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Catalysts for chlorinated VOCs abatement: Multiple effects of water on the activity of VO_x based catalysts for the combustion of chlorobenzene

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Abstract

The influence of H_2O 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. H_2O proves to influence in opposite manners the chlorobenzene conversion depending on its concentration and on the kind of catalysts. The overall influence of water is the sum of three effects, two negative: (1) the reduction of the vanadium phase dictated by its reducibility, itself influenced by the presence of WO_x or MoO_x, (2) the decrease of the number of strong Brönsted acid sites involved in the adsorption of the chlorobenzene and one positive (3) the retrieval of chlorine species from the surface through the production of HCl.

Keywords: Catalytic oxidation; PCDDs/PCDFs; Chlorinated VOC; Chlorobenzene; Vanadia/titania; H_2O

1. Introduction

Over the last years, environmental legislation has imposed stringent limits for atmospheric emission levels. In particular, the release of chlorinated volatile organic compounds (Cl-VOCs) has received much attention. Polychlorinated dibenzo-dioxins and dibenzo-furans (PCDDs and PCDFs), also named dioxins, are very toxic, carcinogenic and environmentally persistent organic pollutants [1]. Dioxins are formed systematically in all the incineration processes in presence of chlorinated compounds, like in municipal waste incinerators or in cogeneration units.

Many methods have been applied to destroy chlorinated VOCs. Among these, catalytic oxidation of chlorinated VOCs is the most viable and economic approach due to its low destruction temperature and its excellent selectivity toward the formation of harmless products [2]. Nevertheless, the catalytic oxidation of chlorinated VOCs presents some problems as the production of HCl and Cl_2, which may attack the catalyst. Based on a systematic screening (10 transition metal oxides supported on 4 different supports), on an investigation of the loading effect, and on the study of the resistance against chlorinated compounds, we spotlighted the very good activity of VO_x submonolayer species supported on titania. Moreover, the dopant effect of WO_x and MoO_x species was also demonstrated.

We report hereafter on our investigation of the influence of H_2O on the total oxidation of chlorobenzene on VO_x/TiO_2 catalysts possibly doped with WO_x or MoO_x. Water is indeed a very special molecule in this reaction. Firstly, water is present in all exhaust gases due to its production in all incineration processes. Secondly, water is a product of the chlorobenzene oxidation. Thirdly, water is commonly regarded as a poison for the catalytic combustion of VOCs [3–6]. In the case of the combustion of Cl-containing VOCs, water could however play an additional interesting role, namely by removing Cl^- left on the surface after the oxidation of the aromatic ring [7]. Finally, water could also react with chlorine to produce HCl by the Deacon [8] reaction and change the selectivity HCl/Cl_2. Therefore, in order to evaluate more accurately the performances of our selected catalysts in a more realistic stream and to have a better understanding of the catalytic mechanism, we

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decided to carry out catalytic tests in presence of different concentrations of water.

2. Materials and methods

2.1. Catalysts synthesis

The VO_x active phases (hereafter noted V) or the combinations VO_x-WO_x (hereafter noted VW) or VO_x-MoO_x (hereafter noted VM) are supported on titania (Millenium PC100, hereafter noted Ts). The support was impregnated with a solution of $(NH_4)VO_3$, $(NH_4)_2WO_4$ or $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and oxalic acid, 2 equivalents of acid for one of transition metal, in distilled water. A classical wet impregnation method was used in order to obtain theoretically 0.75 or 0.75–0.75 monolayer of each transition metal oxide VO_x, VO_x-WO_x or VO_x-MoO_x. After the evaporation of water under vacuum and the drying stage at 110 °C, the catalyst was calcined for 24 h at 400 °C.

2.2. Catalytic tests

Catalytic tests were performed with 200 mg of catalyst (200–315 μm) in a metallic fixed-bed micro-reactor (PID Eng&Tech, Madrid, Spain) operating at atmospheric pressure and fully monitored by computer. The gas stream was composed of 100 ppm of chlorobenzene, 20 vol.% of O_2, 0-1-2-5 vol.% of H_2O and helium as diluting gas to obtain 200 ml min^{-1} (VVH = 37000 h^{-1}). Water was supplied by a controlled evaporator mixer (CEM from Bronkhorst HiTec). The reaction was run at 200 and 250 °C during 150 min at each temperature. Analysis of reactants and products was performed by on-line gas chromatography and by a gas analyser (Horiba PG250). The measured performances were accurate within a range of about 1% (in relative) for the chlorobenzene conversion.

2.3. Characterization

XPS was performed on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments working with a monochromatic Al Kα (1486.6 eV) radiation (10 kV, 22 mA). The surface atomic concentrations were calculated by correcting the intensity with theoretical sensitivity factors based on Scofield cross-sections. Peak decomposition was performed using 85% Gaussian and 15% Lorentzian types and a Shirley non-linear sigmoid-type baseline. The following peak intensities were used for the quantitative analysis: V 2p, W 4d, Mo 3d, Ti 2p, Cl 2p, O 1s and C 1s. Accurate evaluation of the vanadium oxidation state requires to avoid vanadium reduction during time under vacuum, as observed by Nogier et al. [9]. Therefore, "quick XPS analysis" was performed in such a manner that for each sample a unique window with O 1s and V 2p peaks was recorded within less than 10 min. For the decomposition of the V $2p_{3/2}$ into V^{n+} species, we fixed the binding energy of the O 1s at 530 eV as a reference and the gap between O 1s and V^{5+} species between 12.85 and 12.9 eV. For the evaluation of the other oxidation states, firstly, the gap V^{5+}–V^{4+} was fixed at 1.2 eV, secondly the FWHM of the two oxidation states were fixed to be equal.

EPR spectra were recorded at 25 °C with a spectrometer JEOL JES-RE 2X equipped with a cylindrical cavity ES-UCX2 using the following settings: magnetic field (H_0), 300 mT; scan width, 250 mT; microwave frequency ν_0, 9.430–9.440 GHz; microwave radiation power (P_w), 5 mW; modulation amplitude, 0.5 mT; modulation frequency, 100 kHz; time constant, 0.01 s; scan time, 8 min. The data treatment was done with JEOL "esprit 330, 01.521 version" software. The amount of V^{4+} was estimated by the area under the second-derivative curve integrated twice and by comparison with a series of standard mixtures of $VOSO_4$ in K_2SO_4. The vanadium mean oxidation state was evaluated by means of the equation: O.L. (EPR) = 5 × (atomic concentration of V determined by ICP-MS − atomic concentration of V^{4+} determined by EPR) + 4 × atomic concentration of V^{4+} determined by EPR. The 99% confidence interval of these measurements is about ±0.003.

Ammonia chemisorption was conducted on 100 mg of catalyst at 35, 150 and 350 °C using the static volumetric apparatus Micromeritics ASAP 2010C adsorption analyzer.

3. Results

Fig. 1 shows the evolution of the chlorobenzene conversion at 200 °C as a function of the water concentration in the stream for the three catalysts. The effect of water varies greatly with its concentration and the kind of active phases. In the case of VO_x, the chlorobenzene conversion increases from 29%, obtained without water, up to 44% and 42% in the presence of 1 and 2% of water. On the contrary, in the presence of 5% of water, the chlorobenzene conversion decreases to 26%. In the case of VO_x-WO_x, the increase of the water vapour concentration progressively induces a strong deactivation. The conversion decreases from 46% in the absence of water, to 30 and 16%, respectively, in the presence of 2 and 5% of water. The deactivation is much stronger in the case of the VO_x-MoO_x, catalyst which is almost completely deactivated when 2% of water is added in the stream. This deactivation corresponds to a decrease of the chlorobenzene conversion from 48 to 8%. At

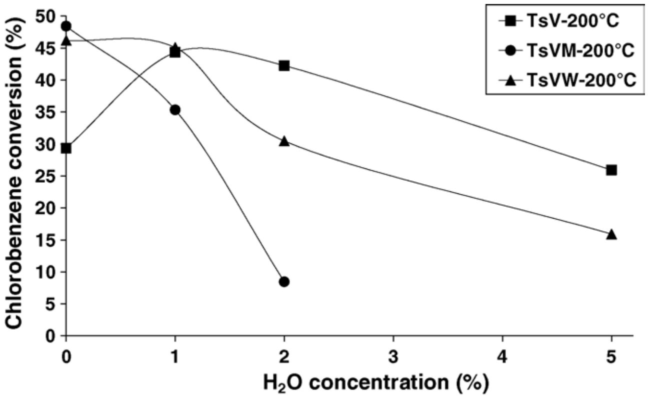

Fig. 1. Chlorobenzene conversion at 200 °C depending on the H_2O concentration (%).

Table 1
Vanadium oxidation level evaluated by EPR and XPS

	TsV		TsVW		TsVM	
	RPE	XPS	RPE	XPS	RPE	XPS
Fresh	4.980	4.97	4.907	4.77	4.944	4.83
0% H_2O	4.971	4.96	4.885	4.74	4.918	4.79
1% H_2O	4.958	4.89	4.867	4.70	4.859	4.67
2% H_2O	4.954	4.80	4.860	4.62	4.832	4.55
5% H_2O	4.950	4.78	4.842	4.57		

Table 2
Acidity of the catalysts after catalytic test (μmole NH_3/g catalyst)

	TsV			TsVM		
	0%[a]	1%[a]	5%[a]	0%[a]	1%[a]	2%[a]
Weak Acidic Sites (35 °C < W.A.S. < 150 °C)	223	219 (−2%)	220 (−2%)	223	221 (−1%)	229 (+3%)
Medium Acidic Sites (150 °C < M.A.S. < 350 °C)	102	98 (−4%)	91 (−10%)	150	132 (−12%)	78 (−48%)
Strong Acidic Sites (S.A.S. > 350 °C)	75	69 (−8%)	67 (−10%)	66	54 (−17%)	46 (−30%)

[a] H_2O concentration.

250 °C, the chlorobenzene conversions are higher and the influence of water is quite weaker. Nevertheless, the tendencies at 250 °C are identical to those noticed at 200 °C.

Table 1 shows the estimated value of the vanadium oxidation level of the catalysts before and after catalytic test. On the one hand, the "bulk" oxidation level estimations are based on the EPR and ICP results. On the other hand, the "surface" oxidation level results are obtained by decomposition of the XPS V $2p_{3/2}$ peak. The "bulk" results (EPR-ICP) show that in the "fresh" catalysts, the second phase (WO_x or MoO_x) induces a stabilisation of the active phase (VO_x) at a lower oxidation level, respectively, 4.907 and 4.944 for TsVW and TsVM rather than 4.980 for TsV. For all the catalysts after test, a progressive reduction of the vanadium was observed with the increase of the water concentration. This reduction is weak in the case of VO_x which goes from 4.971 to 4.950, respectively, in the absence and in the presence of 5% of water, while it is greater in the case of the combined phases. In the presence of WO_x, V undergoes a reduction from 4.885 in the absence of water to 4.842 in the presence of 5% of water. V was most affected in the presence of MoO_x, undergoing a reduction from 4.918 in the absence of water to 4.832 in the presence of 2% of water. The evolutions of the surface vanadium oxidation level (evaluated by XPS) are in very good agreement with the evolutions of "bulk" oxidation level. Nevertheless, surface oxidation level are lower than "bulk" ones. Two hypothesis could account for this: (i) surface vanadium species are more affected by the stream than the "bulk" ones and (ii) the deep vacuum, inherent to the XPS measurement, induces a reduction of the supported vanadium species.

Table 2 shows the amount of acid sites determined by NH_3-chemisorption at different temperatures (35–150–350 °C) for the catalysts after test. Acid sites are arbitrarily classified as Strong Acid Sites (S.A.S. = those on which NH_3 is still adsorbed above 350 °C), Medium Acid Sites (M.A.S. = those on which NH_3 remains adsorbed between 150 and 350 °C) and Weak Acid Sites (W.A.S. = those on which NH_3 remains adsorbed only below 150 °C). The number of W.A.S. was not significantly affected by the presence of water, but the number of M.A.S. and S.A.S. decrease with the increase of water concentration for the investigated catalysts (TsV and TsVM). The VO_x catalyst loses up to 10% of its acid sites (M.A.S. and S.A.S.) in the presence of 5% of water. The disappearance of M.A.S. and S.A.S. is even more marked in the case of the combined phase. For example, the TsVM catalyst loses, respectively, 48 and 30% of its M.A.S. and S.A.S. when 2% of water is added.

4. Discussion

For the two combined catalysts (TsVW and TsVM), adding H_2O in the gas stream is clearly detrimental to the conversion of chlorobenzene. Within the range investigated, the activity decreases with increasing H_2O concentration. Moreover, this depressing effect has also been observed on the TsV catalyst in the presence of 5% of water. The negative effect of water on the activity of vanadium oxide based catalysts has already been observed [4,7,10]. Nevertheless, the hypothesis proposed was based on a competitive adsorption between water and the chlorinated compound on the active sites. This hypothesis is usually only supported by catalytic results and sometimes by IR data, and never considers any possible effect of water on the chemistry of the active phase. Moreover, this hypothesis does not explain the different behaviours that we observed on three catalysts characterized by the same active phase (VO_x loaded at 0.75 monolayer on the same support).

Our characterizations pointed out the effect of water on the oxidation state of the active phase and on the acidity of the catalyst. For the three catalysts, water induces the reduction of the "bulk" and the "surface" of the VO_x phase. The degree of the reduction is progressive within the series: TsV < TsVW < TsVM. It is established that WO_x or MoO_x increase the reducibility of VO_x [11]. Therefore, the reduction of the vanadium phase, in the presence of water, seems to be modulated by the reducibility of the VO_x phase, which itself is dictated by the presence of WO_x or MoO_x. The progressive reduction of the VO_x seems to induce the decrease of the chlorobenzene conversion with the increase of the H_2O concentration.

The acidity characterization revealed the decrease of the number of medium and strong acid sites in the presence of water. The extent of the disappearance of the acid sites is progressive with the concentration of water and is much more marked for the combined catalyst. Strong Brönsted sites are indeed supposed to be the adsorption sites of the chlorinated VOC during the first step of their catalytic combustion [12,13]. The observed decrease of the number of M.A.S. and S.A.S., presumably Brönsted sites on VO_x and MoO_x phases, thus also correspond to a reduction of the number of chlorobenzene adsorption sites. This phenomenon accounts for the observed reduction of the chlorobenzene conversion.

Water thus clearly induces a negative effect on the performance of VO_x catalysts in the oxidation of Cl-VOCs, as it induces a reduction of the active phase and a decrease of the number of acid sites. Nevertheless, TsV catalyst shows an increase of activity in the presence of the lowest water concentrations (1 and 2%). To our opinion only one hypothesis could account for this positive effect, namely the retrieval of Cl^- from the surface by H_2O through the formation of easily desorbed HCl. This phenomenon was already reported in the case of vanadium oxide based catalysts [7,14].

5. Conclusion

Water plays a positive role in the catalytic oxidation of chlorobenzene. A plausible origin of this effect is that water removes the chlorine from the surface of the catalyst. But water vapour additionally influences negatively by two other routes. The first one is the reduction of the active phase (VO_x) which is progressive with the water concentration. This reduction is modulated by the reducibility of the VO_x phase which itself is dictated by the presence of WO_x or MoO_x. The second phase (WO_x or MoO_x), on the one hand, indeed increases the reducibility of the active phase (VO_x). This effect is strongly positive for the total oxidation of chlorobenzene. But, on the other hand, it over-sensitizes the catalysts with respect to water. The second negative route by which water is diminishing the activity of the catalyst is the reduction the medium and strong Brönsted acid sites involved in the chlorobenzene adsorption during the first step of the chlorobenzene oxidation. The relative importance of the three dynamic effects (retrieval of the chlorine, reduction of the active phase and decrease of the number of adsorption sites) allows us to explain the water influence on the VO_x based catalysts.

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