Combined TDPAC and EXAFS Study of InPt/FER Catalysts

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Time Differential Perturbed Angular Correlation (TDPAC) experiments using ^{111}In as probe were performed in order to determine the nature of In-sites in In-ferrierite (In/FER), before and after the incorporation of Pt through the hyperfine interaction between the nuclear quadrupole moment of the probe's nucleus and the extranuclear electric field gradient (EFG). Extended X-ray Absorption Fine Structure (EXAFS) measurements were performed to measure the absorbance above the Pt's L_{III} absorption edge in the transmission mode in order to determine the local environment of Pt atoms in Pt/FER and InPt/FER catalysts.

TDPAC spectra of ^{111}In in In/FER and InPt/FER taken at 500°C in air indicated that there are no changes in the indium surroundings after the incorporation of Pt. Three sites were found for indium in both samples. Two of them correspond to the two sites of indium in In_2O_3 and the third one is attributed to In in exchange sites of the zeolites. Their population, quadrupole frequencies and asymmetry parameters didn't change with the incorporation of Pt. EXAFS experiments showed similar near neighborhood Pt-O distances and Pt coordination number in Pt/FER and InPt/FER samples. There is no evidence of the presence of any In-Pt bimetallic entity in InPt/FER catalyst.

Key words: Hyperfine Interactions; TDPAC; EXAFS; Catalysis; Ferrierite.

Introduction

The cooperation of catalytic species has recently been studied for the selective catalytic reduction (SCR) of NO_x, in order to obtain a suitable catalyst under real conditions [1]. In this vein, the effect of Pt, Rh and Ir on the activity and stability of Co/Zeolites [2] and In/H-ZSM5 [3] in the selective catalytic reduction of wet NO_x with CH_4 has lately been reported. In the present contribution, the role of the Pt-In interaction in the activity and water resistance of bimetallic ferrierite and the nature of the species present is investigated, using Time Differential Perturbed Angular Correlation (TDPAC) and Extended X-Ray Absorption Fine Structure (EXAFS) techniques and catalytic tests.

Experimental

TDPAC technique: An experimental coplanar arrangement of four BaF_2 detectors at 90° for a fast-fast coincidence system was used. The time resolution of the equipment was 0.8 ns for the energies of the 133-242 keV γ-γ cascade of the $^{111}\mathrm{In} \xrightarrow{\mathrm{ec}} {}^{111}\mathrm{Cd}$ probe. The time-differential observation of the perturbed-angular correlation of gamma rays emitted from radioactive ^{111}In allows to characterize different In-species by means of different hyperfine interactions characteristic of each In-site present in the sample. The principle of the application of TDPAC to In compounds consists in determining the hyperfine interaction between the nuclear quadrupole moment of the intermediate level of the γ-γ cascade of the nuclear-probe and the

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electric field gradient (EFG) produced by all extranuclear charges, i. e. the electronic charges of the same atom plus the ionic charges of the lattice (mainly the first neighborhood of the probe).

The EFG is a second-rank tensor and hence it also contains information about the symmetry of the environment of the ^{111}In-probe atoms. This results from the charge density distribution that reflects the nature of the chemical bonds. Inequivalent probe sites in the unit cell or inequivalent sites due to the coexistence of several phases in the sample lead to a superimposing of "perturbation functions" $A_{22}G_{22}(t)$, which are fitted varying the quadrupolar frequency ω_Q and the asymmetry parameter η of each perturbation function. Different weights (relative concentration f) for each function are required in order to obtain the relative population of the different In-surroundings.

EXAFS technique: The absorption fine structure χ is defined as the normalized oscillatory part of the X-ray-absorption cross section in function of the incident photon energy E: $\mu(E)$, i. e. $(\mu - \mu_0)/\Delta\mu_0$, where μ_0 is the embedded-atom background absorption and $\Delta\mu_0$ is the jump in the background at the edge. From a qualitative viewpoint, the probability that an X-ray photon will be absorbed by a core electron depends on both the initial and final states of the electron. The initial state is the localized core level corresponding to the absorption edge. The final state is that the ejected photoelectron, that can be represented as an outgoing photoelectron wave, will be backscattered by the neighboring atom, thereby producing an incoming electron wave. The final state is then the sum of the outgoing and all the incoming waves, one from each neighboring atom. It is the interference between the outgoing and the incoming waves that gives rise to sinusoidal variation of μ vs. E known as EXAFS.

The X-ray absorption spectra were measured at the XAS beamline at the LNLS - National Synchrotron Light Laboratory, Campinas, Brasil. The EXAFS spectra of the Pt L_{III}-edge (11.6 keV) were recorded at room temperature in air using a Si(111) single channel-cut crystal monochromator. Samples of Pt/FER and InPt/FER were measured in order to determine the Pt-surrounding. This enabled us to know if its neighborhood was modified by the incorporation of indium and to see if there was any interaction between Pt and In in the bimetallic catalyst.

Table 1. Fitted values of the parameters characterizing the observed interactions in the TDPAC spectra of Figure 1.

Sample	Population f [%]	Frequency ω_Q [MHz]	Asym. param. η	Distrib. δ [%]	Interaction
In/FER	29(6)	124(2)	0.66(3)	7(2)	I1
	19(6)	151(2)	0.24(3)	4(1)	I2
	53(6)	177(2)	0.35(2)	12(3)	I3
InPt/FER	25(2)	123(1)	0.70(2)	7(1)	I1
	17(1)	157(2)	0.23(2)	3(1)	I2
	58(2)	184(3)	0.29(2)	16(3)	I3
Bulk In_2O_3	77(2)	119.1(5)	0.71(1)	1.4(4)	I1
(Ref. 4)	23(2)	155.2(5)	0	1.0(4)	I2

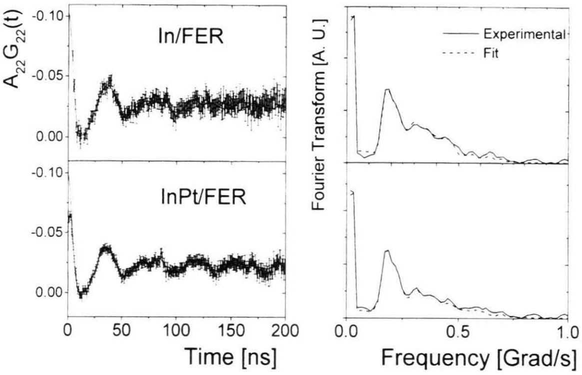

Fig. 1. *Left:* points, PAC spectra taken at 500°C of In/FER and InPt/FER; line, fitted function $A_{22}G_{22}(t)$. *Right:* their corresponding Fourier Transforms.

Samples and Catalytic Test

The starting materials were K-Ferrierites (Si/Al=9). The Ferrierite-based samples were prepared by ion exchange. Further details are supplied in [2]. The solids obtained were: $Pt_{0.5}$/FER, $In_{0.5}$/FER, $In_{0.4}Pt_{0.5}$/FER. For the samples measured by TDPAC ^{111}In was introduced as probe by adding traces of $^{111}InCl_3$ to the solution employed during preparation. The catalytic test was performed in a fixed-bed reactor. The typical mixture was NO = CH_4 = 1000 ppm, O_2 = 2%, H_2O = 2% balanced to 1 atm with He.

Results and Discussion

The calcined In/FER was active for the SCR of NO with CH_4 only at dry reaction conditions. It converted 60% of NO to N_2 under a dry reaction stream. The In/FER reached such conversion at 400°C. The incorporation of 0.5% of Pt did not modify the activity of the oxidized monometallic Ferrierites in the

350 - 500 °C temperature range. After the addition of water to the reaction stream, the activity of InPt/FER was significantly affected at low temperatures: as the temperature increased, the solid recovered the activity, and at 500 °C it reached 85% of NO conversion. Interestingly, when water was removed, the InPt/FER presented a higher activity than the fresh sample.

In/FER and InPt/FER samples were studied by TDPAC in order to determine the number and concentration of inequivalent In-sites and to analyze the difference between these sites after the incorporation of Pt.

Figure 1 shows the time spectra of TDPAC measurements taken at 500°C in air. Their Fourier transforms are also shown. Table 1 shows the fitted hyperfine parameters obtained for these spectra. Both spectra indicate the existence of, at least, three hyperfine interactions. The interactions labeled as I1 and I2 for both samples have the same hyperfine parameters as ^{111}In in In_2O_3 [4]. This indicates that 50% of indium is forming In_2O_3 in both samples. Slight differences with the pure In_2O_3 case should be associated with the small dimensions of the crystallites present in the catalysts [5]. The third interaction has the same hyperfine parameters for both samples. Considering this conversion shown by these catalysts and the fact that In_2O_3 is inactive for the reaction of interest [5], this interaction must be assigned to In in exchange sites, presumably in the form of $(InO)^+$ [6]. The fact that there is no change in the hyperfine parameters corresponding to the catalytic active species of indium indicates that there is no direct interaction between indium and platinum. If this happens, the first neighborhood of In atoms should be different, and hyperfine parameters characterizing the corresponding In-surrounding would change.

When a fraction of In-probes has very similar nearest-neighborhoods – and not identical –, a finite frequency distribution around a mean "precession frequency" due to inhomogeneities can be obtained. In our case, these "inhomogeneities" fitted for I3 can be attributed to ^{111}In-probes located in slight-different sites of exchange in the zeolite.

Figure 2 shows the Fourier transform of Pt L_3-edge k^3-weighted EXAFS spectra of Pt/FER, InPt/FER (Fig. 2a)) and the corresponding backtransform of the only peak present in the spectra (Fig. 2b)), corresponding to Pt-O bonds. Evidence for a higher coordination shell is slight since the peak intensities at appropriate distances are on the order of the noise. Table 2 shows the fitted parameters N (nearest neighbors) and d (distance) for EXAFS oscillations shown in Figure 2b). Fourier transforms were obtained through standard procedures. The resulting data were fitted with experimental phase and amplitude functions from EXAFS measurements of PtO_2.

Table 2. X-ray Absorption spectroscopy results.

Sample	N^a	D^b [Å]	σ^2
Pt/FER	3.3(3)	2.02(1)	0.01(1)
InPt/FER	4.3(4)	2.03(1)	0.01(1)

^{a} The coordination number for the Pt-O pair. ^{b} The nearest-neighbor distance for the Pt-O pair

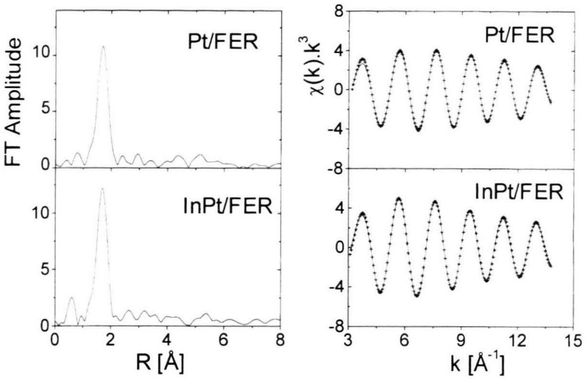

Fig. 2 a) Pt L_3-edge Fourier transform (k^3-weighted, Δk = 3.1 - 12.5 Å^{-1}). Phase shift is not taken into account. b) Crosses, the inverse Fourier transform of the major peak; line, calculated EXAFS function for Pt-O distances.

The fitted parameters (see Table 2) indicate that the Pt-nearest neighborhood is similar in both samples. The Pt-O bonds are the same (within the errors) while the coordination numbers are slightly different. The coordination number of Pt-O in InPt/FER is smaller than that in PtO_2, indicating that Pt is well dispersed over the ferrierite zeolite. The fact that there is no evidence of Pt-In bonds in the bimetallic sample indicates again that there is no direct interaction between In and Pt.

Considering the TDPAC results, which indicate the same In-surrounding in both samples, the difference found in the coordination number for Pt-atoms between both samples through EXAFS experiments should indicate that Pt atoms in InPt/FER catalysts have a higher oxidation state than in the Pt/FER ones.

Conclusions

The combined application of TDPAC and EXAFS techniques is a powerful tool to determine the interaction between highly dispersed metals as in bimetallic catalysts.

The short order sensitivity of the electric field gradient and the extended fine structure of the X-ray absorption spectroscopy let us discard the presence of any In-Pt alloy or any mixed oxide in the bimetallic sample. Thus, the promoting effect of Pt on In/FER catalysts should not be attributed to a direct interaction between In and Pt as in an alloy. The cause of that effect could be some kinetic mechanism of reaction that involves Pt and In atoms in two different steps.

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