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RESEARCH NOTE

Reaction Induced Selectivity Improvement in the Hydrogenation of Crotonaldehyde over Sn–Pt/SiO_2 Catalysts

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Silica-supported Sn–Pt catalysts, prepared by controlled surface reactions between hydrogen adsorbed on platinum and tin tetraethyl, showed high activity and selectivity in the gas phase hydrogenation of crotonaldehyde to crotyl alcohol. The selectivity of the formation of crotyl alcohol (S_{CO}) had a strong dependence of the Sn/Pt ratio. The highest S_{CO} selectivity (around 70%) was obtained at Sn/Pt = 3. The characteristic feature of the Sn–Pt/SiO_2 catalyst in the given reaction is the development of the S_{CO} selectivity during the time-on-stream period. The observed phenomenon was described as a reactant induced catalyst activation.

Key Words: **Sn–Pt/SiO_2 catalyst; hydrogenation; crotonaldehyde; crotylalcohol formation; reaction induced selectivity improvement.**

Recently it has been shown that supported noble metals promoted by Fe, Sn, and Ge modified Pt are very promising catalysts to hydrogenate α,β-unsaturated aldehydes into α,β-unsaturated alcohols (1, 2). It has also been shown that high selectivities of unsaturated alcohols ($S_{C=O}$ selectivity) can be obtained over tin modified Pt catalysts (1–3). The characteristic feature of the above catalysts is the development of the $S_{C=O}$ selectivity during the time-on-stream period (2, 3); i.e., an induction period was required to build up the active sites responsible for the formation of unsaturated alcohol. With respect to the form of tin in the above catalysts the role of ionic species has been suggested and the interaction of metallic Pt with the ionic form of tin has been postulated (1–3). It has also been proposed by different authors that probably the Sn^{+n}–substrate carbonyl interaction is involved in the increased $S_{C=O}$ selectivity (2–8).

The above results have inspired us to apply our Sn–Pt/SiO_2 catalysts prepared by controlled surface reactions (CSRs) between adsorbed hydrogen and tin tetraalkyls (9–12). In the above catalysts, due to the control of the tin anchoring process, the Sn–Pt interaction is exclusive; i.e., the amount of tin introduced onto the catalyst support is negligible (11, 12).

In this study the hydrogenation of crotonaldehyde (CA) has been investigated over Sn–Pt/SiO_2 catalysts prepared by using the above CSRs (9–12). Recently it has been shown that upon using CSRs between tin tetraethyl and hydrogen adsorbed on Pt high Sn/Pt ratios can be obtained if (i) a high concentration of tin tetraethyl is used in the tin anchoring reaction, (ii) a small amount of oxygen is added during or prior to the anchoring process, (iii) the anchoring-type surface reaction is carried out in the presence of gas phase hydrogen, and (iv) the reaction time of tin anchoring is increased substantially (13).

In the hydrogenation of CA over different modified Pt catalysts in a continuous-flow gas phase reactor fast ageing was observed under the time-on-stream condition (1–3). To overcome the ageing-induced deactivation problem in this study the conventional continuous-flow reactor was used in a periodic mode by introducing the substrate–hydrogen mixture in the form of a rectangular long pulse (pulse length = 7 min, product analysis at the end of the pulse) followed by a long pulse of pure hydrogen (7 min). The latter was used to get full or partial restoration of the catalytic activity. After 15–20 pulses a constant activity (and selectivity) period could be achieved allowing us to carry out kinetic experiments by changing the flow rate of the reactant. A similar setup has been used to study hydrocarbon reactions (14).

The aim of this note is to demonstrate that (i) in the gas phase hydrogenation of CA over Sn–Pt/SiO_2 catalyst prepared by CSRs high $S_{C=O}$ selectivities can be obtained and (ii) the overall selectivity is controlled by substrate-induced catalyst activation taking place during the ageing period. The FTIR study of the adsorption of CA onto Pt/SiO_2 and Sn–Pt/SiO_2 catalysts provided further information with respect to the character of surface interactions involved in the substrate-induced activation period.

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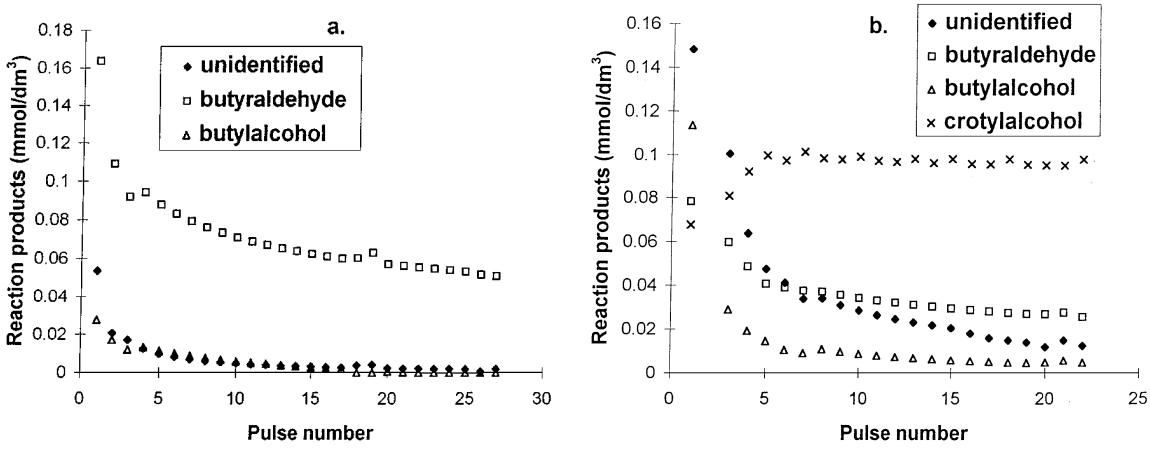

FIG. 1. Formation of different reaction products in the hydrogenation of crotonaldehyde in the ageing period over Pt/SiO_2 (38 mg) (a), and Sn–Pt/SiO_2 catalyst (80 mg) ($Sn/Pt_{surf} = 2.9$) (b). Reaction temperature 80°C, Pt/SiO_2 catalyst (Pt = 3 wt%, D = 0.52) all. All catalysts were prereduced at 300°C for 90 min, flow rate of reactants, 90 cm^3/min, $P_{subst.} = 11$ Torr (0.64 mmol/dm^3).

Figures 1a and 1b show the amount of reaction products formed during the ageing period over Pt/SiO_2 and Sn–Pt/SiO_2 catalysts. As we see from Fig. 1a on the Pt/SiO_2 catalyst, crotylalcohol (UOL) was not formed; i.e., over this catalyst $S_{C=O} = 0$. On the above catalyst during the ageing period three main reaction products were detected, such as butyraldehyde (the major product), butylalcohol, and hydrocarbons (minor products). Contrary to that on Sn–Pt/SiO_2 catalysts a variety of reaction products was detected in the ageing period. The most important observation is that the yield of UOL shows a monotonic increase character, while the formation of unidentified byproducts (mostly hydrocarbons) shows a very pronounced decrease. In the first pulses the formation of hydrocarbons prevails, while in the constant activity period crotylalcohol is the main reaction product and the $S_{C=O}$ selectivity is close to 70%. These observations are in agreement with recent results (2, 3). The observed phenomenon has been attributed "to the modification of the catalyst surface by oxygen retained from the reaction mixture" (3).

Table 1 shows additional activity and selectivity data for different Sn–Pt/SiO_2 catalysts. These data were measured in the constant activity period under a similar conversion range. The role or tin is dramatic, it increases not only $S_{C=O}$ selectivity (S_{UOL},) but the reaction rate too. These data indicate that upon introducing tin onto Pt a new type of active site has been created. The catalyst with Sn/Pt around 3 resulted in almost 70% selectivity to crotylalcohol, without substantial decrease of the reaction rate. Unfortunately catalysts with Sn/Pt > 3 could not be prepared as at higher Sn/Pt ratios the exclusive tin-platinum interaction could not be guaranteed. Data given in Table 1 indicate that the performance of the Sn–Pt catalysts is much better than that prepared by conventional technique, as the highest $S_{C=O}$ selectivity obtained earlier on Sn–Pt/SiO_2 catalyst was around 40% (2, 3).

Figure 2 shows the product selectivity versus the contact time dependencies. These results clearly demonstrate that the long pulse method can provide valuable kinetic information even for reactions with high extent of ageing. The results indicate that on a Sn–Pt catalyst the competition between the carbonyl and the olefinic double bond for the active sites favours the carbonyl group. Figure 2 also shows

TABLE 1

Activity and Selectivity Data Obtained under Steady-State Condition over Different Tin Modified Pt/SiO_2 Catalysts

No.	Catalysts	Sn/Pt_s (at/at)[a] (the mode of tin anchoring)	CO_{br}/CO_{li}[b]	$w_{ini.}$[c] $\frac{\mu mol}{g \cdot s}$	Selectivity (%)[d] SAL	SOL	UOL
1	Pt/SiO_2	0.0	0.07	2.67	100	0	0
2	Pt–Sn/SiO_2	0.7	0.06	6.62	47	6	45
3	Pt–Sn/SiO_2	2.2	0.03	4.70	35	5	59
4	Pt–Sn/SiO_2	2.9	0.01	2.18	20	0	68

Note. For the experimental conditions see Fig. 1. The Pt/SiO_2 catalyst was prepared by ion exchange method using the mixture of $[Pt(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4](OH)_2$, Pt content = 3.0 wt%, H/Pt = 0.52.

[a] 2. Standard experiment, $[Sn]_o/Pt_{surf} = 2.9$, reaction time = 1.5 h. 3. $[Sn]_o/Pt_{surf} = 10.8$, reaction time = 3.5 h. 4. $[Sn]_o/Pt_{surf} = 8.5$, reaction time = 7 h, in the presence of oxygen [13].

[b] FTIR results: the intensity ratio of bridged to linear CO bands obtained upon adsorption of CO on Pt at room temperature.

[c] Initial rates calculated from the conversion-residence time kinetic curves (see Fig. 2).

[d] Measured at 5 ± 0.1% conversion level; SAL = saturated aldehyde (butyraldehyde), SOL = saturated alcohol (butanol), UOL = unsaturated alcohol (crotylalcohol), unidentified reaction products are not shown.

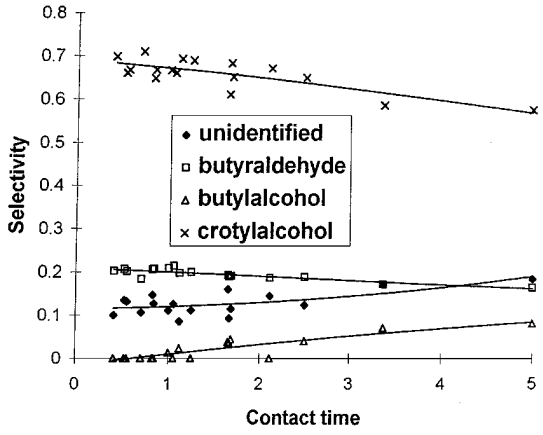

FIG. 2. Product selectivities as a function of contact time. (Experimental conditions; see Fig. 1.) Catalyst, $Sn/Pt_{surf} = 2.9$, 20–150 mg; flow rate: 15–150 cm^3/min. Contact time is given in mg × min × cm^{-3}.

that butylalcohol is a secondary product and $S_{C=O}$ selectivity as high as 60% can be maintained up to high contact time (40–50% conversion).

It is interesting to note that the formation of butylalcohol from butyraldehyde was also strongly suppressed on the Pt/SiO_2 catalyst. On the tin modified catalyst the appearance of butylalcohol implies that not only the carbonyl group of CA, but the carbonyl group of the formed butyraldehyde is also activated by the new type of active site.

Both Pt/SiO_2 and $Sn–Pt/SiO_2$ catalysts were characterized by FTIR spectroscopy. As it emerges from CO adsorption measurements the introduction of tin results in a significant decrease in the ratio of the bridged to linear CO band intensities (see Table 1), but only slight change in the CO frequencies were observed. The shifts in the CO frequencies induced by tin are as follows: 2065 to 2060 cm^{-1} for linear and 1840 to 1830 cm^{-1} for bridged CO.

The adsorption of CA at 80°C onto Pt/SiO_2 catalyst resulted in a sharp peak in the organic carbonyl bond region around 1690 cm^{-1} and broad peaks in the C–H stretching region similar to that found earlier (15). In addition to the above bands two CO bands at 2047 and 1838 cm^{-1} appeared on the Pt/SiO_2 catalyst. The latter two peaks were attributed to adsorbed CO on platinum formed in the decarbonylation of the aldehyde group, similar to that observed recently by Englisch *et al.* (8). Neither the organic carbonyl nor the C–H stretching frequencies were altered by the addition of tin. However, the two CO carbonyl bands showed marked differences upon tin introduction. These results are shown in Fig. 3.

The FTIR results indicate that the introduction of tin onto Pt strongly diminishes the intensity of the above CO bands and on catalysts with high Sn/Pt ratio the intensity of these CO bands is almost negligible. This observation implies that the introduction of tin changes the route of "the reactant induced catalyst modification"; i.e., on $Sn–Pt/SiO_2$ catalysts with high Sn/Pt ratio the decarbonylation reaction taking place in the ageing period is strongly suppressed. It is more likely that over these catalysts CA is, rather, deoxygenated than decarbonylated. The deoxygenated species upon subsequent hydrogenation should result in hydrocarbons. Over $Sn–Pt/SiO_2$ catalysts the formation of hydrocarbons at the beginning of the ageing period was really pronounced (see Fig. 1). As the ageing process proceeded the latter reaction was suppressed; however, the hydrocarbon formation was not completely suppressed as hydrocarbons have been observed even in the constant activity period.

Contrary to that, the Pst sites in Pt/SiO_2 catalyst are covered by CO that originated from CA. The adsorbed CO decreases the intrinsic activity of Pt/SiO_2. Thus, the appearance of CO can explain the lower activity of the Pt/SiO_2 catalyst, as well as the loss of activity during the ageing period. Additional explanation for the loss of activity during ageing is the catalyst poisoning by organic residues that originated from the substrate. Similar interpretation was given in earlier studies (1–3, 8).

The above observations are in accordance with a recent suggestion (3) that the ageing period is responsible for the formation of highly selective catalysts in the hydrogenation of CA to crotylalcohol. It has been suggested that in catalysts with high $S_{C=O}$ selectivity the surface of the Sn–Pt bimetallic entities is modified with oxygen retained from the reaction mixture. In our Sn–Pt bimetallic catalysts

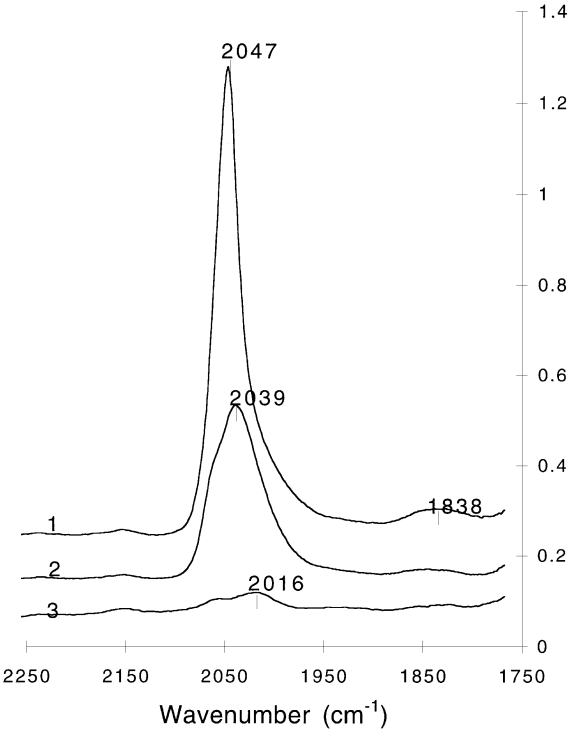

FIG. 3. Adsorption of crotonaldehyde onto Pt/SiO_2 and $Sn–Pt/SiO_2$ catalysts followed by FTIR. Temperature of adsorption: 80°C, catalyst prereduced in hydrogen at 300°C for 90 min. 1. Pt/SiO_2, 2. $Sn–Pt/SiO_2$ ($Sn/Pt_{surf} = 0.5$), 3. $Sn–Pt/SiO_2$ ($Sn/Pt_{surf} = 2.3$).

prepared by CSRs all of the tin introduced is in contact with platinum and the Sn/Pt ratio is high. High Sn/Pt ratio is required to obtain supported platinum clusters decorated by SnO_x species. We believe that the high surface concentration of SnO_x species over Pt is crucial to activate the aldehyde group prior to its hydrogenation, similar to the suggestion given recently by Ponec (3). The character of SnO_x species formed at the top of the Sn–Pt bimetallic cluster is very unique, as none of the attempts to use molecular oxygen in the temperature range of 25–300°C resulted in selectivity improvement or led to a shortened "induction period."

To summarize this study it has been shown that Sn–Pt/SiO_2 catalysts prepared by CSRs are excellent catalyst to hydrogenate CA to crotylalcohol. In order to obtain high $S_{C=O}$ selectivities in the above reaction the Sn/Pt ratio should be high. The high $S_{C=O}$ selectivity is attributed to the reactant-induced activation. In this process the surface of the Sn–Pt bimetallic particle is mildly oxidized by the aldehyde group of the substrate. Further studies are in progress to elucidate the character of the reactant-induced activation process.

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