presence of oxygen, the increase in the NO concentration induces a dramatic enhancement of the chlorobenzene conversion on VO_x-, VO_x–WO_x-, and VO_x–MoO_x-based catalysts. We proposed a mechanism in three steps for the oxidation of chlorobenzene in the presence of NO and oxygen. In the first step, the vanadia phase gives its lattice oxygen to oxidize the chlorobenzene, following a Mars and van Krevelen mechanism. In parallel, in a second step, the NO is oxidized to NO_2, principally on the doping phases WO_x and MoO_x. The produced NO_2 is able to replace or assist O_2 for the reoxidation of the reduced vanadia sites, which stands for the third step. This third step leads to the regeneration of the reduced vanadia sites, which could then give again their lattice oxygen atoms, and to the liberation of NO in the same amount in which it had been introduced in the stream. The higher oxidation power of NO_2 than of O_2, for the reoxidation of the vanadia-reduced sites, induces a speed-up of the Mars and van Krevelen mechanism. The objective of this contribution was to evaluate whether VO_x-

based supported catalysts known to be efficient in abating chlorobenzene production in oxidizing conditions would remain as efficient in the presence of NO as a co-pollutant. It appears that NO is not definitively a poison; on the contrary, it acts as dopant of chlorinated aromatics combustion on VO_x-based catalysts.

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