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## IMPROVEMENTS IN SELECTIVITY AND STABILITY OF Rh CATALYSTS MODIFIED BY SnBu<sub>4</sub>. DEHYDROGENATION OF ISOBUTANE TO ISOBUTENE

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### Abstract

RhSn/SiO<sub>2</sub> bimetallic catalysts prepared via an organometallic route have proved to be very active and selective toward several hydrogenation reactions. In this work these catalysts were studied for the dehydrogenation of isobutane to isobutene. It was found that Rh/SiO<sub>2</sub> monometallic catalysts had a null selectivity to isobutene, and this selectivity increased up to more than 90 % after the addition of tin, using SnBu<sub>4</sub> as precursor.

*Keywords:* RhSn/SiO<sub>2</sub>, surface organometallic chemistry, SnBu<sub>4</sub>, isobutane dehydrogenation

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## INTRODUCTION

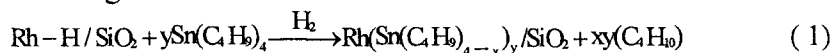
Surface organometallic chemistry on metals can be a new route to generate supported bimetallic and organometallic materials, according to previous works [1-3]. For example, the selective reaction of Group 14 organometallic complexes with Group 8 metals supported on silica gave rise to a new generation of bimetallic materials with high activity and selectivity in heterogeneous catalysis. For instance, it has been shown that SnBu<sub>4</sub> reacts with supported rhodium, ruthenium or nickel to give the corresponding bimetallic catalysts (RhSn, RuSn

or NiSn), which are highly selective and active in the hydrogenation of ethyl acetate to ethanol [4]. This fact was interpreted as an isolation of the transition metal by tin neighbors [5]. Bimetallic systems can be obtained as well as phases where several organic fragments are retained by using this preparation method [6]. For these organometallic catalysts the activities and selectivities are much higher than those of the corresponding bimetallic catalysts for selective hydrogenation of citral to geraniol [7].

The aim of this work is to describe the catalytic properties of bimetallic catalysts prepared by the reaction between Rh/SiO<sub>2</sub> and SnBu<sub>4</sub> in the dehydrogenation of isobutane to isobutene. This olefin is an intermediate of interest in the production of non-pollutant naphtha (MTBE) or polymeric materials (polyisobutylene). In dehydrogenation reactions of paraffins to olefins, thermodynamic limitations force the reaction to be carried out under severe operating conditions (high temperatures, low H<sub>2</sub> to paraffin ratios) resulting in catalyst deactivation mainly caused by coke formation. Therefore, stability, selectivity and regeneration ability are very important features to be improved in dehydrogenation catalysts.

## EXPERIMENTAL

Rh was deposited on silica (Aerosil, Degussa, 380 m<sup>2</sup> g<sup>-1</sup>) by cationic exchange of amine complexes [RhCl(NH<sub>3</sub>)<sub>5</sub>]<sup>++</sup> at pH=10 [8], and the resultant materials were calcined in air at 623 K and then reduced in H<sub>2</sub> at 623 K to obtain Rh/SiO<sub>2</sub> monometallic catalysts. Bimetallic catalysts were prepared under H<sub>2</sub> atmosphere by reaction of Rh/SiO<sub>2</sub> with SnBu<sub>4</sub> in *n*-C<sub>7</sub>H<sub>16</sub> between 298 to 363 K, according to:



Tetra *n*-butyltin and *n*-butane (the only hydrocarbon detected) were monitored by gas chromatographic analysis. The catalyst was then washed with *n*-heptane and treated under hydrogen at 623 K. After this treatment all the butyl groups evolved as shown by Didillon *et al.* [6], obtaining a RhSn bimetallic catalyst. The content of metals on the resulting materials was determined by atomic absorption. H<sub>2</sub> adsorption was followed in a conventional volumetric equipment [8]. Temperature programmed reductions (TPR) of Rh<sub>2</sub>O<sub>3</sub> and Rh<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> / SiO<sub>2</sub> were conducted in a conventional dynamic equipment under flow of a mixture of Ar and H<sub>2</sub> (95/5, 20 cm<sup>3</sup> min<sup>-1</sup>, 10 K min<sup>-1</sup>). Transmission Electronic Microscopy (TEM) and Scanning Transmission Electronic Microscopy (STEM) experiments were made using JEOL 100 CX and Vacuum Generator HB5 electron microscopes, respectively.

Isobutane dehydrogenation was carried out in a dynamic reactor according to the following procedure: 2 h in H<sub>2</sub> flow at 823 K, then the temperature was set to 723 K. The reaction started by feeding a mixture of H<sub>2</sub> and isobutane to the reactor (66/34, flow rate 42 cm<sup>3</sup> min<sup>-1</sup>, mass 0.1 g). The latter temperature was kept for an initial period of 2 h and increased up to 773 K for another 2 h, then up to 823 K for further 2 h and finally decreased to the initial value (723 K) for two additional hours to complete eight hours of reaction and to determine the stability of the samples.

## RESULTS AND DISCUSSION

Rh/SiO<sub>2</sub> monometallic material showed high dispersion in the metallic phase. TEM observations indicated that the particle size distribution was centered at about 1.5 nm, in close agreement with the results of H<sub>2</sub> volumetric adsorption (H/Rh=1.2, D ≈ 80%, considering H/Rh<sub>s</sub>=1.5 for an equilibrium pressure of 150 mbar at room temperature [8]).

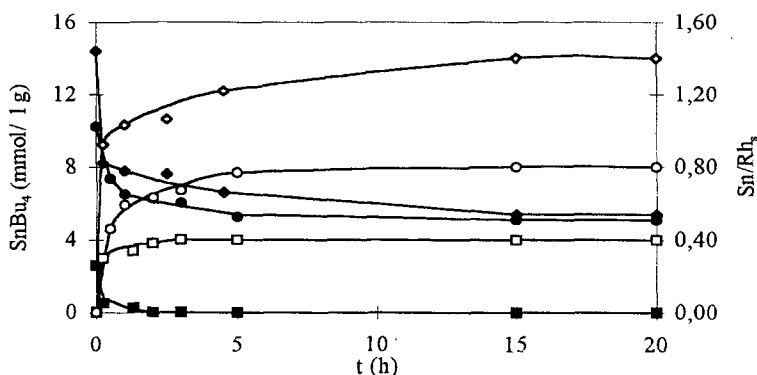


Fig. 1. SnBu<sub>4</sub> concentration (filled symbols) and Sn/Rh<sub>s</sub> atomic ratio (empty symbols) as a function of time.

(Squares) T=298 K; (circles) T=298 K; (diamonds) T=363 K

When reaction (1) is carried out at 298 K, all the SnBu<sub>4</sub> in solution reacts with Rh/SiO<sub>2</sub> monometallic catalysts until a Sn/Rh<sub>s</sub> ratio of *ca.* 0.8 is reached. When Sn/Rh<sub>s</sub> ratios higher than 0.8 are required, the temperature must be increased [9]. Kinetic results of reaction (1) are shown in Fig. 1.

Previous papers [1,3,9] provided evidence on the interaction of Rh with Sn, and this was confirmed in this work by STEM and TPR. The STEM analyses

always showed the peak of Sn (3.44 keV) associated with that of Rh (2.69 keV). Sn peak was never found alone on the support. TPR of the samples obtained on calcined Rh and RhSn/SiO<sub>2</sub> catalysts, exhibit only one peak at about 370 K and 450 K for monometallic and bimetallic catalysts, respectively. Hydrogen consumption corresponded approximately to the complete reduction of Rh<sub>2</sub>O<sub>3</sub> and Rh<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> to Rh<sup>(0)</sup> and to Rh<sup>(0)</sup>-Sn<sup>(0)</sup>, respectively.

The reaction test led to complete decomposition of isobutane to methane (hydrogenolysis reaction) and coke when using Rh/SiO<sub>2</sub> catalyst. In contrast, the addition of Sn caused noticeable changes in selectivity toward isobutene, as is shown in Table 1. In this sense, the catalyst having Sn/Rh<sub>s</sub>= 0.5 produced, besides methane, a small amount of isobutene together with much less coke. The catalyst became as selective to isobutene as it was to methane when increasing the amount of tin to Sn/Rh<sub>s</sub>= 0.8. The best results in selectivity to isobutene (>90%) were reached for a catalytic material with Sn/Rh<sub>s</sub>=1.4. Moreover, from coke analysis data taken at the end of the tests, a direct relationship was found between the inhibition of coke formation and the tin concentration used.

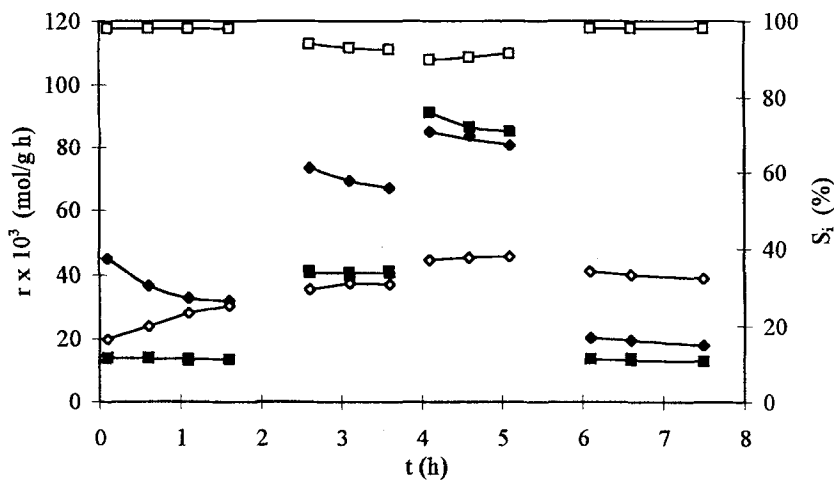


Fig. 2. Rate of reaction (filled symbols) and selectivity to isobutene (empty symbols) as a function of time.

(Diamonds) Sn/Rh<sub>s</sub>=0.8; (squares) Sn/Rh<sub>s</sub>=1.4

On the other hand, skeletal isomerization was low on all the catalysts most possibly because of the weak acidity of silica.

The above mentioned geometrical effect of Sn on Rh (isolation of Rh "ensembles") addressed to explain the high activities and selectivities in the reaction of ethyl acetate to ethanol [10] could also explain the inhibition of coke and methane formation (hydrogenolysis reactions are favored by Rh "ensembles").

Concerning the catalyst with Sn/Rh<sub>s</sub> ratio = 1.4, the stability of these bimetallic catalysts was very high (Fig. 2) almost undoubtedly because of the lower coke formation rate. It was observed that, while the selectivity was not much affected by temperature (above 90% between 723 and 823 K), the activity increased considerably. For the working conditions covered here, the apparent activation energy was in the order of 80 kJ mol<sup>-1</sup>, in agreement with those obtained for a Pt-based commercial catalyst. Catalysts with Sn/Rh<sub>s</sub> ratios of 0.5 and 0.8 deactivated noticeably during the experimental runs (see behavior of the latter in

**Table 1**  
Results of the catalytic tests for different Sn/Rh<sub>s</sub> ratios

Sn/Rh <sub>s</sub>	T (K)	r (mol/h g <sub>cat</sub> )	S <sub>i</sub> (%)	S <sub>H</sub> /S <sub>i</sub>	C (%)
0.5	723	0.116	2.3	42.50	
0.5	773	0.123	3.0	32.33	
0.5	823	0.128	3.4	28.41	1.50
0.8	723	0.069	26.3	2.80	
0.8	773	0.088	36.7	2.46	
0.8	823	0.104	45.2	1.22	1.12
1.4	723	0.014	96.2	0.04	
1.4	773	0.041	93.3	0.07	
1.4	823	0.104	90.6	0.09	0.29

S<sub>i</sub>: selectivity to isobutene  
r: reaction rate

S<sub>H</sub>: selectivity to hydrogenolysis  
C: coke content

Fig. 2). These results evidence the inhibition effect on coke formation produced by tin, but coke still affects the catalytic activity. A very interesting property of this kind of catalysts is their ability to regenerate when treated in a flow of air at 673 K for 8 h, after which coke is eliminated and the activity is restored to the values of fresh catalysts.

In this work the promotion effect of Sn on Rh was observed. Monometallic Rh catalysts are characterized by high hydrogenolysis activity and high rate of coke formation, and, after the addition of tin, switch to excellent selectivity (higher than 90%) and stability in the reaction of isobutane to isobutene. The reaction between transition metals and tin organometallic compounds is a very interesting way to produce catalysts with a controlled amount of promoters. For dehydrogenation reactions of paraffins to olefins, tin could be used to promote other elements (apart from Rh) such as Ni, Ru, Ir, *etc.*, giving rise to a new family of dehydrogenation catalysts.

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