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HYDROGENATION OF C=C AND C=O GROUPS ON RUTHENIUM-TIN CATALYSTS

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The effect of addition of tin on the catalytic activity of Ru/C catalysts has been investigated in the liquid phase hydrogenation of β-methylstyrene and hydrocinnamaldehyde. On increasing the Sn content, the amount of CO chemisorbed decreases, indicating a decrease in the number of Ru surface atoms. In the hydrogenation of β-methylstyrene the specific activity of Ru (calculated per Ru surface atom) remains constant regardless of the Sn/Ru ratio. An increase of specific activity is however observed in the hydrogenation of hydrocinnamaldehyde. It is suggested that tin, present mainly as Sn ions, enhances the reactivity of the C=O group.

1. Introduction

Previous results have shown that addition of Sn to Pt/nylon modifies strongly the activity of the noble metal [1–8]. The rate of hydrogenation of double and triple carbon-carbon bonds has been found to decrease continuously on addition of tin [3,8], whereas the rate of hydrogenation of carbonyl groups increases, up to three orders of magnitude, for addition of about 30% Sn. At higher Sn/Pt ratios the rate of reaction decreases [3]. Results qualitatively similar to those obtained in the hydrogenation of the C=O group were observed also in the hydrogenation of benzonitrile [7] and nitrobenzene [5]. It has been suggested that tin plays two different roles: a) it poisons the active platinum sites; b) it increases the reactivity of the polar groups by enhancing their polarization charge. Due to the difficulty of measuring, on Pt/nylon, the number of active sites by chemisorption it has not been possible to verify the above hypothesis on the basis of the reactivity measured per atom of platinum on the surface.

In this paper we have extended our study to Ru catalysts with the aim of:
a) verifying the general validity of the hypotheses previously expressed on

platinum catalysts; b) finding a less expensive catalyst for the hydrogenation of C=O groups.

Ruthenium is known to be a good catalyst for the hydrogenation of aldehydes [9,10]. Moreover, addition of stannous chloride to Ru/C has been reported to increase the rate of hydrogenation of aldehyde [11]. Ru-Sn catalysts, promoted with boron, have been shown to catalyze the selective hydrogenation of esters and unsaturated aldehydes to alcohols [12,13].

2. Experimental

Ru/C and Ru-Sn/C samples were prepared by impregnation of activated carbon (CHEMVIRON SCXII 80–100 mesh, surface area 900–1100 m^2/g) with aqueous solutions of $RuCl_3$ and $SnCl_2$ having the appropriate concentration of metals. The amount of solution used was slightly greater than the pore volume. After impregnation, the catalysts were dried at 393 K and stored in air. Before use catalysts samples were reduced at 573 K under flowing H_2. In all catalysts the amount of Ru was kept constant at 2 wt% whereas the Sn content was varied between 0 and 2.0 wt%.

Catalytic activity of the Ru-Sn/C samples was tested in the hydrogenation of hydrocinnamaldehyde (Fluka, purity 90–95%) and β-methylstyrene (Fluka, purity $> 98\%$). Hydrogenations were carried in a 100 ml four-necked flask fitted with a reflux condenser, dropping funnel, thermocouple and a stirrer head. The catalyst was added to the required amount of solvent (25 ml of 95% ethanol) then treated at 343 K for 1 h under H_2 flow. After cooling at reaction temperature (333 K, unless otherwise specified), the organic substrate (0.5 ml) was injected through one arm of the flask. The reaction mixture was stirred at 500 rpm. The reaction was carried out at atmospheric pressure under H_2 flow.

The progress of the reaction was followed by analyzing a sufficient number of microsamples withdrawn from the reaction mixture. Chemical analysis was performed with a gas chromatograph (Carlo Erba Model 4200) equipped with a flame ionization detector. The gas chromatograph column used was a 10% GP over SP2100.

Chemisorption of CO was measured in a conventional pulse system operating at room temperature. Negligible amounts of CO were found to chemisorb on the support and on the Sn/C sample.

3. Results and discussion

The Ru-Sn catalysts were characterized by CO chemisorption and the results are reported in table 1. The CO/Ru ratio is 0.26 on the monometallic Ru/C sample and decreases with addition of tin, reaching a value of about 0.003 on the

Table 1
Chemical composition and CO uptakes of Ru-Sn/C catalysts

Catalyst code	Ru (wt%)	Sn (wt%)	100 Ru/(Ru+Sn) [a]	CO uptakes (cc(STP) $gcat^{-1}$)	CO/Ru
Ru 100/C	2.0	–	100	1.160	0.261
Ru 95/C	2.0	0.12	95	0.977	0.220
Ru 90/C	2.0	0.26	90	0.520	0.115
Ru 80/C	2.0	0.58	80	0.427	0.096
Ru 70/C	2.0	1.01	70	0.017	0.003
Ru 60/C	2.0	1.56	60	[b]	[b]

[a] atomic ratios.
[b] not detectable.

sample (Ru 70/C) which contains 30 at% Sn. Samples having a higher Sn content showed a CO chemisorption below the detection limit of our equipment. The decrease of CO chemisorption on addition of Sn cannot be ascribed to an increase of Ru particle size. A TEM analysis of samples Ru 100/C and Ru 70/C showed no increase in the metal particle size (always in the range 50–60 Å). For the hydrogenations of β-methylstyrene (MST) and of hydrocinnamaldehyde (HCALD) samples of Sn/C pretreated under the same conditions were found inactive. Preliminary runs carried out with different catalyst loadings, stirring conditions and catalyst grain size showed the absence of diffusional limitations.

Under the conditions used, hydrogenation of MST produces only phenylpropane without any side product. The kinetic analysis of the rate of consumption of MST showed an order of reaction with respect to the organic substrate of about 0.5–0.6 on all catalysts regardless of the Sn content.

In order to compare the catalytic activity of the Ru-Sn samples towards MST hydrogenation, in fig. 1 are reported the initial rates of reaction, V_i, as a function of Sn. Increasing the level of Sn the catalytic activity decreases steadily. Samples having a Sn content higher than 30 at% were found practically inactive. In fig. 1 the specific catalytic activity (per Ru surface atom), N_i, is also reported. Ru surface atoms have been calculated from table 1 on the assumption that CO chemisorption occurs with a stoichiometry $CO/Ru = 1$. It is noted that the specific activity of Ru towards MST hydrogenation is constant in all range of composition investigated. This suggests that, in this reaction, the main effect of tin is the blocking of the Ru surface atoms. The specific activity of the available Ru surface atoms remains constant.

A different effect of addition of Sn to Ru has been instead observed in the hydrogenation of HCALD. Under the condition used the only reduction product observed is phenylpropanol which is formed through the hydrogenation of the C=O group. Hydrocinnamaldehyde diethylacetal is also formed through the reaction between the substrate and ethanol used as solvent. This is in agreement with previous results over platinum catalysts [1,3]. The diethylacetal is readly

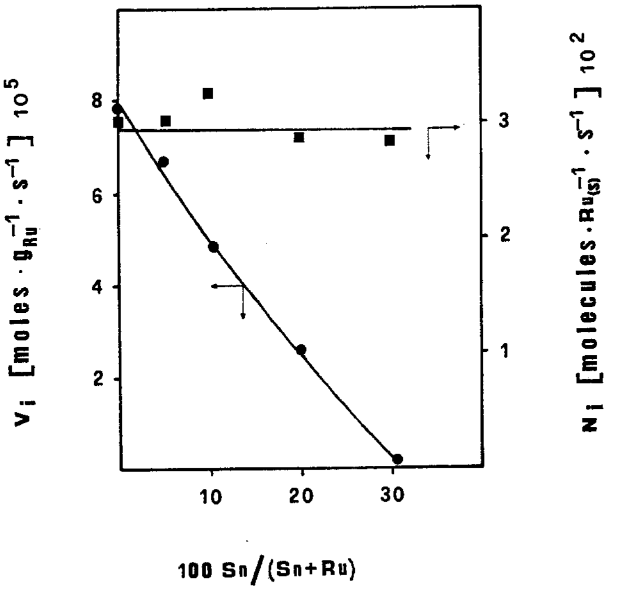

Fig. 1. Hydrogenation of β-methylstyrene. Initial rate of reaction, per gram of Ru (v_i) and per Ru surface atom (N_i), as a function of Sn content.

obtained and is essentially at equilibrium with HCALD, which made them kinetically indistinguishable. On all catalysts the rate of disappearance of the aldehyde was first order with respect to the organic substrate. In the hydrogenation of HCALD a zero order of reaction has been previously reported on Pt-Sn/nylon [3]. It should be however noted that over Pt-Sn/nylon a lower reaction temperature was used ($T_r = 283$ K) and it is therefore possible that under this condition a saturation of the catalyst surface with the organic substrate is reached. Fig. 2 shows the effect of addition of tin on the initial rate of hydrogenation of HCALD. Increasiny the amount of tin the catalytic activity increases reaching a maximum at a Sn content of about 20 at%. A further addition of Sn causes a drastic decrease.

In the same fig. 2 the specific rate of reaction (N_i) is also reported. It can be noted that, in contrast with the hydrogenation of MST (fig. 1), the specific activity for HCALD reduction shows an increase at increasing Sn contents, revealing a promoting effect of Sn in the hydrogenation of the C=O group.

The above reported results show clearly that the role played by tin on the catalytic activity of Ru depends strongly on the organic substrate which is hydrogenated. In the case of non-polar groups such as C=C double bonds the main effect of tin is that of decreasing the number of Ru surface atoms, the reactivity of which remains constant (fig. 1). In addition to this effect, it should be considered that in the hydrogenation of HCALD tin activates the C=O group facilitating the hydrogen transfer from adjacent Ru sites. The activating effect of tin can be ascribed to Sn ions present on the catalytic surface which polarize the

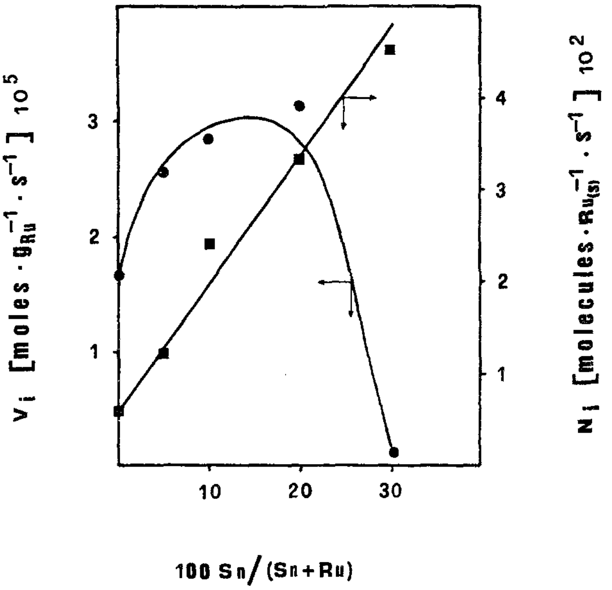

Fig. 2. Hydrogenation of hydrocinnamaldehyde. Initial rate of reaction, per gram of Ru (v_i) and per Ru surface atom (N_i), as a function of Sn content.

carbonyl group. Under our conditions it is in fact likely that tin is not reduced to the zero valent state [12]. The hypothesis that Sn ions are mainly responsible for C=O activation has been confirmed by runs carried out on monometallic Ru/C catalysts by adding $SnCl_2$ directly into the reaction mixture.

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