INVESTIGATION OF THE CATALYTIC ACTIVITY OF METAL COMPLEXES FIXED ON A SOLID SUPPORT.

10. SELECTIVE HYDROGENATION OF ALLYLBENZENE IN THE PRESENCE OF HETEROGENEOUS Pt–Sn-CITRATE COMPLEXES

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UDC 541.49:541.128:542.941.7:547:313.6

New heterogeneous catalysts based on the complexes of platinum with tin(II) citrate were prepared. The catalysts exhibit high selectivity in the hydrogenation of allylbenzene to propylbenzene without increasing the rate of isomerization of the C=C bond. The activity of the complexes depends on the conditions and decreases with increase in the Sn:Pt ratio.

Key words: *synthesis, selective hydrogenation, allylbenzene, activity of complexes, heterogeneous Pt—Sn-citrate complexes.*

The complexes of platinum with Sn(II)halides are well known as catalysts of the hydrogenation and isomerization of unsaturated hydrocarbons [1]. The catalytic characteristics of Pt–Sn complexes are determined by their ability to activate hydrogen, and this is due to the high *trans* effect of the tin-containing ligands. The nature of the substituent at the tin atom makes a substantial contribution to the properties of these complexes [2-4]. In the present work we investigated for the first time the catalytic characteristics of the complexes of platinum with tin citrate ligands. In order to increase the stability of the catalyst [5] we used the complexes fixed on a support.

EXPERIMENTAL

The complexes fixed on the anion-exchange resin AV-17-2P were prepared by two methods. In the first method 2 ml of a 1 M solution of H_3Cit and 1 ml of water with 0.050 g of K_2PtCl_4 dissolved in it were added to 2 g of the resin. When the platinum had been completely sorbed, a solution of Sn(II) in 1 M citric acid was added to the resin. The Sn(II):Pt molar ratio was varied between 2 and 5. The mixture was stirred thoroughly and kept for 2 h. The solution was then decanted, and the support was washed with 1 M citric acid solution and with ethanol and dried in air. In method 2 in order to obtain bimetallic complexes with platinum in a low degree of oxidation mixtures containing the Sn(II) and Pt(II) compounds in initial molar ratios of 3 and 4 were heated in the presence of the resin on a boiling water bath for ~0.5 h. The resin was then treated according to the first method.

The bimetallic Pt–Sn-complexes fixed on the support were characterized by means of their γ-resonance (GR) spectra (^{119}Sn). The GR spectra were recorded at liquid nitrogen temperature on a YaGRS-4M spectrometer with an AI-1024-95 pulse analyzer. The isomer shifts are given with reference to SnO_2.

Hydrogenation with hydrogen at atmospheric pressure was conducted in a thermostated glass hydrogenation flask attached to a rocker and connected to a gas buret. Hydrogenation at increased pressure was realized in a rotating autoclave fitted with a special insert that excluded contact between the reaction mixture and the walls of the autoclave. In the experiment we used 1 ml of allylbenzene (AB) in 5 ml of methanol and 0.05 g of the catalyst, calculated on the platinum content. The reaction products were analyzed by GLC on an LKhM-8MD instrument with a flame-ionization detector (3 mm × 3 m column, 15% of Triton X-305 on Zeolite, analysis temperature 100°C).

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TABLE 1. Parameters of the GR Spectra (^{119}Sn) and the Composition of the Pt–Sn-Complexes

Compound	Complex	δ	Δ	Sn:Pt molar ratio
		± 0.04 mm/sec		
1	$[Pt(SnCit)_2(H_2Cit)_2]^{2-}$	1.23	2.04	2 : 1
2	$[Pt(SnCit)_5]^{3-}$	1.20	2.40	5 : 1
3	$[Pt_2(SnCit)_5]^{3-}$	1.45	2.04	2.5 : 1
4	$[Pt_2(SnCit)_8]^{6-}$	1.49	2.10	4 : 1

TABLE 2. Hydrogenation of Allylbenzene in the Presence of the Catalysts (25°C, 50 atm)

Catalyst	Length of experiment, h	Composition of catalyzate, wt. %	
		AB	PB
1	1	64	36
	3	20	80
2	1	78	22
	3	29	71
3	1	37	63
	3	–	100
4	1	54	46
	3	35	65

DISCUSSION OF RESULTS

The nature and the parameters of the GR spectra of the Pt–Sn-compounds fixed on the support (Table 1) did not differ from those for the bimetallic complexes of platinum with tin citrate ligands in solutions or isolated in the solid phase [6]. The isomer shifts (δ) were 0.30-0.40 mm/sec lower than for the analogous tin chloride complexes. This effect is due to the higher electronegativity of the citrate ions compared with the Cl ions. The Pt(II) complexes (Table 1, samples **1** and **2**) are characterized by isomer shifts in the region of 1.20-1.23 mm/sec. The compounds with platinum in a degree of oxidation close to unity are characterized by higher δ values of 1.45-1.49 mm/sec (Table 1, samples **3** and **4**). It was suggested on the basis of these results that the composition and structure of the complexes fixed on the support are similar to those of Pt–Sn compounds isolated in the solid phase from 1 M citric acid solution [6].

The bond between Pt(II) and the functional group of the resin (a quaternary ammonium base) during the sorption of the $PtCl_4^{2-}$ ions is formed through the Cl ions. Complete substitution of the Cl ions occurs as a result of the reaction of the $PtCl_4^{2-}$ with tin(II) citrate. The bond between the Pt–Sn-complex and the functional groups of the resin may be formed through the citrate ions attached to the tin(II) atoms by two or three five- or six-membered rings through the oxygen atoms. The presence of a Pt–Pt bond is possible in diamagnetic complexes with platinum in a low degree of oxidation (Table 1, samples **3** and **4**).

With hydrogen at atmospheric pressure and 20-50°C the indicated complexes fixed on the resin did not exhibit catalytic activity in the hydrogenation of allylbenzene. At elevated temperatures and pressures (50°C, 50 atm) almost complete transformation of allylbenzene into propylbenzene (PB) was observed on all the tested catalysts after only 3 h. A series of experiments at 25°C and 50 atm were conducted in order to compare the activities of the various complexes.

It is seen from the obtained results that the most active catalyst is compound **3** with platinum in a low degree of oxidation and with the minimum Sn:Pt ratio (Table 2). The bimetallic compounds of Pt(II) (Table 2, samples **1** and **2**) and also of Pt(I) but with a higher tin content than in catalyst **3** (Table 2, sample **4**) differ little from each other in activity and in the direction of the reaction. It can be supposed that under harsh experimental conditions in an atmosphere of hydrogen the Pt(II) compounds are reduced with the formation of bimetallic complexes with the platinum in a lower degree of oxidation, which are similar to compounds **3** and **4** (Table 1) and are probably responsible for the catalytic transformation of allylbenzene.

The activity of the catalysts depends on the Sn:Pt ratio in the initial compounds. With low Sn:Pt ratios the complex with platinum in a low degree of oxidation is formed effectively. This gives rise to the high activity of catalyst **1**, comparable with the activity of catalyst **3** (Table 2). The reason for the lower activity of catalysts **2** and **4** is the higher tin content.

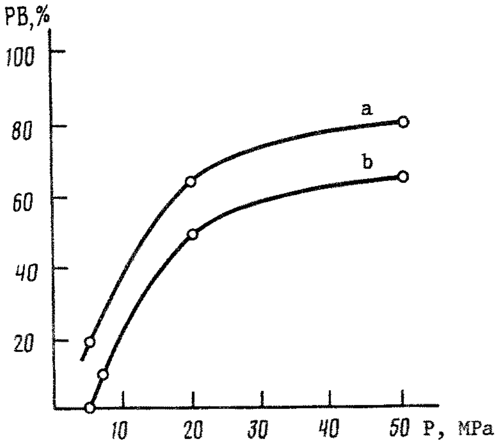

Fig. 1. Effect of pressure on the degree of transformation of allylbenzene and propylbenzene on catalyst **1** (a) and **4** (b); length of experiment 3 h, 25°C.

TABLE 3. Effect of Temperature on the Hydrogenation of Allylbenzene (5 atm, 3 h)

Catalyst	T, °C	Composition of catalyzate, wt. %	
		AP	PB
1	25	82	18
	50	–	100
2	25	91	9
	50	16	84
3	25	54	46
	50	–	100
4	25	100	–
	50	28	72

The hydrogen pressure (Fig. 1) and the temperature at which the process is conducted (Table 3) have a substantial effect on the activity of the catalysts.

It should be noted that in contrast to previously studied trichlorostannide complexes of platinum, which mostly accelerate the isomerization of α-olefins [3], bimetallic compounds with tin citrate ligands catalyze the hydrogenation of allylbenzene to propylbenzene strictly selectively. The formation of propenylbenzene was not observed in any of the experiments with these complexes. This fact can be regarded as an argument in favor of the idea that bimetallic complexes with platinum in a low degree of oxidation are catalytically active.

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