

Letter

Bimetallic Pd–Zn silica-supported catalyst for CO hydrogenation. In situ DRIFT study

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Abstract

We report the behaviour of a silica-supported Pd–Zn catalyst in the hydrogenation of CO (total pressure=20 bar, $T=548\text{--}598$ K). Unusual high selectivity to higher hydrocarbons and higher oxygenated products (ethanol and acetaldehyde) was observed. An in-situ DRIFT study under reaction conditions, with analysis by mass spectrometry of products evolved, was carried out. The presence of surface acetate species is related to the production of acetaldehyde, which is proposed to be the primary C₂-oxygenated product. © 2000 Elsevier Science B.V. All rights reserved.

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Palladium-based catalysts have been extensively studied in the synthesis of methanol. In particular, the effect of alkali, alkaline-earth and lanthanide metals as promoters has been deeply analyzed [1–4]. In some cases, besides methanol and methane, low selectivity to ethanol and higher hydrocarbons has been obtained [1]. Some proposals for the active site of these catalysts in the chain growing have been given. For lithium-promoted Pd/CeO₂ catalysts, the coordination of CO to Pd and Li⁺ has been cited to explain the catalytic behaviour in the synthesis of ethanol and higher hydrocarbons [5]. In other cases, the effect of promoters which can alloy with palladium has been related to the formation of bimetallic phases. In this context, the Pd₃Fe phase may be responsi-

ble for the C₂+ hydrocarbon production in Pd–Fe catalysts [6].

However, few studies deal with the influence of inactive metals which could alloy with palladium. Here we report the catalytic behaviour of a silica-supported PdZn catalyst which shows high selectivity to higher hydrocarbons and alcohols in CO hydrogenation. An “in situ” DRIFT study under reaction conditions, with on-line analysis of evolved products, was carried out. This study allowed the identification of some surface species involved in the reaction.

Bimetallic catalyst was prepared by successive impregnations of PdCl₂ and ZnCl₂ solutions onto aerosil-type silica (Degussa, BET surface-area 200 m² g⁻¹). For Pd impregnation the incipient-wetness method was used with an acidified aqueous solution, then catalyst was dried under vacuum at 373 K and Zn was impregnated by free adsorption from an acetone solution of ZnCl₂. Sample was then dried under vacuum at 373 K and subsequently reduced at 673 K

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under flowing hydrogen. The catalyst composition was Pd (%)=2.53 (w/w), Zn (%)=0.52 (w/w). Catalytic tests were carried out in a stainless-steel microreactor under flowing CO/H₂=1 mixtures (total flow 40 ml/min) at 20 bar total pressure and temperature up to 598 K using 0.4–0.6 g of powdered catalyst. Catalytic data were obtained 3 h after any experimental change. For the DRIFT study ca. 20 mg of catalyst was placed in a catalytic chamber (Spectra Tech, 0030-102) which allowed thermal and pressure operations under flowing reactant gases. Helium-diluted CO/H₂=1 mixtures (total flow ca. 30 ml/min) were used under 20 bar of total pressure and temperature up to 598 K. All spectra were acquired at 4 cm⁻¹ resolution in a Magna 750 Nicolet FTIR apparatus. Blank spectra of the gas phase and the background of the catalyst were subtracted at each experimental condition. Products evolved from the infrared chamber were monitored continuously by on line mass spectrometry. The outlet of the DRIFT chamber was connected through a capillary tube held at 393 K to a Balzers instrument equipped with a QMS 200 quadrupole mass spectrometer. Products evolved were also analyzed by gas chromatography when necessary. Chemisorption of different reactants was also carried out in separate experiments in order to identify some adsorbed species under the reaction conditions [7].

Table 1 shows the results of some catalytic tests carried out at 20 bar. Besides methane, methanol and CO₂, higher hydrocarbons (C₂–C₅), acetaldehyde and ethanol were produced. An increase in temperature from 548 to 598 K produced an increase in the CO conversion. Under these conditions, temperature had little effect on the selectivity values to CO₂ or methane. However, the selectivity to oxygenates in-

Table 1

CO hydrogenation reaction over Pd–Zn/SiO₂ catalyst. CO/H₂=1, 40 ml/min, total pressure 20 bar

T (K)	CO conversion (%)	Selectivity (%) ^a				
		CO ₂	CH ₄	C _{2+HC} ^b	MeOH	C _{2ox} ^c
548	1.8	10	19	36	10	25
573	4.4	10	21	45	9	15
598	9.8	11	21	48	6	14

^a(CO converted to a product/total CO converted)×100.

^bC₂–C₅ hydrocarbons.

^cAcetaldehyde and ethanol.

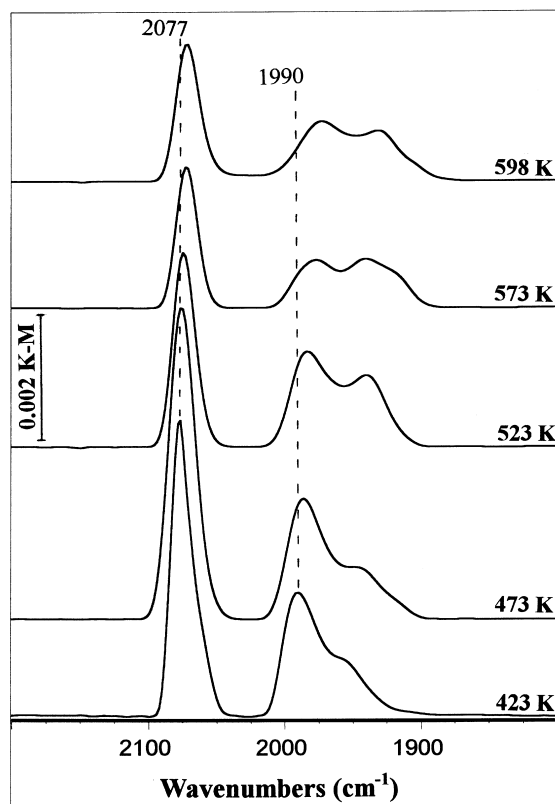


Fig. 1. DRIFT spectra of the PdZn/SiO₂ catalyst under a flow of He:CO:H₂=24:2:2 ml/min at 20 bar of total pressure. Evolution with the reaction temperature.

cluding methanol and higher oxygenates decreased and selectivity to higher hydrocarbons increased when the temperature rose from 548 to 598 K.

DRIFT experiments were carried out under CO hydrogenation conditions (He:CO:H₂=24:2:2 ml/min) also under a total pressure of 20 bar. Fig. 1 shows the spectra in the region 2200–1800 cm⁻¹ as a function of reaction temperature (423–598 K). In all cases, bands due to coordinated CO, linear and bridged, were observed. When temperature increased from 423 to 598 K, the wave numbers corresponding to linear CO species decreased from 2077 to ca. 2072 cm⁻¹. The pattern corresponding to bridged CO also changed as a function of reaction temperature (Fig. 1). At 423 K, a main absorption centered at 1990 cm⁻¹ and a shoulder at 1949 cm⁻¹ appeared. The increase in temperature produced a progressive shift of the bands to lower

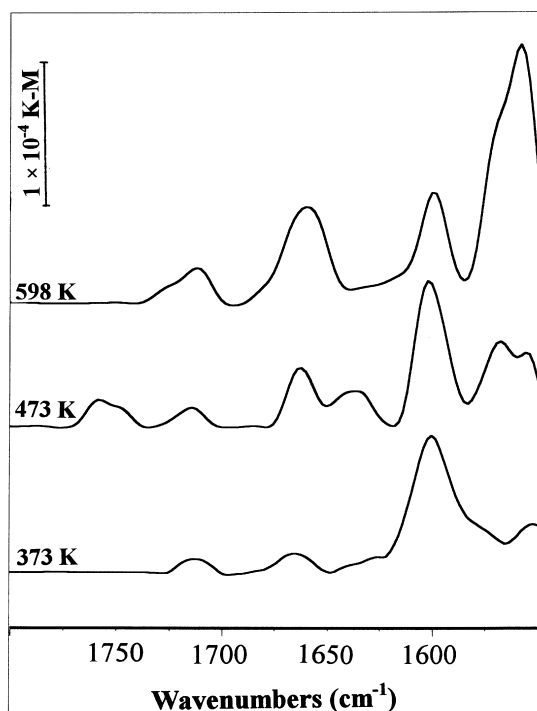


Fig. 2. DRIFT spectra of the PdZn/SiO₂ catalyst under a flow of He:CO:H₂=24:2:2 ml/min at 20 bar of total pressure. Evolution with the reaction temperature.

wave numbers, accompanied by a change in their relative intensity. At 598 K, the spectrum showed two main adsorptions in the zone corresponding to ν_{stretch} of bridged CO (see Fig. 1). These bands are centered at 1974 and 1929 cm⁻¹, however shoulders appeared at lower wave numbers. This indicates that when temperature increases new coordinated CO species are generated in which the C–O bonding becomes progressively weaker.

Fig. 2 shows the evolution of the spectra in the region below 1800 cm⁻¹, as a function of temperature. At 373 K, a well-defined band centered at 1600 cm⁻¹ appeared, which may be related to the presence of formiate species [8,9]. This band remained up to 598 K. At 473 K, bands at 1760–1740 cm⁻¹ appeared, which could be related to acetic acid on the silica support [10–12]. New bands in the region 1570–1550 and 1640 cm⁻¹ are also generated at this temperature. Even if these bands may correspond to carbonate and hydrogenocarbonate species, bands at 1570–1550

cm⁻¹ can also be assigned to bidentate acetate species [11]. The band at 1638 cm⁻¹, by comparison to the spectra of palladium acetate complexes, may be assigned to monodentate acetate species on palladium [13]. Simultaneously to the DRIFT analysis, products evolved were analyzed by on-line M.S. At 473 K, the evolution of C₁ and C₂ hydrocarbons, acetaldehyde and a smaller amount of ethanol was determined. Production of oxygenates increased with temperature up to 598 K. However, methanol was not detected under these experimental conditions. At 598 K, no bands due to physisorbed acetic acid were present (Fig. 2, bands at 1760–1740 cm⁻¹), simultaneously the intensity of the bands at 1570–1500, 1660 and 1713 cm⁻¹ increased (Fig. 2). This indicates an increase in plausible bidentate acetate species at this temperature. The band at 1660 cm⁻¹, whose intensity increased with temperature, may correspond to acyl species. Over supported Rh catalysts a relation between the presence of bidentate acetate species and ethanol synthesis through acetaldehyde has been proposed [10,11]. In our case, the production of acetaldehyde and ethanol increased with the temperature under these conditions, as determined from MS and GC analysis. The defined band at 1713 cm⁻¹ may be attributed to the presence of acetaldehyde, which was the main oxygenated product under the experimental conditions used in the DRIFT experiments [7]. Taking into account that methanol was not detected under these conditions but it was produced in the catalytic tests (Table 1), at 598 K, the reagent flow was enriched in CO and H₂, to give reaction mixtures He:CO:H₂ = 16:6:6; and He:CO:H₂=0:14:14 (cm³/min). Only when this last mixture (with higher partial pressure of reactants) was used in the DRIFT experiments was methanol identified in the reaction products.

The bimetallic PdZn silica-supported catalyst prepared in this work showed unusual behaviour in CO hydrogenation, its ability to produce the chain-growing and to insert CO on a M-alkyl bond may be responsible for the high selectivity to higher hydrocarbons and C₂-oxygenates shown by this catalyst. Probably, this is due to a decrease in the hydrogenating properties of palladium produced by Zn. Although the CO dissociation is favoured over this bimetallic catalyst, the formation of CH₄ from CH_x hydrogenation is not. The probability of chain growth through CH_x species increases and higher

hydrocarbons are obtained. On the other hand, DRIFT experiments indicated that the presence of bidentate and monodentate acetate species may be related to the production of acetaldehyde, which would be the primary C₂-oxygenated product; ethanol would be produced from acetaldehyde reduction.

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