

HYPERFINE/CHEMICAL CHARACTERIZATION OF HETEROGENEOUS CATALYSTS: Pt-In/Nb₂O₅ SYSTEMS

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ABSTRACT - Pt-In/Nb₂O₅ catalysts were investigated using Temperature Programmed Reduction and Time Differential Angular Correlation experiments. The results indicated the presence of In-O complexes for low loading In/Nb₂O₅ and Pt-In/Nb₂O₅ catalysts after calcination. These complexes did not form In₂O₃ crystalline phase. After reduction for Pt-In/Al₂O₃, although it was not possible to determine univocally the surface structure, it was evidenced In is present in different states. A fraction of In atoms is bonded to niobia surface, as a surface complex that does not show crystalline structure similar to bulk In₂O₃. Other fraction of In atoms interacts with platinum, in the form of an alloy, in locations that present trigonal symmetry.

Keywords: angular correlation, niobia, platinum.

1. Introduction

Niobia (Nb_2O_5) supported platinum catalysts have been investigated as alternative catalysts for hydrocarbon conversion^[1-3]. After reduction at 773 K, platinum particles are decorated by partially reduced niobia species, with the creation of new interfacial sites^[4]. The dehydrogenation of paraffins is commercially carried out using an alumina supported platinum catalyst, containing indium as a promoter^[5]. Indium is able to dilute the platinum particles in these catalysts and improve the selectivity and activity in n-heptane dehydrogenation^[6].

In this work we report Temperature Programmed Reduction (TPR) and Time Differential Angular Correlation (TDAC) results obtained from experiments on the Pt-In/ Nb_2O_5 catalytic system.

TDAC is a nuclear spectroscopy which enables us to characterize material systems in an atomic scale through the determination of the hyperfine interactions (HI) parameters, here represented by the interactions between the nuclear electric quadrupole moment of a suitable probe-isotope and the electric field gradients originated from the probe-isotope neighbourhood; in this sense, announcing those neighbourhood dynamics. Characteristic measured parameters, obtained via detection of emitted γ -rays originated from the nuclear cascade of the probe-isotope, are *quadrupole frequency interactions* and *assymetry parameters*^[7]. Although the application of this technique in materials characterization have been used intensive and sistematically, only recently it started to be applied to catalytic systems^[8-10].

2. Experimental

2.1- Catalyst Preparation:

Niobia (BET area= 65 m^2/g) was obtained by calcination of niobic acid (CBMM HY340) for 2h.

Pt/ Nb_2O_5 was prepared by incipient wetness using an aqueous solution of H_2PtCl_6 (Merck). After impregnation, the sample was dried at 373K for 24 h followed by calcination at 773K for 2h.

Pt-In/ Nb_2O_5 catalysts were prepared by impregnating the calcined Pt/ Nb_2O_5 catalyst with an aqueous solution of $\text{In}(\text{NO}_3)_3$ (Aldrich) followed by drying at 373K and calcination at 773K.

2.2 - Temperature Programmed Reduction:

Temperature Programmed Reduction (TPR) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples (300 mg) were dehydrated at 423 K for 30 min in a He flow prior to reduction. After cooling to room temperature (RT), a mixture of 5% H_2 in Ar flowed through the sample at 30 cm^3/min , raising the temperature, at a heating rate of 10 K/min, up to 773 K.

2.3 - Time Differential Angular Correlation:

In the present work we used for the TDAC measurements the ^{111}Cd (172keV-247 keV) nuclear cascade resulting from the decay of ^{111}In . Twelve simultaneous γ - γ coincidence spectra were measured for each system and the experimental data were worked out according convenient data treatment in order to obtain adjustable functions.

The carrier free ^{111}In TDAC suitable probe-isotope was added to all the samples by diffusing ^{111}In (10^{-4} at. %) to the $\text{In}(\text{NO}_3)_3$ impregnation solution; so, the probe-isotope would go to the same positions as In atoms. The samples were placed in an experimental setup that allowed to perform *in situ* TDAC experiments as well as their treatment. The samples were reduced at 773K for 2 hours under a flow of H_2 ($30 \text{ cm}^3/\text{min}$).

3. - Results and Discussion

3.1- Temperature Programmed Reduction

TPR profiles of the catalysts are presented in Fig. 1. The profile of $\text{Pt}/\text{Nb}_2\text{O}_5$ presented reduction peaks at RT and 355 K that correspond to PtO_2 reduction^[11]. A peak at 500K was also observed and it is usually ascribed to an oxychloroplatinum surface complex^[12]. The broad peak centered at 648 K is related to partial reduction of the support.

$\text{Pt-In}/\text{Nb}_2\text{O}_5$ presented similar spectra to $\text{Pt}/\text{Nb}_2\text{O}_5$ with the reduction of In taking place at lower temperatures than in the case of $\text{In}/\text{Nb}_2\text{O}_5$. The difference between H_2 uptakes during TPR of 1%Pt-0.7% $\text{In}/\text{Nb}_2\text{O}_5$ and of 1% $\text{Pt}/\text{Nb}_2\text{O}_5$ indicates that approximately 50% of In is in a zero valent state. This is in the same range as observed previously for $\text{Pt-In}/\text{Al}_2\text{O}_3$ catalysts.

3.2 - Time Differential Angular Correlation

TDAC results are displayed in Fig. 2, while Table I shows the HI parameters adjusted from the experiments. After calcination, the 1% $\text{Pt}/\text{Nb}_2\text{O}_5$ ^{111}In doped catalyst showed a frequency distribution pattern, indicating the atoms of ^{111}In were not located in translational repetitive crystalline lattice sites. Probably there was the formation of In-O bonds, with the spectrum displaying a pattern different from those well known of bulk In_2O_3 ^[13]. Similar results were previously obtained for $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts^[9-10] and for oxidized In implanted Pt^[14]. After reduction of the above 1% $\text{Pt}/\text{Nb}_2\text{O}_5$ catalyst, at 773K, the TDAC displayed a typical Pt-In alloy spectrum^[15]. This is a strong indication of the tendency of alloy formation in $\text{Pt-In}/\text{Nb}_2\text{O}_5$, and it is consistent with previous results for $\text{Pt-Sn}/\text{Nb}_2\text{O}_5$ ^[11] where the formation of Pt-Sn alloys was observed. In the case of $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts, an interaction of Pt and In was also noted^[9-10], but there was not the formation of regular Pt-In alloy structures. Thus, the interaction between active metal and promoter is higher when Nb_2O_5 is used as support. The system Pt-(diffused ^{111}In impurity) displayed spectra were similar at RT and 773K (Figs. 2b-2c), indicating same structures at both temperatures. The exposure of the $\text{Pt}/\text{Nb}_2\text{O}_5$ sample to air caused the oxidation of the alloy as well as the formation of In-O bonds that were not in a regular crystalline-like structure (Fig. 2d). The Pt-In alloy was formed again after repeating the reduction treatment (Fig.2e).

For all the samples, after reduction at 773K a relaxation pattern was also observed. This is related to a mobility of the neighborhood of the probe isotope in the samples^[10].

The 1% $\text{In}/\text{Nb}_2\text{O}_5$ system, after calcination, presented the frequency distribution pattern (Fig. 2f) (In_2O_3 pattern absent). Our recent work demonstrated in the case of Al_2O_3 supported catalysts the formation of In_2O_3 structure only for high In contents of the sample. For low In contents, In-O bonds are formed but are well dispersed and thus they are not arranged in a regular crystalline-like structure. After reduction we could not observe the formation of a In^0 structure, as there was again the display of a frequency distribution pattern. This finding is consistent to the TPR experiments, that showed there was only the reduction of a fraction of In atoms. Thus the combination of some In^0 formation and the remaining In-O irregular structures lead to a frequency distribution pattern.

For the 1%Pt-1%In/Nb₂O₅ catalyst, after calcination, a frequency distribution pattern concerned to the In-O bonds was obtained. The reduction of this sample lead to a pattern that can be interpreted as the combination of the formation of Pt-In alloy and the formation of In-O bonds. This picture also agrees with the TPR experiments that showed that around 50% of the In atoms is in a zero-valent state.

4- Conclusions

The TDAC results indicated the presence of In-O complexes for low loading In/Nb₂O₅ and Pt-In/Nb₂O₅ catalysts after calcination. These complexes do not form In₂O₃ crystalline phase. After reduction for Pt-In/Al₂O₃, although it was not possible to determine univocally the surface structure, it was evidenced In was present in different states. A fraction of In atoms is bonded to niobia surface as a surface complex that does not show crystalline structure similar to bulk In₂O₃. Other fraction of In atoms interacts with platinum, in the form of an alloy, in locations that present trigonal symmetry.

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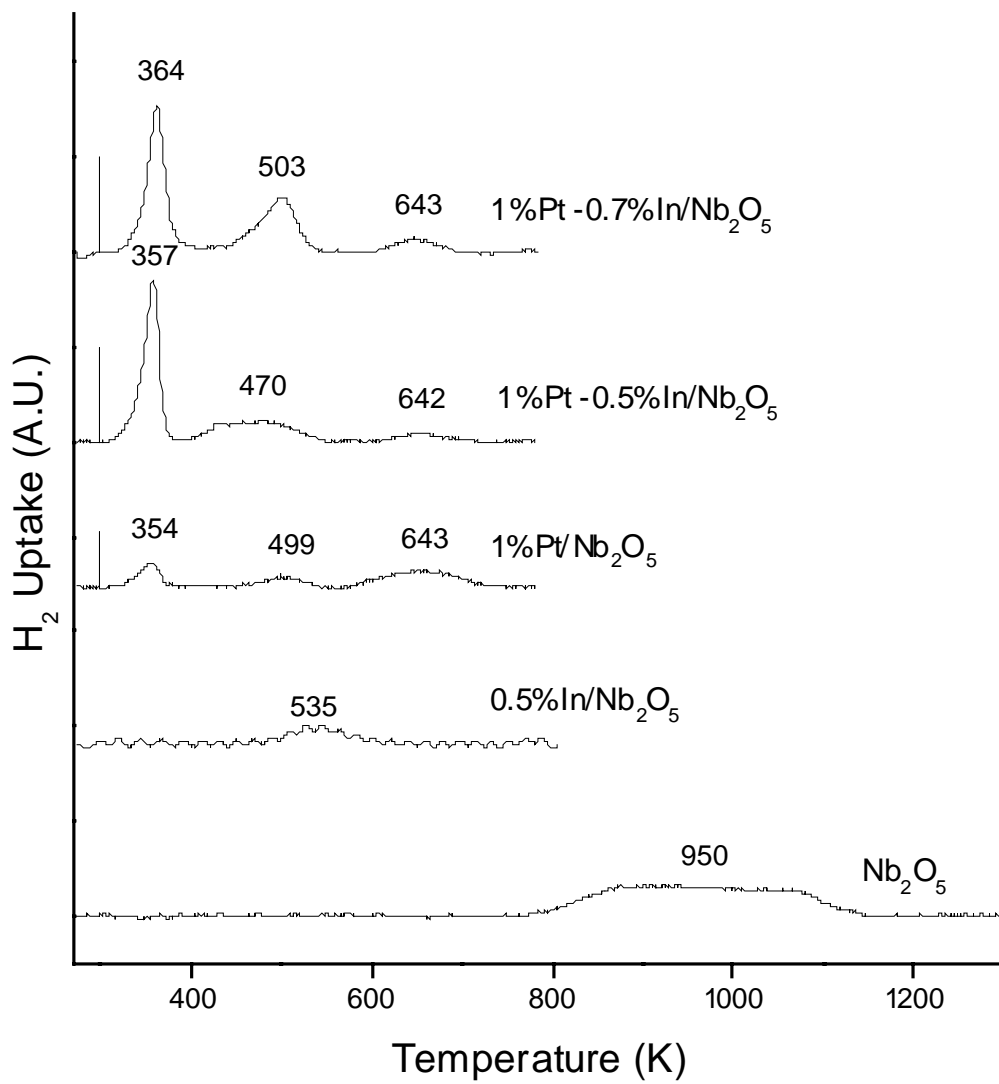


Figure 1- Temperature Programmed Reduction of Pt-In/Nb₂O₅

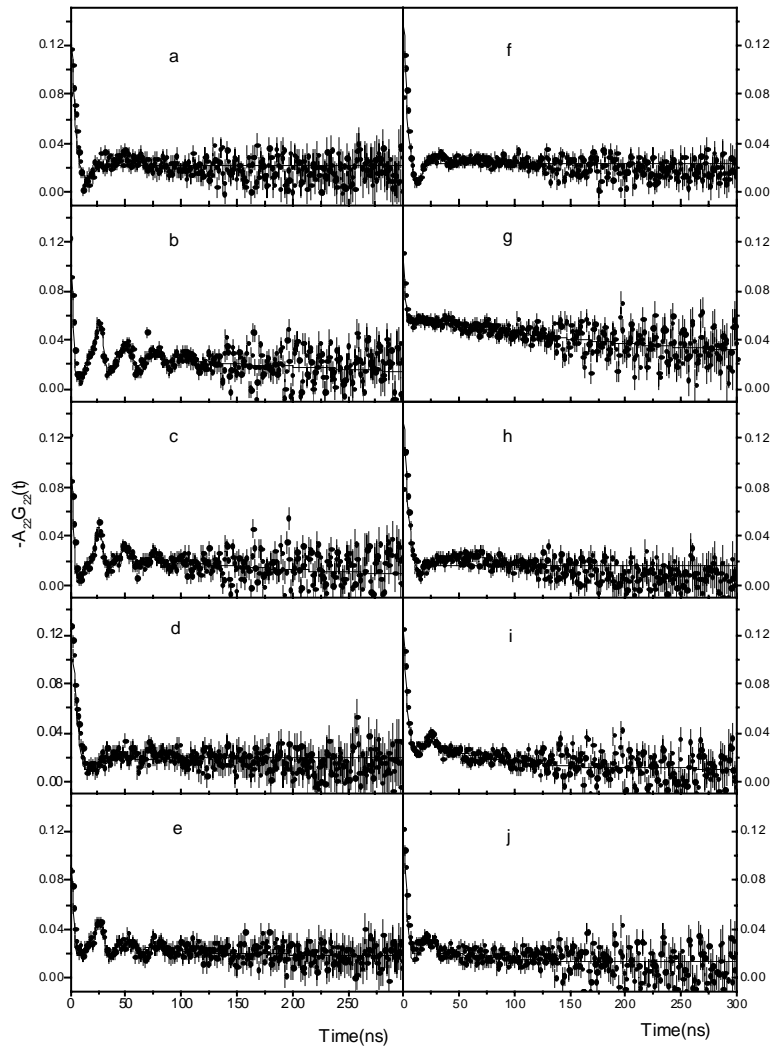


Figure 2- Adjusted Measured TDAC Spectra

1%Pt/Nb₂O₅: a) calcinated, b) after reduction at 500C, c) reduced; measurement at RT, d) after air exposure at RT, e) after new reduction at 500C

1%In/Nb₂O₅: f) calcinated, g) after reduction at 500C

1%Pt/1%In/Nb₂O₅: h) calcinated, i) after reduction at 500C, j) reduced; measurement at RT

