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Chromia on silica and zirconia oxides as recyclable oxidizing system: structural and surface characterization of the active chromium species for oxidation reaction

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Abstract

Chromium oxide samples supported over silica and zirconia were prepared by wet impregnation of the supports with aqueous solution of CrO_3. In order to investigate the influence of the preparation method on the chromium dispersion and oxidation state, one sample was prepared by sol–gel technique. The materials were structurally characterized by XRD analysis. The oxidation states of chromium species were investigated by XPS, DRS and TPR/TPO techniques. EPR analyses were also carried out for the sample Cr/SiO_2, that due to the low crystalline state exhibits broad XPS signals. In this case, particular attention was paid to the presence of Cr(V) and Cr (III) species and their concentration.

The oxidizing performances of the chromia supported reagents have been evaluated for the liquid phase oxidation of benzyl alcohol to benzaldeyde, in absence of molecular oxygen. With the aim to investigate the redox behaviour of anchored Cr and to evaluate the amount of regenerable Cr species (upon TPR/TPO process), oxidation tests were carried out on fresh and aged samples (i.e. after 7 redox cycles up to 600 °C). A correlation was found between the benzyl alcohol conversion and the amount of chromium reduced by TPR of used samples (i.e. after 22 h of reaction).

Keywords: Chromium supported oxides; XPS; TPR/TPO cycles; Benzyl alcohol oxidation

1. Introduction

Supported chromium oxides are industrially important catalytic materials. They are used in oxidation, polymerisation, dehydrogenation–hydrogenation, $deNO_x$ reactions [1]. Particularly, a huge amount of different methods using chromium (VI) reagents has been developed for the oxidation of alcohols to aldehydes and ketones [2,3]. However, the Cr(VI) oxidant is usually not regenerated and the toxic effluents result in serious drawbacks, especially on an industrial scale. In order to overcome this problem, the use of reagents adsorbed on inert supports, that can be easily recovered, has been applied in organic synthesis. Chromium reagents adsorbed on alumina and zirconia supports have been reported to give high yields in alcohols oxidation [4,5]. Recently, we have reported that chromium oxidants over silica and zirconia, prepared by both wet impregnation and sol–gel method, are useful reagent for oxidation of alcohols [6,7]. These materials were easily recovered from the reaction mixture without any leaching of chromium in solution. Moreover, recycling studies have indicated that they can be regenerated by calcinations at 400–600 °C, depending on the support [7]. Therefore, a deep structural investigation of these materials is desirable in order to detect the chromium species in the fresh and aged (i.e. after 7 redox cycles) samples and their importance in the oxidation of benzyl alcohol.

In the present paper, Cr/silica and Cr/zirconia samples were investigated by several techniques, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR) and oxidation (TPO). Particular attention was devoted to the characterization of chromium species in the Cr/silica sample, that was studied also by electron paramagnetic resonance (EPR) spectroscopy.

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2. Experimental

All the chemicals (Aldrich) used were analytically graded.

2.1. Samples preparation

Chromia samples (Cr 2 wt.%) were prepared by wet impregnation of the supports, silica (BET 450 m^2/g, pore size 10 Å) and zirconia (BET 35 m^2/g, pore size 30 Å) with aqueous solution of CrO_3, as previously reported [7]. The so prepared chromium specimens (labelled as Cr/SiO_2 and Cr/ZrO_2) were calcined at 600 °C for 1 h (fresh samples), in order to anchor the chromium to the –OH groups of the support. A second zirconia sample (Cr 9 wt.%), labelled as sgCrZrO_2, was prepared by one pot sol–gel method, using $CrCl_3{\cdot}6H_2O$ and $Zr(OCH_2CH_2CH_3)_4$ as precursors [7]. After calcination at 600 °C for 1.5 h (fresh sample), the material showed surface area of 40 m^2/g and pore size 20 Å. In order to study the influence of ageing on the redox properties, Cr/silica and Cr/zirconia fresh samples were subjected to seven TPR/TPO cycles (aged samples), according to the procedure described in the following section.

2.2. Characterization

XRD patterns were recorded with a Philips apparatus, using nickel filtered Cu Kα radiation. Diffraction peaks were fitted by using a pseudo-Voight function and the crystalline phases were identified by comparison with the ICDD files [8]; card no. 38-1479 for α-Cr_2O_3, no. 37-1484 and no. 17-923 for monoclinic and tetragonal ZrO_2 phases, were used, respectively. XPS analyses were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the non-monochromatised Al Kα source (1486.6 eV) run at 14 kV and 15 mA.

Temperature programmed reduction and oxidation studies were carried out on a Micromeritics 2910 instrument, equipped with a thermal conductivity detector (TCD). In a typical experiment TPR/TPO, H_2 (5% in Ar, flow rate 30 ml/min) and O_2 (5% in He, 30 ml/min) were flowed, respectively, over the sample (100 mg), heating from room temperature up to 600 °C.

DRS measurements were collected at room temperature, in air with a PC Shimadzu UV-2401 spectrometer, in the wavelength range 300–800 nm, using Eastman white reflectance standard as reference.

EPR spectra were recorded at room temperature and at −196 °C on a Varian E-9 spectrometer (X-band). The g values were determined taking as reference the sharp peak at $g = 2.0008$ of the E'_1 centre [9] (marked with an asterisk in Fig. 3, see later). The absolute concentration of the paramagnetic species was determined from the integrated area, using as standard the Varian strong pitch ($5 \times 10^{15} \pm 20\%$ spin cm^{-1}) [9].

2.3. Benzyl alcohol oxidation tests

The benzyl alcohol oxidation by using Cr supported samples was carried out in a magnetically stirred glass reactor (stirring rate 1200 rpm), at room temperature, under argon atmosphere (see [7] for experimental details). The benzyl alcohol concentration in CH_2Cl_2 was 0.05 M and a molar ratio of Cr/alcohol of 2/3 was used. Oxidation tests were carried out on both, fresh and aged samples (i.e. after 7 redox cycles TPR/TPO up to 600 °C). The conversion of benzyl alcohol to benzaldehyde was monitored by withdrawing periodically (every 30 min for the first 6 h, then every 1 h) samples of the solution and analysing them by GC–MS analysis. The reaction was stopped in any case after 22 h, because no more conversion was observed. After the reaction, the materials were easily recovered from the reaction mixture without any leaching of chromium in solution, as determined by atomic adsorption spectroscopy (AAS).

3. Results and discussion

In a previous paper we have reported that Cr/silica and Cr/zirconia samples are useful reagents for oxidation of alcohols in absence of oxygen and that they are easily regenerable [7]. However, we have found that the oxidizing performances along with the recyclability of these Cr samples by calcination treatments, strongly depend on the type of support and on the preparation method. Therefore, in order to correlate structure and reactivity we have investigated the structural and chemical modifications by XRD, TPR, XPS and DRS techniques. For a selected sample, Cr/SiO_2, the nature of chromium species has been studied also by EPR spectroscopy. The oxidation step up to 600 °C, in the preparation of the materials, favours anchoring of chromium species by esterification with the hydroxyl groups of the support [10]. The extent of the anchoring is strongly dependent on the nature of the support and on the Cr loading. According to the literature [11–14], being silica more acidic than zirconia, Cr(VI) is better anchored to the zirconia than to silica. On the other hand, many other parameters as the surface area, number of –OH groups and Cr loading could influence both, the chemical state of supported chromium and their degree of reoxidability.

Fig. 1 shows the XRD patterns of aged Cr supported samples, i.e. after seven redox cycles (TPR/TPO up to 600 °C) along with the pure ZrO_2 pattern. In both samples, Cr/ZrO_2 and sgCr/ZrO_2, chromia appears well dispersed. No chromium phases were detected in the XRD patterns of fresh samples as well as after seven redox cycles. On the other hand, although no chromium diffraction peaks were detected in the fresh Cr/SiO_2, sintering of the chromium species is likely to occur over the acid silica support, after successive cycles. Indeed, crystalline peaks of the more stable α-Cr_2O_3 oxide were observed after the redox cycles. Monoclinic (m) and tetragonal (t) phases coexist in the

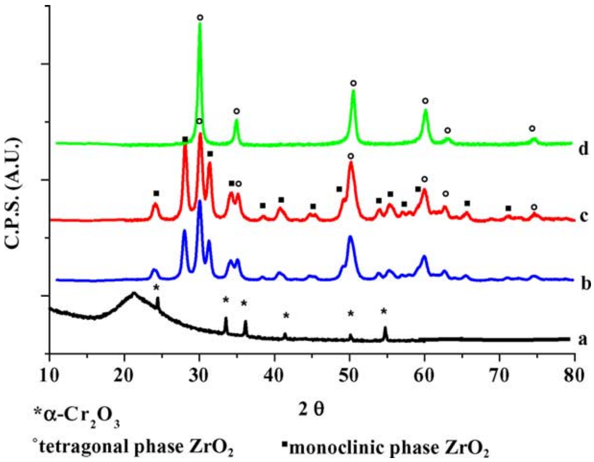

Fig. 1. XRD patterns of Cr supported samples after seven redox cycles (TPR/TPO up to 600 °C). The diffractogram of the ZrO_2 support is reported for comparison: (a) Cr/SiO_2; (b) ZrO_2 support; (c) Cr/ZrO_2; (d) sgCr ZrO_2.

Cr/ZrO_2 sample as well as in the zirconia support [15], as shown in Fig. 1. Upon seven redox cycles, the monoclinic modification of zirconia predominates in the impregnated sample. It is worth noting how different is the development of textural properties with the temperature for the sgCr/ZrO_2 sample, in comparison with Cr/ZrO_2 and pure zirconia. The protective effect of Cr(III) to prevent the structural transition (tetragonal to monoclinic) of the zirconia is evident from the inspection of Fig. 1. In agreement with the literature [16] the observed stabilization of metastable t-ZrO_2 could be ascribed to a mutual interaction between Cr(III) and zirconia in our sgCr/ZrO_2 sample. As a result, sgCr/ZrO_2 displays only the diffraction lines of the tetragonal phase. In Table 1 the TPR results (I and VII redox cycles) of Cr supported samples are summarized. From the amount of hydrogen consumption, the changes of oxidation state $(n - m)$ were calculated [13]. Similarly, the percentage of Cr(VI) reduced was calculated by the hydrogen consumption, considering simply the reduction Cr(VI) to Cr(III), see Table 1. In any case, an incomplete reduction of Cr(VI) was observed.

The oxidation state change $(n - m)$ reaches a value of 2.37 with the fresh Cr/SiO_2, then after seven redox cycles decreases. Considerable deviations of $(n - m)$ values from the theoretical 3 were observed with both chromium zirconia samples. These findings suggest that beyond a saturation coverage which depends on the nature of the support (surface area and number of –OH groups) excess of chromium species not stabilized on the support, is converted by calcination treatment at 600 °C (during the samples preparation step) into Cr with lower oxidation state, not reoxidable.

Moreover, in the case of sol–gel Cr/ZrO_2 sample the Cr(III) species in close contact with the support should be stabilized into the low oxidation state.

Comparing the redox behaviour of Cr/SiO_2, Cr/ZrO_2 and sgCr/ZrO_2, we can conclude that although a smaller portion of Cr(VI) is stabilized over zirconia, it appears more regenerable ($n - m$ values stables) compared to Cr over silica. In Fig. 2 the first TPR profiles of the Cr samples are showed. Both Cr zirconia samples are reduced at lower temperature than Cr/SiO_2 (Fig. 2), for each sample the position of maximum reduction temperature after seven redox cycles does not change. Information concerning the near-surface composition as well as the chromium oxidation state have been obtained from XPS analysis (Table 1). The simultaneous presence of different oxidation states was detected, depending on the nature of the support and treatment conditions [17]. The presence of Cr(VI) along with some Cr(III) was detected at once in the fresh samples, Cr/ZrO_2 and sgCr/ZrO_2; then, in the aged ones (after 7 redox cycles) the ratio Cr(III)/Cr(VI) doubles. The fresh Cr/SiO_2 exhibits a broad band centred at 578.2 eV. The poor quality of the spectrum probably is attributable to the morphology of the sample. However, due to the broadness of the signal no definite assignment of the Cr species can be done, only the presence of several oxidation states can be inferred. After 7 redox cycles, the XPS signals become well resolved and the

Table 1
Summarized TPR and XPS results on Cr supported samples, before benzyl alcohol oxidation

Samples before benzyl alcohol oxidation	TPR (mmol H_2/mmol Cr)	Changes of oxidation state $(n - m)$[a]	% Cr(VI) reduced to Cr(III)[b]	Cr 2p 3/2 (eV) (Cr oxidation state)	Ratio Cr(III)/Cr(VI) (XPS)	at.% Cr, XPS (at.% Cr analytical)
Cr (2 wt.%)/SiO_2 (fresh sample)	TPR (I) 1.18	2.37	79	578.2 (6 eV) Cr(VI)	–	1.6 (0.78)
After seven redox cycles	TPR (VII) 0.99	1.98	66	576.4 (3.8) Cr(III), 579.5 (3.2) Cr(VI)	4.0	1.1
Cr (2 wt.%)/ZrO_2 (fresh sample)	TPR (I) 0.90	1.80	60	576.3 (2.4) Cr(III), 578.8 (2.9), Cr(VI)	0.7	3.3 (1.58)
After seven redox cycle	TPR (VII) 0.88	1.76	59	576.9 (2.6) Cr(III), 579.2 (2.6) Cr(VI)	1.4	2.2
sgCr (9 wt.%)/ZrO_2 (fresh sample)	TPR (I) 0.53	1.06	35	576.3 (2.5) Cr(III), 578.3 (3.2) Cr(VI)	1.4	3.3 (7.11)
After seven redox cycle	TPR (VII) 0.52	1.03	34	576.5 (2.5) Cr(III), 578.8 (2.5) Cr(VI)	3.0	3.9

FWHM (full-width half-maximum) values are given in parentheses.

[a] The $(n - m)$ values were calculated from the hydrogen consumption (mmol H_2/mmol Cr) during the TPR, according to the reaction: $Cr^n + [(n - m)/2]H_2 \Leftrightarrow Cr^m + (n - m)H^+$.

[b] The percentage of reduced Cr was calculated by supposing that Cr(VI) is reduced to Cr(III).

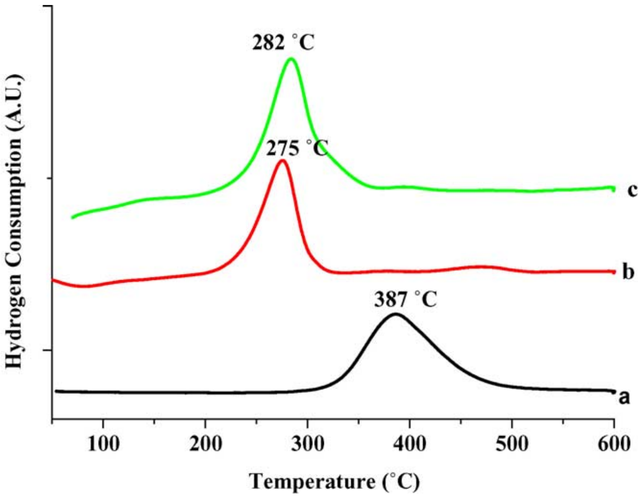

Fig. 2. First TPR (H_2 5% in Ar) profiles for the Cr supported samples (as-prepared): (a) Cr/SiO_2; (b) Cr/ZrO_2; (c) $sgCr/ZrO_2$.

two bands, assigned to Cr(VI) and Cr(III), respectively, are visible. Moreover, the ratio Cr(III)/Cr(VI) increases to the value 4, indicating that most of the chromium converts to Cr_2O_3 oxide, in agreement with the XRD picture (Fig. 1).

Finally, it results from XPS analysis that both samples Cr/SiO_2 and Cr/ZrO_2 prepared by wet impregnation, show a chromium enrichment over the surface, see Table 1. Upon successive redox treatments, the Cr at.% decreases to some extent. On the contrary, a surface depletion of Cr seems to occur in the $sgCr/ZrO_2$ sample. Indeed, through the sol–gel procedure, some chromium may have been encapsulated insight the zirconia framework, in accord with the XRD pointing to some Cr(III)–ZrO_2 interaction. By comparison, the TPR and XPS data of each sample (Cr/SiO_2, Cr/ZrO_2, $sgCr/ZrO_2$), a different distribution of the chromium species [Cr(VI)/Cr(III)] results. However, it should be considered that the TPR gives a complete picture of all the reducible species, whereas the XPS technique concerns mostly with the surface composition.

In order to assign more specifically the oxidation state of chromium species over silica, fresh and aged samples were analysed by EPR spectroscopy, with particular attention to Cr(V, III) species. After evacuation treatment at RT for 1 h (1×10^{-5} Torr), Cr/SiO_2 fresh and aged samples showed similar EPR spectra (Fig. 3). The predominant part of the spectrum is a broad ($\Delta H_{pp} \approx 500$ G) isotropic signal with g value near 2 (see Fig. 3a). This signal is well documented in literature and assigned to surface Cr^{3+} clusters, like α-Cr_2O_3 small particles [9,18]. The spectrum also shows, as a minor component, an axial signal ($g_{\parallel} = 1.958$, $g_{\perp} = 1.975$), due to surface Cr^{5+} ions (chromyl species), Figs. 3a and b [19]. In the aged samples a peak at $g = 1.985$ was also detected, probably due to a ligand different from oxygen in the chromyl species (carbonaceous impurity). When the spectrum were recorded at −196 °C, the Cr^{3+} signal undergoes a small broadening ($\Delta H_{pp} \approx 600$ G), whereas Cr^{5+} signals remain unchanged. The concentration of Cr^{3+} clusters markedly differs in the two samples, being 45% of total Cr-content in aged sample and 14% in the fresh one. While, the Cr^{5+} concentration is ≈300 ppm in both, fresh and aged samples. EPR measurements recorded at −196 °C are in good agreement with the data so far discussed.

Finally, DRS data (not reported for sake of conciseness) confirm the presence of Cr(VI) species, as chromate [14] (two bands at $\lambda = 260$–280 and 370–380 nm) in all the fresh samples, whereas features attributable to Cr(III) [14] (two bands at $\lambda = 450$–465 and 580–600 nm) were detected in the aged ones. However, it should be noted that the quality of the spectra strongly depends on the nature of the support and preparation method of Cr system, the best resolved band being that of the sample Cr/ZrO_2.

In Table 2, the data concerning the benzyl alcohol oxidation, in absence of oxygen, over fresh and aged samples

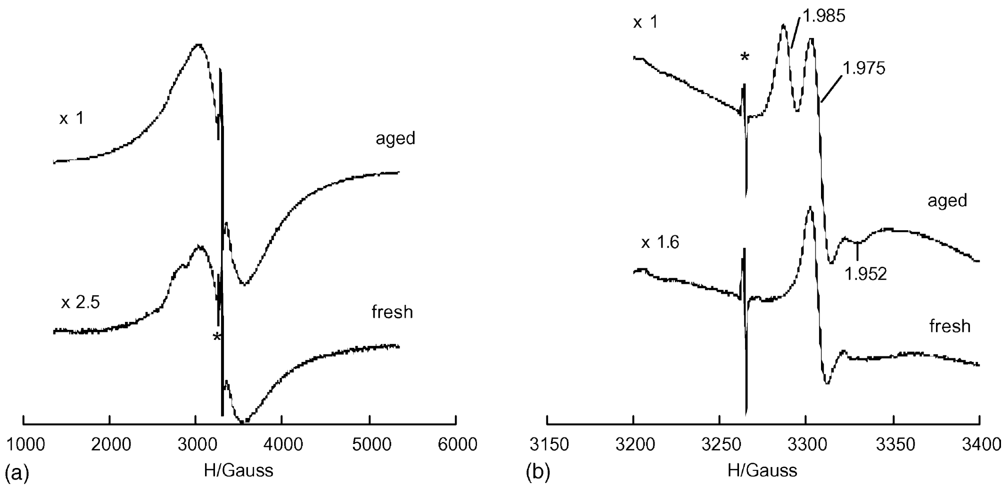

Fig. 3. EPR spectra recorded at room temperature of Cr (2 wt.%)/SiO_2, fresh and aged samples: (a) in the range 1000–6000 H/G; (b) in the range 3150–3400 H/G. * Sharp peak at $g = 2.0008$ of the E'_1 centre [9], as reference.

Table 2
Oxidation of benzyl alcohol (0.05 M) with Cr supported reagents: relationship between benzyl alcohol conversion % and H_2 consumption (mmol H_2/mmol Cr) for the used samples (i.e. after reaction, 22 h)

Samples	Time (h)	Benzyl alcohol conversion (%)	Constant rate[a] (h^{-1})	TPR (mmol H_2/mmol Cr) after reaction, 22 h	Percentage[b] of active Cr species
Cr (2 wt.%)/SiO_2 (fresh sample)	2	30.5	0.133	0.12	90
	22	82.0			
After seven redox cycles	2	19.6	0.076	0.11	88
	22	53.0			
Cr (2 wt.%)/ZrO_2 (fresh sample)	2	17.2	0.043	0.09	89
	22	49.0			
After seven redox cycles	2	14.0	0.038	0.09	84
	22	45.0			
sgCr (9 wt.%)/ZrO_2 (fresh sample)	2	8.7	0.020	0.07	80
	22	27.0			
After seven redox cycles	2	8.2	0.018	0.06	78
	22	25.0			

[a] The constant rates (h^{-1}) were calculated by fitting the experimental data (moles of benzyl alcohol converted versus time) with a pseudo-first-order kinetic with respect to the benzyl alcohol concentration, for the first 5 h of reaction.

[b] The percentage of Cr species active in the benzyl alcohol oxidation was calculated on the basis of the alcohol conversion after 22 h of reaction, taking into account the percentage of Cr(VI) reducible to Cr(III) determined by TPR.

(after 7 redox cycles) are listed. In order to compare the oxidizing activities of the different systems, the benzyl alcohol conversion after 2 and 22 h, was reported in Table 2. The experimental data (moles of benzyl alcohol converted versus time) fit well a pseudo-first-order kinetic with respect to the benzyl alcohol concentration, for the first 5 h of reaction. The first-order rate constants (h^{-1}) calculated are reported in Table 2. With the aim to estimate the percentage of Cr species active in the benzyl alcohol oxidation, TPR experiments were carried out also on the used samples, i.e. after 22 h of reaction. On the basis of benzyl alcohol conversion and taking into account the percentage of Cr(VI) reducible to Cr(III) (see Table 1), an estimate of the chromium active in the alcohol oxidation was calculated (Table 2). In any case, it appears that almost 90–80% of Cr(VI) is able to oxidize the probe molecule, depending on the system.

Considering that the oxidizing performances of the Cr reagents depend on the total amount of Cr(VI) reversibly reducible to Cr(III) species (as determined by TPR), it can be concluded that in the alcohol oxidation all Cr species with high oxidation state are involved and not only those at the surface. Surface and bulk oxygen diffusion phenomena are indeed involved in the redox process of other reducible oxides, as ceria-based materials [20].

4. Conclusions

Cr(VI) oxide on silica and zirconia appears an useful oxidizing reagent for benzyl alcohol oxidation and a valuable system in preventing environmental pollution, since no leaching of chromium in solution was observed. The relative abundance of different Cr species (by XPS, TPR, DRS and EPR) was found to be mainly controlled by the nature of the support, as well as by the preparation method (impregnation or sol–gel entrapment). The oxidation activity of both fresh and aged samples, is correlated with the amount of Cr(VI) that can be reversibly reduced, as determined by TPR measurements. On this basis, the alcohol oxidation appears to occur via a reduction process, involving both, surface and bulk Cr species. After seven redox cycles, Cr/ZrO_2 appears to be more regenerable compared to Cr/SiO_2 system.

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