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Necessary conditions for a synergy between Ag and V_2O_5 in the total oxidation of chlorobenzene

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ABSTRACT

V_2O_5/TiO_2 catalysts are widely developed for the total oxidation of dioxins. However, this study presents an innovative way to improve the performances of V_2O_5/TiO_2 catalysts by the addition of silver. Three kinds of catalysts were synthesized: Ag/TiO_2, V_2O_5/TiO_2 and Ag–V_2O_5/TiO_2. The vanadia loading always corresponds to a 0.75 theoretical monolayer while 9 different loadings of silver were explored (0.02–12.5%). This new kind of catalysts is tested in the total oxidation of chlorobenzene which is a classical model molecule for dioxins. The samples were characterized by BET, XPS, XRD, ICP-AES and TEM before and after catalytic tests. The specific surface decreases with the increase of the silver loading for Ag/TiO_2 and Ag–V_2O_5/TiO_2 catalysts. XPS results show that the addition of silver to a V_2O_5/TiO_2 formulation induces a higher oxidation state of the vanadium which should be beneficial on the performances. A synergy is indeed observed for several loadings of silver with a maximum at a loading of 0.05 wt.%. This synergistic effect between silver and vanadia can only be achieved in the total oxidation of chlorobenzene by choosing appropriate operating conditions, namely conditions avoiding AgCl formation. This synergy is directly linked to an optimal silver loading which offers the best compromise between a high oxidation state of vanadia without a significant decrease of the specific surface of the catalyst.

1. Introduction

The abatement of dioxins constitutes a major concern in the field of atmospheric pollution. Dioxins, which refer to polychlorinated dibenzo-furans (PCDFs) and polychlorinated dibenzo-dioxins (PCDDs), are systematically formed in all kinds of combustion processes of organic fuels in the presence of chlorinated compounds, e.g. in municipal waste incinerators or in cogeneration units [1,2]. These molecules are very toxic and responsible for carcinogenic and hormonal problems even in very low concentrations [3]. Moreover, dioxins being very stable structures, their destruction is necessary directly at the source of emission. In this context, catalytic total oxidation is the most promising solution [4]. Vanadium-based catalysts are widely developed for this application and different ways were already explored to improve the activity of V_2O_5/TiO_2 catalysts [5–7]. Classically, the performances of this formulation are improved by the addition of molybdenum or tungsten oxides [8–10]. These improvements lead to a higher acidity which is generally considered as a determining factor for the adsorption of the pollutant. However, these conclusions were obtained with model molecules while our group has recently shown that this approach is not fully relevant [11,12]. The oxidation of dioxins is indeed negatively influenced by the addition of these doping phases in their total oxidation on V_2O_5/TiO_2 catalysts [13]. Recently, some authors tried an innovative way to improve the efficiency of vanadium based catalysts by the addition of noble metals [14–17]. Synergistic effects were claimed between the noble metal and supported vanadia in the total oxidation of aromatic VOC. However, these new systems were generally not used in the oxidation of chlorinated compounds. This aspect is a major drawback regarding to the oxidation of dioxins. The potential poisoning effect of the chlorine species is indeed well known and has to be studied in this reaction. The mechanism of this synergy is actually not really understood.

To further progress in this direction, silver is added to V_2O_5/TiO_2 catalysts by a wet impregnation method. The addition of silver could potentially bring electrophilic oxygens [18,19] which are interesting species in a reaction of total oxidation. This new kind of catalysts is characterized by ICP-AES, XRD, N_2-physisorption, TEM and XPS before and after the catalytic tests. These characterizations allow to describe the effect of the addition of silver on the physico-chemical properties of V_2O_5/TiO_2 catalysts. These catalysts are tested in the total oxidation of chlorobenzene which is a classical model molecule for dioxins. The aim of this work is to determine whether a synergy can be achieved between silver and vanadium and which conditions are required to observe this synergy. In this context, we will assume that there is a synergy between silver and vanadium if the catalytic performances of the Ag–V_2O_5/TiO_2

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catalyst are higher than the sum of the performances of the two corresponding reference catalysts, namely Ag/TiO_2 and V_2O_5/TiO_2.

2. Experimental

2.1. Preparation of the catalyst

Three kinds of catalysts were supported on TiO_2 (Degussa P25: 49 m^2/g; 85% anatase–15% rutile): Ag/TiO_2, V_2O_5/TiO_2 and Ag–V_2O_5/TiO_2. Silver and vanadia were introduced by a wet impregnation method. The $AgNO_3$ precursor (Aldrich, >99%) was dissolved in distilled water while the NH_4VO_3 precursor (Vel, >99%) was dissolved in distilled water and complexed with oxalic acid (Aldrich, >99%, molar ratio vanadium:oxalic acid = 1:2 [8]). An appropriate amount of titania was then added to the solution. The suspension was mixed for 2 h at room temperature and water was evaporated in a rotary evaporator under reduced pressure at 40 °C. The material was dried overnight in an oven at 110 °C and finally calcined in air in a muffle furnace (20 h, 400 °C). The vanadia loading always corresponds to a 0.75 theoretical monolayer while 9 different loadings of silver were explored (0.02–12.5 wt.%). The V_2O_5/TiO_2, Ag/TiO_2 and Ag–V_2O_5/TiO_2 catalysts are labelled TV, AgT-*x* and AgTV-*x*, respectively, where *x* denotes the silver content in wt.%.

2.2. Catalytic tests

The catalytic tests were performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The reactor was made of an inconel tube of 1 cm internal diameter. The catalytic bed was composed of 200 mg of catalyst powder selected within the granulometric fraction 200–315 μm and diluted in 800 mg of inactive glass spheres (diameter in the range 315–500 μm). The gas stream contained 100 ppm of chlorobenzene in He (Praxair), 20% of O_2 (Praxair; 99,995%) and He (Praxair; 99,996%) as diluting gas to obtain 200 ml/min (VVH = 37,000 h^{-1}). Two different procedures were used to evaluate the catalytic activity. In the "light-off" procedure, after stabilization at 100 °C, the reaction was run from 100 to 400 °C in a step mode. In the "alternative" procedure, the stabilization step was realized at 200 °C and the catalysts performances were measured at 200 and 250 °C. The interest of this alternative will be evoked later. In both procedures, the catalysts were stabilized for 150 min at each temperature. The analysis of reactants and products (CO_2, CO) was continuously performed by on line gas chromatography (GC). This equipment allowed to detect potential intermediate products of the reaction like hydrocarbons and chlorinated hydrocarbons. In both procedures, the conversion of chlorobenzene always corresponds to total oxidation. The selectivity of CO_2 is systematically 100% except when the conversion of chlorobenzene reached 100%. In this case, CO can sometimes be produced and its selectivity can reach up to 3%. The conversion is defined as the ratio reactant transformed/reactant in the inlet (in %). More details of the operating conditions can be found elsewhere [5,8,9].

2.3. Characterization

The weight percentages of V and Ag in the catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Iris Advantage apparatus from Jarrell Ash Corporation.

The BET specific surface area of the catalysts was measured by nitrogen adsorption at 77 K with a Micromeritics TriStar 3000 instrument. The samples were outgassed overnight at 150 °C under vacuum before the measurement.

Table 1
Specific surface area (SSA) and silver and vanadium contents (wt.%) of Ag/TiO_2, V_2O_5/TiO_2 and Ag–V_2O_5/TiO_2 catalysts.

Nominal Ag loading (%)	Ag/TiO_2		Ag–V_2O_5/TiO_2		
	SSA ($m^2\,g^{-1}$)	Ag (%)	SSA ($m^2\,g^{-1}$)	Ag (%)	V (%)
0	50.0	–	48.3	–	2.4
0.02	49.3	n.m.	47.0	n.m.	2.4
0.05	49.2	0.06	46.9	0.07	2.3
0.12	49.7	0.11	46.4	0.14	2.3
0.24	48.6	n.m.	46.3	n.m.	2.5
0.49	49.1	0.47	46.7	0.45	2.3
1.24	44.2	1.12	44.2	1.12	2.4
2.49	44.0	n.m.	37.8	n.m.	2.3
4.98	36.3	4.85	38.6	4.76	2.3
12.50	33.3	12.37	30.0	12.30	2.2

n.m. = not measured.

X-ray diffraction (XRD) measurements were performed on the catalysts with a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The 2θ range was recorded between 5 and 75° at a rate of 0.028° s^{-1}. The ICDD-JCPDS database was used to identify the crystalline phases.

TEM measurements were performed on a JEOL 2000FX, working under an acceleration voltage of 200 kV. For the analysis, the sample was dispersed in ethanol and homogenized by agitation. A droplet of the suspension was deposited on the grid and the solvent was allowed to evaporate.

Surface characterization was done with an X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra spectrometer (Kratos-Analytical, Manchester, UK) equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). The pressure in the analysis chamber was about 10^{-6} Pa. The analyzed area was 700 mm × 300 mm. The pass energy of the hemispherical analyzer was set at 160 eV for the wide scan and 40 eV for narrow scans. Charge stabilization was achieved by using the Kratos Axis device. The electron source was operated at 1.8 A filament current and a bias of −1.1 eV. The charge balance plate was set at −2.8 V. The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Ti 2p, Ag 3d, V 2p, Cl 2p and C 1s again to check for charge stability as a function of time, and the absence of degradation of the sample during the analyses. Special care was taken to make sure that vanadium and silver were measured fast enough in order to avoid potential reduction under vacuum. This was done by measuring these elements at first as soon as the vacuum level was low enough to allow proper XPS measurements (quick XPS procedure). The binding energy (BE) values were referred to the C–(C, H) contribution of the C 1s peak at 284.8 eV. Molar fractions (%) were calculated using peak areas normalized on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors, and transmission factors provided by the manufacturer. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). More details of the exact settings and peak analysis can be found elsewhere [16,20].

3. Results and discussion

3.1. Physico-chemical characterization

Elementary analyses reveal a good agreement between experimental and nominal data for all catalysts (Table 1). There are no significant differences between AgTV catalysts and the corresponding AgT and TV catalysts.