Dehydrogenation of isobutane on Pt-In and Pt-In-Sn Supported Catalysts

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Introduction
The catalytic dehydrogenation of light paraffins has been the subject of an important research effort due to the growing demand in several applications (polymers, oxygenated compounds, raw materials for other processes). Platinum is an active component for the dehydrogenation reaction. However, it deactivates fast and needs to be promoted with other components, like tin.

Platinum-tin catalysts supported on non-acidic supports like SiO₂, KL-zeolite, and Al₂O₃ neutralized with K have been studied by several groups [1,2]. However, it has been reported that during regeneration there is a disruption of the alloy, and that during reaction a surface tin enrichment takes place, leading to a deactivation that cannot be recovered by air treatment [3].

Due to these problems of the Pt-Sn system, we decided to investigate the Pt-In and Pt-In-Sn catalysts. Indium has a slightly different electronic structure than tin, and therefore is a good candidate to be used as a promoter for Pt in the dehydrogenation reaction.

Experimental
Catalysts were supported on SiO₂ and on K-neutralized alumina. They were prepared by incipient wetness impregnation using solutions obtained from In₂O₃ dissolved in HCl, SnCl₂ and H₂PtCl₆ as the precursors of the metals. The amounts of impregnated In varied from 0.25 to 1.2 wt.%. All samples were calcined in air at 500°C for 2 h, and contained 1wt.% Pt. Catalyst were therefore labeled as 1:X, to indicate 1wt.%Pt and Xwt.% In, and 1:X:Y to indicate 1wt%Pt, Xwt% In, Ywt% Sn. The isobutane dehydrogenation activity was measured at 500°C, using pure isobutane or a mixture isobutane-H₂ as feed, with a weight hourly space velocity (WHSV) of 350 h⁻¹. Regeneration cycles were also carried out with selected catalysts. Catalysts were characterized by Temperature-programmed reduction (TPR), H₂ and dynamic CO chemisorption measurements and XPS. Coke was analyzed by TPO.

Results and discussion
Fig. 1 shows results of activity of the Pt-In catalysts with different compositions, both when using pure isobutane as feed (Fig. 1 A) and isobutane plus hydrogen as feed (Fig. 1 B). There is an important effect of the Pt:In ratio on the catalyst activity. The influence is different, depending upon the feed composition. If pure isobutane is fed to the reactor, the catalyst with the same composition of Pt and In (1:1) displays the highest activity. There is a well-defined maximum in the activity for this catalyst composition. On the other hand when H₂ is co-fed, the catalyst that has higher activity is the
In this case, although there is a maximum in the activity for this composition, after this maximum there is little difference among the catalysts with Pt:In weight ratios of 1:1, 1:0.8, and 1:0.5. In all cases, with and without hydrogen, the selectivity is 100%, except in the initial few minutes of the runs carried out with hydrogen in the feed and catalysts with low In content. Nevertheless, selectivity is always higher than 98%. The catalyst stability is different depending upon the feed is pure isobutane or isobutane with hydrogen. The activity decay in the former is evident even during the four-hours activity test. When hydrogen is present, the activity is almost constant during this 4 h time-on-stream. The pure platinum has a very low activity, both in pure isobutane and in isobutane + hydrogen feed. The catalyst can be considered as formed by three types of metal particles: composed by pure platinum, pure indium, and by both metals. In addition, the bimetallic particles may have different compositions. The system Pt-In has three known intermetallic compounds: Pt<sub>2</sub>In<sub>3</sub>, Pt<sub>3</sub>In<sub>7</sub>, and the third one that can only exist at very high temperatures. These two compounds have a Pt:In weight ratio of 1:0.88 and 1:1.37, respectively. The pure platinum particles display very low activity, due to either a quick deactivation, or due to a low dispersion. The pure indium particles have no activity for dehydrogenation. Therefore, it can be expected that the bimetallic Pt-In particles are responsible for the type of activity curves observed, and the dependence of the hydrogen composition in the feed.

The TPR profiles for Pt-In catalysts display a peak at low temperature (150-200°C approximately) that corresponds to the coreduction of Pt and In that are forming an alloy, which is the active metallic phase. As the In content increases, the peak that correspond to the non-alloyed In increases (peak at 400°C). Successive oxidation-reduction cycles, indicate that there is a modification in the metallic phase, mainly in the first cycles.

Both the CO dynamic chemisorption, and the H<sub>2</sub> chemisorption experiments indicate that the Pt dispersion is very low. In the case of the pure Pt catalyst, the dispersion is in the order of 8%. When the chemisorption experiments are carried out in any of the bimetallic catalysts, chemisorption values are extremely low. It has been shown that the hydrogen uptake in Pt-In/Al<sub>2</sub>O<sub>3</sub> [4] is much smaller than in the case of the Pt/Al<sub>2</sub>O<sub>3</sub>. This means that the bimetallic Pt-In particles either do not chemisorb H<sub>2</sub> or chemisorb in a much smaller amount than the platinum. This suggests that an electronic effect is present in the system Pt-In.

The EXAFS analysis clearly indicates that in the Pt:In 1:0.8 catalyst there is an interaction between Pt and In. One possibility is that there is an increase in Pt dispersion in this catalyst as compared to the monometallic Pt catalyst.

In all catalysts, the hydrogen inhibits the coke formation, being the amount of coke smaller when hydrogen is in the feed. Nevertheless, the amount of coke in all the catalysts and under any experimental conditions is at most close to 1%. The regeneration at 500°C allows the recovery of activity, although the activity of the first cycle is not fully restored, in spite of a complete coke removal. Phase segregation as indicated by TPR might be one of the reasons why the activity cannot be recovered after the regeneration in air. However, results indicate that this is not the only reason for this behavior. As in the case of the Pt-Sn catalysts, a change in the metallic phase in a reductive environment could be the reason.

The trimetallic catalysts Pt-In-Sn did not show an improved initial activity behavior compared to the bimetallic systems Pt-Sn and Pt-In. However, certain formulations in this catalytic system display a very good stability even in the absence of hydrogen, with a very high turnover number.

References