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Nitrate hydrogenation on Pt,In/Al_2O_3: EXAFS and XANES characterization of fresh and used catalysts

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ABSTRACT

Pt,In/Al_2O_3 catalysts were characterized by EXAFS and XANES. Among the catalysts studied, the one that contained 1 wt.% of Pt and 0.25 wt.% of In had a remarkable high initial activity which decreased with reaction time. EXAFS characterization showed that the fresh solid consisted of a mixture of bimetallic Pt,In particles and monometallic Pt ones. After reaction, the amount of bimetallic particles decreased and unalloyed Pt considerably increased, which led to a partial deactivation of the catalyst.

1. Introduction

In a previous work [1], bimetallic Pt,In catalysts supported on alumina were studied for the reduction of nitrate in water. Pt(1 wt.%)In(0.25 wt.%) was the most active one, showing a high conversion rate at low time-on-stream. However, the conversion decreased with time, and we suggested that this effect was due to the segregation of Pt and In oxide phases under reacting conditions. This speculation was made taking into account XPS and TPR results. However, an EXAFS–XANES characterization was necessary to further confirm our hypothesis, and the results obtained are now presented in this communication. In addition, TEM and dynamic CO chemisorption experiments were carried out to further support the proposed catalytic behavior.

2. Experimental

Aqueous solutions of $PtCl_4H_2$ and $InCl_3$ were added to 20–40 mesh Al_2O_3 pellets in order to obtain the desired loading of Pt and In. The solids were dried overnight at 120 °C and calcined for 2 h, at 500 °C. Samples of the catalysts were pretreated under a flow of H_2 (100 ml min^{-1}) at 450 °C. More details about catalysts preparation and kinetic experiments are given in our previous work [1].

The sizes of metallic particles were measured from TEM images using a Jeol electronic microscopy, Model 100 CX II operating at 100 kV with 6 Å resolution. Dynamic CO chemisorption measurements were carried out by sending 250-μl pulses of 2.5% CO/N_2 on 0.10 g samples of fresh and used catalysts.

X-ray absorption spectroscopy (XAS) spectra were measured using the XAFS2 beamline at the LNLS, Laboratorio Nacional de Luz Síncrotron (Campinas, Brazil). EXAFS and XANES spectra of the Pt L_3 edge (11.6 keV) were recorded at room temperature using a Si(111) single channel-cut crystal monochromator in transmission mode with two ion chambers as detectors. The samples were reduced in H_2 at 450 °C for 2 h in a glass reactor. The powdered samples were then transferred under H_2 to glass cells with kapton windows, which were then sealed for the XAS experiments.

3. Results and discussion

3.1. Reaction results

In Table 1 it is shown that the catalyst with the lowest amount of In presents the highest activity and that it steeply decreases when the In content increases. Since the non-promoted Pt(1%)/Al_2O_3 catalyst presents little activity, an optimum Pt:In ratio at about 1%;0.25% is observed. Probably, higher loadings of In hinder the access of H_2 molecules to the Pt crystals, as suggested by the CO chemisorption results, discussed below.

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Table 1
Reaction and CO chemisorption results

Pt,In(wt.%)	Atomic relationship	Reaction rate[a]	μmol CO/μmol Pt[b]
1,1.2	0.5	1.48	ND[c]
1,1	0.6	2.89	ND
1,0.5	1.2	2.60	0.01 (0.17)
1,0.25	2.4	11.15	0.16 (0.21)
1	–	–	0.26

[a] (N-ppm) (min)$^{-1}$ (g catalyst)$^{-1}$. Calculated at conversions lower than 10%.
[b] Fresh catalysts. For used catalysts values are between brackets.
[c] Non-detectable.

3.2. CO chemisorption and TEM characterization

CO chemisorption results are shown in Table 1. It can be seen that the addition of small amounts of Indium to the Pt/Al_2O_3 provokes a strong decrease in CO chemisorption. This effect has been reported by Meriaudeau et al. for Pt-In/NaY Zeolite [2] and it occurs because bridged CO species are strongly depressed by In addition when Pt and In are forming bimetallic particles. Since no electronic modification is observed with IR studies of the adsorbed CO phases, In acts as a diluent of Pt atoms. Interestingly, in Table 1, it can also be observed that CO chemisorption increases for used catalysts, suggesting that the components of the bimetallic particles partially segregated under reaction conditions. A redispersion of the catalytic phases after reaction should be discarted, since TEM pictures of those shows that the crystals present in the used catalysts are bigger than those of the fresh ones. Fresh catalysts have particles of about 4 nm, and after use their size is more than two fold increased. These results, together with XPS and TPR experiments previously reported [1] suggests the importance of the presence of Pt,In bimetallic particles upon the reaction behavior.

3.3. EXAFS and XANES characterization of Pt(1 wt.%),In(0.25 wt.%)/Al_2O_3 fresh and used catalysts

Fig. 1 shows k^3-weighted fourier transforms of EXAFS signals of Pt and Pt,In samples (those of a foil of Pt are also shown for comparison). It can be seen that the fourier transform of the EXAFS spectrum of the monometallic sample is very similar to that of the foil of Pt, showing one main peak at 2.5 Å (without phase correction) with an appreciable decrease of its amplitude indicating that Pt is forming metallic clusters. For the bimetallic samples, two peaks at 2.20 and 2.75 Å approximately (without phase corrections) are observed, showing that Pt atoms are immersed in a more complex structure than in the monometallic catalyst and that there might be more than one scatterer around the Pt atoms.

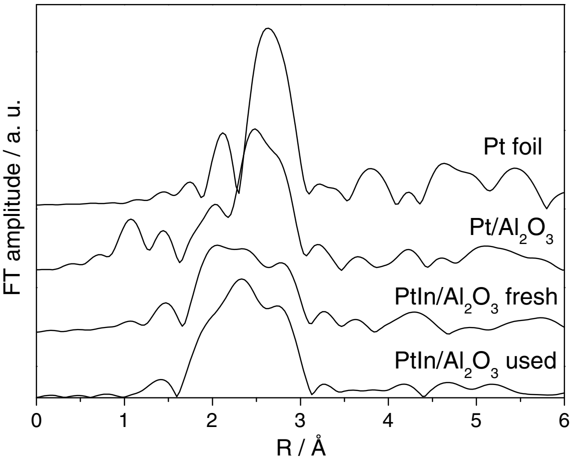

Fig. 1. Pt L_3 EXAFS results. k^3-weighted Fourier transform of the extracted EXAFS signals for the three catalysts and a foil of Pt.

In order to quantitatively analyze these data, the main peaks were isolated and fitted using standard procedures. Different combinations of shells were used to fit each spectrum. Theoretical standards were generated by the FEFF program [3]. The results obtained from the fits are shown in Table 2. The monometallic sample was fitted with only one Pt–Pt shell. Fig. 2.a shows the resulting fit for this sample. The existence of only Pt atoms in the vicinity of the absorber is indicating that in this sample the Pt is in metallic form. However, the average coordination number of the Pt–Pt shell is smaller than the value of 12, which is the coordination number for the Pt in a Pt foil. This is an indication of the high dispersion of Pt on the catalyst which would be forming very small metallic particles. It is possible to make an estimation of the size of these particles from the average coordination number making some assumptions on their shape [4]. Under the supposition of spherical particles, the fitted average coordination number of 6 ± 1 would correspond to 0.8 nm particles, approximately.

The fourier transform of the EXAFS signal corresponding to the fresh bimetallic catalyst was first fitted in the region between 1.5 and 3 Å using the same strategy as the monometallic one but a single Pt shell was not enough to fit the whole region. Very poor fits were obtained and it was not possible to reproduce the signal with only one Pt shell. For that reason the EXAFS signal was fitted using two coordination shells around Pt: one formed by indium atoms and the other one formed by platinum atoms. Different Pt-In alloys were considered to perform this fit. If we analyze the In-Pt phase diagram, at the Pt concentration of our samples (70% approximately), the stable phases would be Pt_2In and Pt_3In, if we assume a completed and balanced alloying [5]. However, at the nanoscale it may be possible to form nanoalloy structures that are not normally favorable at given compositions. For this reason, different alloys rich in Pt and rich in In were be considered. In particular, Pt_3In and Pt_3In_7 alloys were chosen for the EXAFS analysis. Pt,In phase and amplitude were obtained from the crystallographic data of the In_7Pt_3 alloy taken from Schubert and Pfisterer [6] and of the Pt_3In alloy taken from Ellner [7] using the FEFF program. The main difference between these two alloys is the distance from a Pt atoms to the first neighbor indium atoms which are located at 2.82 Å in Pt_3In and at 2.51 Å in Pt_3In_7 alloy. Fig. 2b shows the good results considering this fitting strategy. Table 2 shows the parameters fitted for both shells.

The existence of an indium shell around Pt absorbers is a clear indication of the formation of a Pt,In alloy in the catalyst, which is an important result by itself but it is not possible to quantify this phase directly from this result. The second shell of Pt atoms could be forming part of two different phases: the alloy itself and a segregated phase of metallic Pt. We have seen this behavior previously in Pt,Sn catalysts [8] so we cannot rule out this possibility. The Pt,In distance obtained from the fit is 2.51 Å, the same distance in the Pt_3In_7 alloy, indicating that an alloy rich in indium would be present in the catalyst. However, we have 70% of Pt atoms and a 30% of In atoms in the catalyst, so a rich in Pt atoms alloy would be ex-

Table 2
Results obtained form the fittings shown in Fig. 2

Sample	Scatterer	N	R(Å)	$\sigma^2 \times 10^2(Å^{-2})$
Pt/Al_2O_3	Pt	6 ± 1	2.71 ± 0.01	0.89 ± 0.08
$In,Pt/Al_2O_3$ fresh	In	1.9 ± 0.4	2.51 ± 0.01	1.2 ± 0.1
	Pt	4.2 ± 0.3	2.70 ± 0.01	0.93 ± 0.06
$In,Pt/Al_2O_3$ used	In	1.6 ± 0.4	2.51 ± 0.01	1.5 ± 0.2
	Pt	7.5 ± 0.4	2.69 ± 0.02	1.12 ± 0.03

N, average coordination number; R, interatomic distance; σ^2, Debye–Waller factor.