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Relationship between surface properties of PtSn–SiO_2 catalysts and their catalytic performance for the CO_2 and propylene reaction to yield hydroxybutanoic acid†

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The catalytic coupling of CO_2 and propylene has been studied on a silica-supported platinum–tin catalyst containing the well-defined PtSn phase. Microcalorimetry of adsorption has been applied to investigate the interaction of the reactants with the surface of the catalyst. When the adsorption properties of the bimetallic catalyst are compared with those of monometallic counterparts, significant differences in the strength and number of adsorption sites concerning CO_2 and propylene are evidenced. The adsorption properties of the bimetallic catalyst have been related to its catalytic behaviour. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: catalytic activation of CO_2 in heterogeneous phase; microcalorimetry of adsorption on bimetallics; carboxylic acids from CO_2; heterogeneous catalysis in CO_2–olefin reactions

INTRODUCTION

The reaction of CO_2 with a mono-olefin is an interesting synthetic route to obtain the formation of new C—C bonds. This way can allow the synthesis of useful organic compounds from CO_2 and alkenes, a cheap feedstock available from the petrochemical industry. There exist in the literature various reports in which the coupling between CO_2 and unsaturated hydrocarbons yields to the formation of different types of carboxylic acid, ester and lactone.[1,2] For instance, propylene, CO_2 and methanol react yielding the corresponding *n*- and *iso*-butanoic esters using ruthenium complexes and pressures in the range 150–250 bar.[3] However, minor attention has been devoted to this topic using catalysts in the heterogeneous phase, and only a few examples have been reported.[4,5] In this context, silica-supported platinum–tin catalysts containing the well-defined PtSn phase have been shown to be active in the catalytic activation of CO_2 and ethylene to give lactic acid selectively, in the presence of H_2 or water.[5–7] Here we report the behaviour of this material in the reaction of CO_2 and propylene. The purpose of this research is to progress the understanding of the surface requirements for supported metallic catalysts to be selective for the simultaneous activation of an olefin and carbon dioxide, and their subsequent coupling. A study of the adsorption of the reactants on the catalyst has been carried out by microcalorimetry, and the capability of adsorption of the bimetallic sample has been compared with that of monometallic counterparts.

EXPERIMENTAL

Preparation of catalysts

Aerosil-type SiO_2 (Degussa, 200 $m^2\ g^{-1}$) was used

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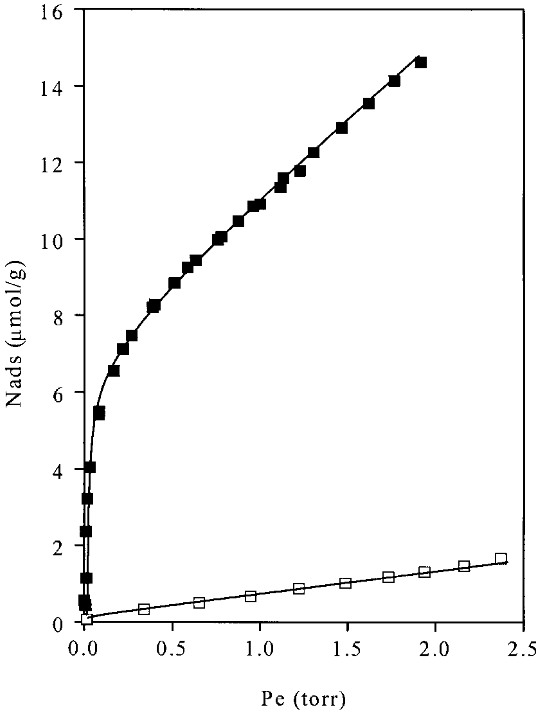

Figure 1 Isotherms of hydrogen adsorption at 330 K on: (■), Pt–SiO_2; (□), PtSn–SiO_2.

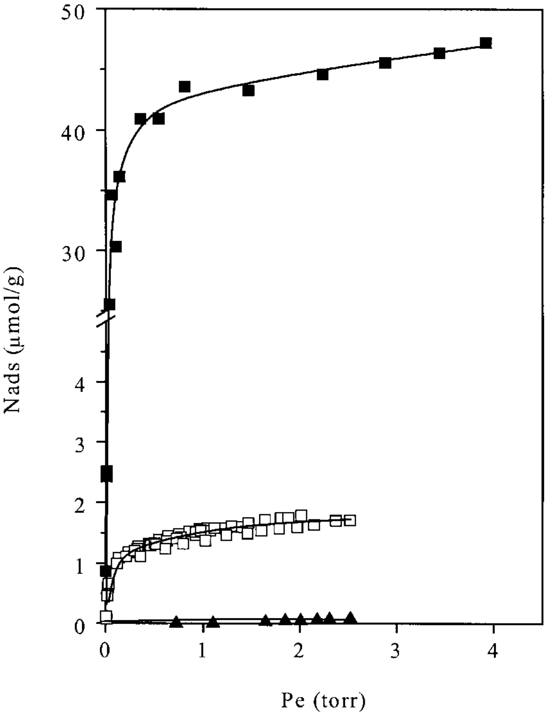

Figure 2 Isotherms of carbon monoxide adsorption at 330 K on: (■), Pt–SiO_2; (□), PtSn–SiO_2; (▲), Sn–SiO_2.

as support. The bimetallic sample PtSn–SiO_2 was prepared by successive impregnations from methylene chloride $[PtCl_2(PPh_3)_2]$ and acetone–$SnCl_2$ solutions as reported elsewhere.[5] By using these metallic precursors, the two monometallic samples Pt–SiO_2 and Sn–SiO_2 were prepared as reference materials. After each impregnation the samples were dried under vacuum at 373 K, and then reduced under hydrogen at 2 K min^{-1} up to 673 K for 16 h.

Adsorption experiments

The heats of adsorption were measured in a differential heat-flow microcalorimeter of the Tian–Calvet type (C80 from Setaram). Details about the experimental set-up can be found elsewhere.[8] The adsorption vessels containing the samples were introduced in the calorimeter and connected to a calibrated dosing system. This apparatus consists of a Pyrex volumetric line equipped with a greaseless stopcock that allows the introduction of small pulses of probe molecules. All samples were exposed to a previous reduction treatment under hydrogen at 673 K for 1 h, and outgassed at the same temperature under high vacuum (10^{-6} mbar) for 16 h; they were then cooled to the adsorption temperature. The hydrogen, carbon monoxide, propylene and carbon dioxide chemisorption behaviours were examined at 330 K. Once the calorimeter containing the reduced sample was thermally stabilized, successive doses of probe molecules were introduced from the volumetric apparatus, until a final pressure of several torrs was reached. The equilibrium pressure relevant to each adsorbed amount was measured by means of a temperature-controlled pressure transducer heated at 373 K (MKS Baratron 628) in the case of propylene and carbon dioxide and a room temperature operating transducer (MKS Baratron 627) was used for hydrogen and carbon monoxide. The differential heats of adsorption Q_{diff} were obtained as the ratio between the exothermic integrated values of each pulse ΔQ_{int} and the adsorbed amount n_a. Gases with a minimum purity of 99.9% were supplied by S.E.O. (Air Liquide). Hydrogen was passed through a trap of liquid nitrogen, whereas propylene, carbon dioxide and

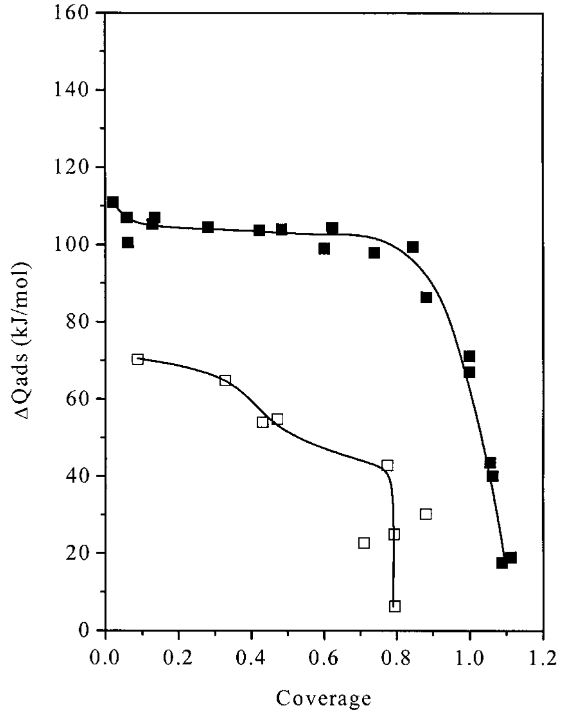

Figure 3 Differential heat of carbon monoxide adsorption on: (■), Pt–SiO$_2$; (□), PtSn–SiO$_2$.

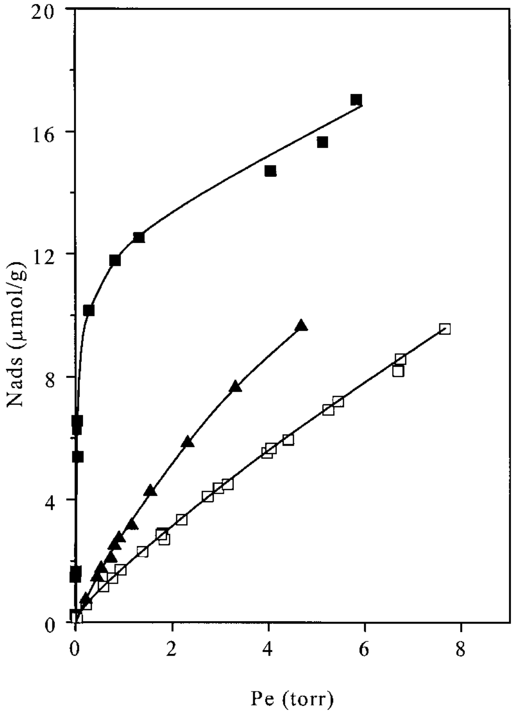

Figure 4 Isotherms of propylene adsorption at 330 K on: (■), Pt–SiO$_2$; (□), PtSn–SiO$_2$; (▲), Sn–SiO$_2$.

carbon monoxide were further purified by performing freeze–pump–thaw cycles.

Catalytic reaction

Catalytic studies were carried out in two different reaction systems: a batch reactor (reaction conditions P_T = 39–59 bar, C_3H_6:CO_2 = 2:3, catalyst charge 0.8 g, T = 393–423 K), and a microreactor operating under continuous flow and differential conditions (reaction conditions P_T = 9 bar, T = 393–453 K, C_3H_6:CO_2:H_2 = 5:5:1). When the batch reactor was used, after 12 h of reaction the solid was treated with a water–methanol mixture. Subsequently, the filtered solution was acidified with HCl, and then analysed. While operating under a continuous flow of reactants, the outlet reactor was automatically sampled on-line using gas chromatography apparatus (Varian 3400 CX). Conversion values were calculated on the basis of propylene consumption. In all cases the reaction products were identified by mass spectrometry using an HP 5920 GC instrument equipped with a mass-selective detector.

RESULTS AND DISCUSSION

A full structural characterization of PtSn–SiO$_2$ and Pt–SiO$_2$ has been reported elsewhere.[5] Briefly, in the PtSn–SiO$_2$ catalyst the presence of the single, well-defined PtSn bimetallic phase has been evidenced (mean particle size 24 nm). The mean particle size determined for Pt–SiO$_2$ has been 1.8 nm. Volumetric isotherms corresponding to hydrogen and carbon monoxide are shown in Figs 1 and 2. In the PtSn–SiO$_2$ sample the number of metallic surface sites able to chemisorb these molecules is very small, according with its structural characteristics. In this catalyst, as stated above, only big particles of the silica-supported well-defined PtSn bimetallic phase had been detected, and a dilution effect of Pt by Sn had been proposed.[9] Figure 3 depicts the differential heats of carbon monoxide adsorption as a function of the coverage. The PtSn–SiO$_2$ sample presents weaker adsorption sites for carbon monoxide than the Pt–SiO$_2$ sample. On the other hand, no adsorption of hydrogen or carbon monoxide was detected for the Sn–SiO$_2$ sample. Concerning the propylene inter-

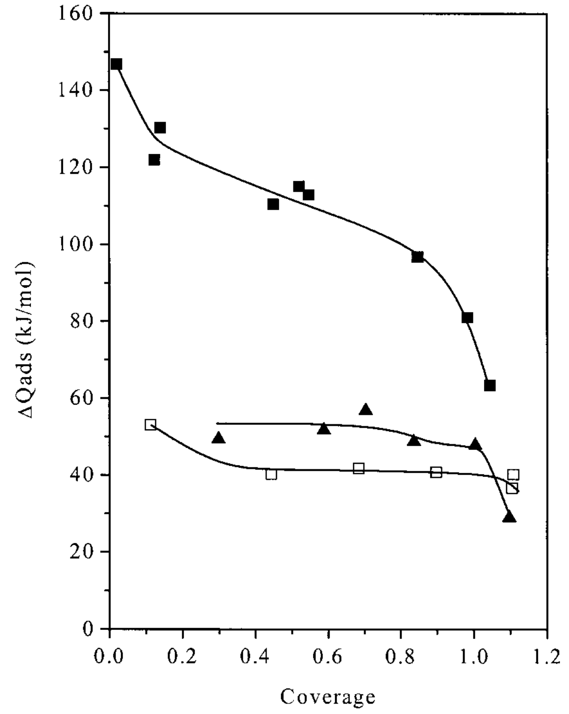

Figure 5 Differential heat of propylene adsorption on: (■), Pt–SiO_2; (□), PtSn–SiO_2; (▲), Sn–SiO_2.

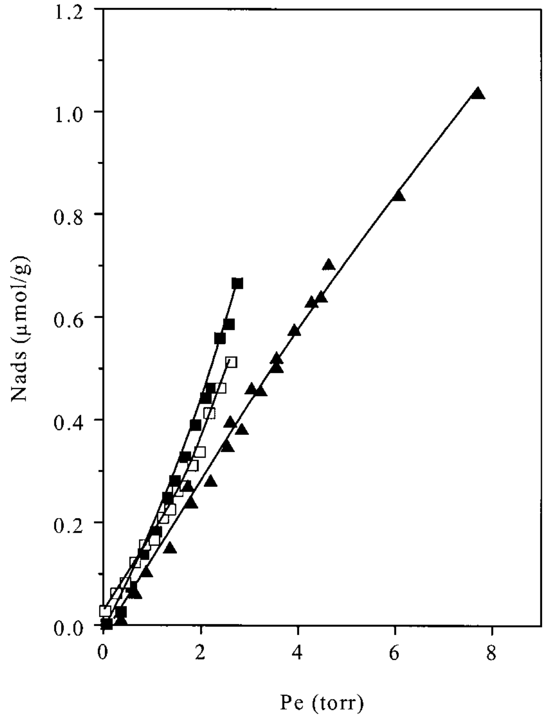

Figure 6 Isotherms of carbon dioxide adsorption at 330 K on: (■), Pt–SiO_2; (□), PtSn–SiO_2; (▲), Sn–SiO_2.

action with the surfaces, a different behaviour of the samples was again evidenced. Figures 4 and 5 show the volumetric adsorption and the differential heats as a function of propylene coverage respectively. Although the adsorption capacities of PtSn–SiO_2 and Sn–SiO_2 are not negligible, they are lower than that of Pt–SiO_2. Besides that, the Pt–SiO_2 sample shows propylene chemisorption heats much higher than that of the PtSn–SiO_2 and Sn–SiO_2 samples. When the carbon dioxide chemisorption is analysed, a distinct behaviour between the different samples is also observed. In Fig. 6 the isotherms of carbon dioxide adsorption are shown for the different samples and Fig. 7 shows the adsorption heats as a function of the amount of adsorbed carbon dioxide. The analysis of these results reveals that even if, under our experimental conditions, the amount of carbon dioxide adsorption surface sites is very low for all catalysts, the initial adsorption heats are significantly higher for PtSn–SiO_2 and

Table 1 Product distribution under dynamic conditions (C_3H_6:CO_2:H_2 = 5:5:1, 9 bar) over the PtSn–SiO_2 catalyst (0.86 g) during a 22 h experiment at different flow rates and temperatures

				Selectivity (%)				
T (K)	C_3H_6 conv. (%)	Total flow (ml min^{-1})	*t* (h)	EtOH	i-PrOH	*n*-PrOH	2-OH-butanoic	HC
393	0.8	11	4	46.0	15.2	24.8	—	14.0
423	1.6	11	6	18.0	33.4	30.3	1.3	17.0
423	0.4	22	8	—	38.3	14.9	—	46.8
453	2.2	11	14	3.0	58.7	14.0	1.8	22.5
423	1.2	5.5	22	9.2	59.7	13.0	0.8	17.3

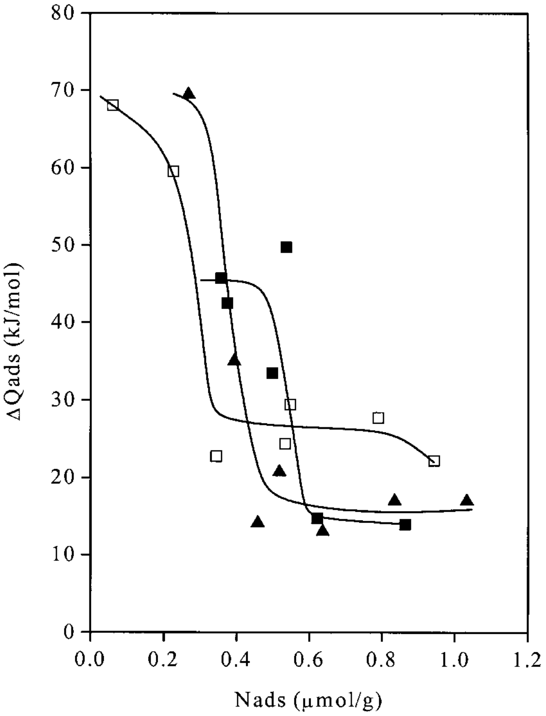

Figure 7 Differential heat of carbon dioxide adsorption on (■), Pt–SiO_2; (□), PtSn–SiO_2; (▲), Sn–SiO_2.

Sn–SiO_2 (70 kJ mol^{-1}) than for the Pt–SiO_2 sample (45 kJ mol^{-1}).

These results indicate that there are significant differences between the behaviour of the PtSn–SiO_2 and Pt–SiO_2 samples in front of reactants. Differences in the carbon monoxide and carbon dioxide adsorption have also been revealed by infrared spectroscopy. The carbon dioxide coordination to PtSn–SiO_2 has been evidenced by the appearance of a band at 2339 cm^{-1}, and this sample has shown a preferred coordination for carbon dioxide rather than for carbon monoxide. In contrast, when the monometallic Pt–SiO_2 catalyst was contacted with carbon dioxide, a band due to coordinated carbon monoxide evolved.[9]

Catalytic studies of the reaction between propylene, carbon dioxide and hydrogen indicate that the PtSn–SiO_2 bimetallic catalyst produces the coupling reaction with formation of hydroxybutanoic acids. Taking into account that the PtSn–SiO_2 catalyst has been shown to be active in the reverse water-gas shift reaction,[5] we interpret these results via the formation of water, which takes part in the reaction with propylene and carbon dioxide.

Table 2 C_4 carboxylic derivatives extracted from the coupling reaction between propylene and carbon dioxide over the PtSn–SiO_2 catalyst

T (K)	*P* (bar)	mmol 3-OH–butanoate/g cat[a]
393	39	1.3
423	59	3.9

[a] Includes 3-OH–butanoic acid and 3-OH–butanoic methyl ester.

However, the process to obtain hydroxybutanoic acids is not selective and the distribution of products changes under different reaction conditions.

Table 1 compiles the catalytic data for the process carried out under a continuous flow of reactants. 2-Hydroxybutanoic acid is produced at temperatures higher than 423 K through:

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

$$C_3H_6 + H_2O + CO_2 \longrightarrow CH_3CH_2CH\ (OH)\ COOH$$

However, ethanol, isopropanol and *n*-propanol constitute the main products of the reaction in any condition. When the reaction is carried out in the batch reactor at higher pressure and longer contact time, besides isopropanol, 3-hydroxybutanoate is extracted (3-hydroxybutanoic acid and 3-hydroxybutanoic methyl ester). The higher the temperature and pressure the greater is the amount of 3-hydroxybutanoate extracted (see Table 2). The reactivity of propylene versus water determines the selectivity of the process as a function of the reaction conditions used.

In this work, the differences in the properties of PtSn–SiO_2 and Pt–SiO_2 catalysts for the adsorption of hydrogen, carbon monoxide, carbon dioxide and propylene have been determined and related to their structural characteristics. All these characterization results can be used to understand the improved catalytic properties of the PtSn–SiO_2 for the simultaneous activation of carbon dioxide and lower olefins. In particular, the unique properties of the bimetallic sample for carbon dioxide adsorption may contribute to its capability to give the coupling reaction.

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