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Organometallics derived $(Pd + Ln)/SiO_2$ catalysts for the reactions of synthesis gas conversion

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C_3H_6 hydroformylation and CH_3OH synthesis on organometallics derived $(Pd + Ln)/SiO_2$ and Pd/SiO_2 catalysts have been studied. The activity and selectivity towards methanol in $CO + H_2$ reaction were observed to increase for all the modified catalysts while both the hydroformylation activity and selectivity towards oxygenates in C_3H_6 hydroformylation decreased for the catalysts in comparison to those of Pd/SiO_2. The FTIR, TPD data and characteristic catalytic properties of the catalysts studied allow to suggest that C_3H_6 hydroformylation on $(Pd + Ln)/SiO_2$ catalysts occurs on monometallic Pd clusters without participation of mixed active sites and CO complexes activated thereon.

Keywords: Palladium; rare earth elements; silica; temperature programmed desorption; CO hydrogenation; C_3H_6 hydroformylation

1. Introduction

During the last two decades abundant experimental data have been summarized supporting the assumption of the effective application of rare earth elements to modify the catalytic properties of supported group VIII metals [1–3]. Studies of the activity and selectivity of Pd/SiO_2 and $(Pd + Ln)/SiO_2$ catalysts for CO hydrogenation have been the subject of a number of investigations [4–14]. The catalysts were prepared either by incipient wetness impregnation or by ion exchange or via organometallics [10,11,14] and produced mainly methane and methanol. Hydroformylation of olefins is a widely used industrial process in C_1-chemistry for aldehyde and alcohol production with homogeneous catalysts. When light olefins are used as a substrate heterogeneous catalysts could be of interest. Moreover, there is some analogy between olefin hydroformylation and C_{2+}-oxygenate synthesis from $CO + H_2$ mixture. Oxygenates in the last reaction appear to result from migratory insertion of CO adsorbed into the bond between surface metal atom and surface alkyl formed in turn from adsorbed CO and H_2 by the consequence of elementary steps [15–17]. The key step of olefin hydroformylation is also migratory CO insertion [18]. However, few papers are concerned with vapor phase hydroformylation of olefins on supported Pd catalyst [19–23] and there are no papers on hydroformylation for supported Pd + Ln catalysts.

The goal of the present study is to compare the adsorptive and catalytic properties in the reactions of CO hydrogenation and propylene hydroformylation of organometallics derived Pd/SiO_2 catalyst and $(Pd + Ln)/SiO_2$ ones containing surface sites of palladium clusters stabilized on silica anchored lanthanide ions.

2. Experimental

Vacuum dehydrated silica with specific surface area of 250 $m^2\ g^{-1}$ was used as a support. Pd/SiO_2 catalyst was obtained by interaction of pentane solution of allylpalladiumcyclopentadienyl with hydroxyl groups of SiO_2. $(Pd + Ln)/SiO_2$ catalysts were prepared as described elsewhere [10,11]. Silica was modified by chemisorption of tris(isopropylcyclopentadienyl) complex of a lanthanide from pentane solution and anchored lanthanide complexes were decomposed in a flow of O_2 to remove organic ligands and to obtain ions of the rare earth elements in the requisite oxidation state. Then allylpalladiumcyclopentadienyl from pentane solution was supported on modified silica. Concentration of lanthanides in the catalyst samples was determined by means of the weight method [24]. Pd loading in all cases was determined by X-ray fluorescence spectroscopy. Metal loadings in the catalysts studied are listed in the tables. The preparation and testing of catalysts were performed in a glass apparatus without contact with air.

Chemisorption measurements were carried out in a pulse flow reactor, with the gases analysed by using gas chromatography. To remove organic admixtures, samples were oxidized in air at 573 K and then reduced with H_2 and evacuated at the reduction temperature up to 0.1 Pa. Then pulse oxidation with O_2 at 298 K and hydrogen titration at the same temperature were carried out.

IR spectra were recorded on a Bruker IFS-113 V Fourier spectrometer within 1300–4000 cm^{-1} with a resolution of 4 cm^{-1} as described elsewhere [14].

Temperature programmed desorption (TPD) of hydrogen was carried out following treatment of catalysts with hydrogen at 323 K and cooling the sample in H_2 flow to room temperature. Moreover, the TPD of H_2 was carried out upon hydrogen treatment at 573 K, catalysts exposing in Ar flow at the same temperature for 2 h, cooling the catalyst in argon to 323 K and H_2 adsorption. TPD of CO was performed following reduction of the catalysts with hydrogen at 773 K exposing them in He flow at the same temperature for 2 h, cooling the sample in helium to room temperature and CO adsorption. The evolving gases were registered with a catharometer. Helium was used as carrier gas to treat CO, while argon was employed for hydrogen.

CO hydrogenation was performed on catalysts reduced at 573 K in a copper flow reactor at 523 K, 10 atm, CO : H_2 = 1 : 2, with space feed velocity 20000 h^{-1}, with $<1\%$ conversion as described previously [11]. The activity and selectivity were determined in 30 min on stream. Only negligible amount of methane and methanol was formed in the empty reactor at the reaction conditions and it took into account when activity and selectivity of the catalysts were calculated. Propylene hydroformylation was performed on catalysts without any preliminary treatment in the glass flow reactor at 323 K, 1 atm, CO : H_2 : olefin = 1 : 1 : 1 with $<5\%$ conversion. Steady state activity and selectivity were determined. The reaction products were analyzed by means of gas liquid chromatography.

3. Results and discussion

When SiO_2 is treated with pentane solution of $(i\text{-}C_3H_7C_5H_4)_3Ln$ decoloration of colored solution and coloration of support due to irreversible complex adsorption are observed. The highest amount of Ln complex adsorbed is approximately equal to the hydroxyl group concentration on the silica surface [25]. It is reasonable to suggest that treatment of Ln/SiO_2 in oxygen flow at 873 K removes organic ligands and leads to formation of surface Ln ions in the highest oxidation state. Contact of pentane solution of $C_3H_5PdC_5H_5$ with Ln/SiO_2 also results in decoloration of the solution. Probably, the palladium complex interacts both with the anchored Ln ions and with reactive surface hydroxyl groups consumed after Ln complex adsorption.

The results of H_2-O_2 titration presented in table 1 demonstrate the dispersions of Pd in (Pd + Ln)/SiO_2 catalysts to be rather high. Moreover, the dispersion is the same for the reduction temperatures of 573 and 873 K. Similar observations have also been reported for Ln_2O_3-, CeO_2-, Pr_6O_{11}-, Sm_2O_3- and Nd_2O_3-promoted Pd/SiO_2 [12]. Under the same conditions the dispersion of silica supported Pd in unmodified catalyst decreased from 0.66 to 0.40.

The results of the H_2 TPD study for a number of (Pd + Ln)/SiO_2 catalysts and that of Pd/SiO_2 are presented in fig. 1. There are two adsorbed modes of H_2 desorbing within 358–398 and 638–693 K, with negligible amount of hydrogen desorbed at low temperature. The lower temperature peak in H_2 TPD spectra of (Pd + Ln)/SiO_2 might be assigned to the H_2 desorption from homonuclear Pd clusters. The higher temperature peak might be due to (i) H_2 activation on Pd atoms of mixed Pd$-Ln^{n+}$ sites or to (ii) H_2 desorption from rare earth ions [26], to which hydrogen was spilled from Pd. The presence of this peak can give a reason for some interaction between Pd atoms and Ln ions anyway (Ln/SiO_2 catalysts have not the H_2 TPD spectrum). The initial coverages by adsorbed H atoms, H/Pd, are calculated

Table 1
Adsorptive properties of (Pd + Ln)/SiO_2 catalysts

Catalyst composition (wt%)	Temperature of reduction (K)	H/Pd ratio	CO/Pd ratio	H/Pd ratio (HT)	Pd_s/Pd_t [a] ratio
1.4% Pd + 2.5% La	573	–	–	2.19	0.73
	873	–	–	1.74	0.58
1.6% Pd + 2.9% Ce	573	–	–	2.25	0.75
	873	–	–	1.86	0.62
3.8% Pd + 5.0% Pr	573	0.32	0.45	2.13	0.71
	873	–	–	2.17	0.72
2.3% Pd + 2.7% Sm	573	0.32	0.28	1.79	0.60
2.1% Pd + 2.8% Dy	573	0.15	0.23	2.05	0.68
2.1% Pd + 7.7% Ho	573	0.34	0.32	2.13	0.71
	873	–	–	2.08	0.69
2.5% Pd + 4.3% Tm	573	–	–	2.11	0.70
2.1% Pd + 0.6% Yb	573	–	–	2.05	0.68
3.2% Pd	573	0.63	0.59	2.01	0.67
	873	0.40	–	1.2	0.40

[a] Pd dispersion calculated from the results of hydrogen titration assuming the stoichiometry equal to 3.

from the amount of H_2 desorbed up to 773 K and are listed in table 2. High H/Pd ratios could be due to H_2 spillover. It has been observed that only small adsorption of CO determined from CO TPD data occurred on the catalysts studied.

It is worth noting that the moles of exposed Pd determined by H_2–O_2 titration are quite different from those determined by H_2 or CO chemisorption (see table 1). These differences can be assigned (i) to the formation of M_{VIII}–Ln alloy particles

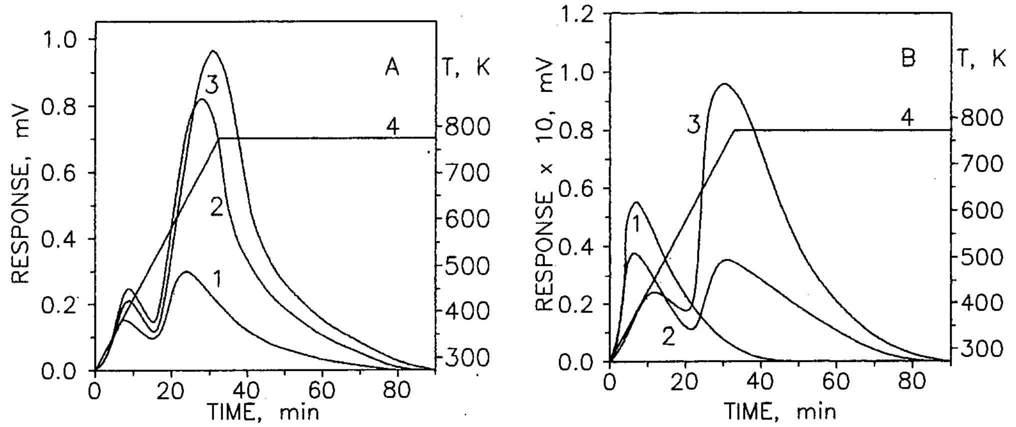

Fig. 1. The H_2 TPD spectra for 3.2% Pd/SiO_2 (1), (1.6% Pd + 2.9 Ce%)/SiO_2 (2) and (3.8% Pd + 5.0% Pr)/SiO_2 (3) catalysts. Curve 4 is the catalyst bed temperature versus time. (A) Pretreatment in hydrogen at 323 K, (B) at 573 K.

Table 2
The parameters of H_2 TPD spectra for some Pd + Ln and Pd catalysts

Catalyst[a]	T_{max}[b]		S_β/S_α[c]	H/Pd	
	α	β		323 K	573 K
(1.6% Pd + 2.9% Ce)/SiO_2	398 (423)	673 (773)	13 (1.4)	13.7	1.0
(3.8% Pd + 5.0% Pr)/SiO_2	398 (443)	693 (773)	16 (12)	15.2	2.8
(2.5% Pd + 4.3% Tm)/SiO_2	358 (413)	638 (693)	12 (0.5)	12.2	0.4
3.2% Pd/SiO_2	393 (383)	623	7	5.2	0.5

[a] Before H_2 adsorption the catalysts were reduced at 323 K or 573 K.

[b] The temperature of a peak location (in parentheses the reduction temperature of 573 K is illustrated).

[c] Peak surface ratio (in parentheses the reduction temperature of 573 K is illustrated).

during high temperature catalyst reduction yielding a decrease in moles of the exposed group VIII metal atoms [27], (ii) to the wetting of the Pd surface by the oxide promoter [12,28–30], (iii) to the changes in electron state of Pd in the presence of Ln-ions resulting in the suppression of H_2 and CO adsorption [12,29]. In the present paper the suppression of H_2 and CO chemisorption (see table 1) was observed for (Pd + Ln)/SiO_2 catalysts reduced at moderate temperature (573 K). Pd dispersion in the catalysts remained high, Ln_xO_y-phases or Pd–Ln alloy particles have not been observed [10,14]. Therefore, the changes in adsorptive properties of silica supported Pd modified by Ln-ions is not related with the blockage of Pd surface by Ln_xO_y particles, but these changes could be due to an electron interaction between Pd and surface Ln-ions. This viewpoint is supported by H_2 TPD data (fig. 1b). They allow to conclude that most of the Pd surface in (Pd + Ln)/SiO_2 catalysts reduced at 573 K is blocked by hydrogen which could not be removed by a continuous flow of inert gas at the reduction temperature. Hence adsorbed hydrogen is also not removed by evacuation following reduction at the same conditions in the measurements of H_2 and CO chemisorption.

FTIR studies of CO adsorption were performed for Ln-containing and unmodified supported Pd catalysts. Two absorption bands within 2103–2060 and 1975–1900 cm^{-1} were reasonably assigned to linear and bridging carbonyl on Pd atoms, respectively [31]. A low-frequency band within 1629–1600 cm^{-1} on modified catalysts can be attributed to CO adsorbed on mixed $Pd–Ln^{n+}$ sites. For (2.0% Pd + 7.7% Ho)/SiO_2 catalyst the last band is situated within 1629–1622 cm^{-1} depending on CO pressure (fig. 2).

Some results for the hydroformylation of propylene at 323 K and methanol synthesis are shown in table 3. Upon adding rare earth elements to silica supported palladium its activity and selectivity towards methanol in the CO + H_2 reaction increase. The highest promoting effect is observed for Pr and Ho. Both the hydroformylation and hydrogenation activities appeared to decrease in C_3H_6 hydroformylation for all (Pd + Ln)/SiO_2 catalysts in comparison to those of Pd/SiO_2. The selectivity towards hydroformylation also decreased for Ln-containing Pd cata-

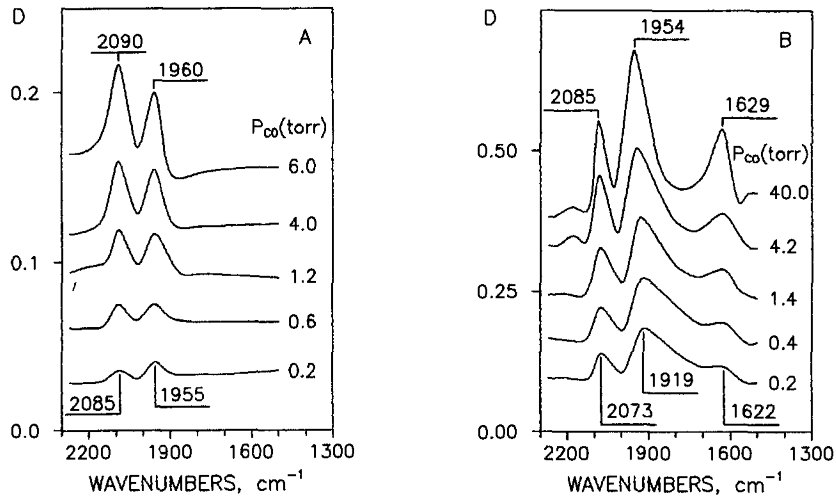

Fig. 2. IR spectra of CO adsorbed at 0.2–40 Torr pressure on 3.2% Pd/SiO_2 (A) and (2.0% Pd + 7.7% Ho)/SiO_2 (B) catalysts reduced with H_2 at 573 K.

lysts. Hydrogen pretreatment of the studied catalysts leads to the decrease of hydroformylation activity in proportion to rising reduction temperature. In general, the catalysts of highest hydroformylation activity exhibit the lowest activity in methanol synthesis. There seems to be a correlation between H/Pd ratio of the catalysts studied and their catalytic properties (compare the data of tables 2 and 3).

Table 3
Hydroformylation of propylene at 323 K and methanol synthesis at 523 K on silica supported Pd + Ln catalysts

Catalyst	Activity in propylene hydroformylation[a]		i/n[c]	Activity in methanol synthesis[d]
	C_3H_8	oxygenates[b]		
(1.4% Pd + 2.5% La)/SiO_2	7.4	1.6	2.3	3.0
(1.6% Pd + 2.9% Ce)/SiO_2	4.7	0.7	4.0	7.3
(3.8% Pd + 5.0% Pr)/SiO_2	4.5	0.0	–	10.0
(2.3% Pd + 2.7% Sm)/SiO_2	5.5	0.6	3.2	6.0
(2.1% Pd + 4.8% Dy)/SiO_2	6.4	0.0	–	6.1
(2.1% Pd + 7.7% Ho)/SiO_2	4.3	0.0	–	8.2
(2.5% Pd + 4.3% Tm)/SiO_2	5.0	0.5	4.5	4.7
(2.1% Pd + 0.6% Yb)/SiO_2	7.9	1.3	1.6	2.7
3.2% Pd/SiO_2	9.6	3.0	1.5	1.0

[a] In mmol (mmol Pd)$^{-1}$ min^{-1}.

[b] n-C_3H_7CHO + i-C_3H_7CHO.

[c] i-C_3H_7CHO/n-C_3H_7CHO ratio among oxygen-containing products of propylene hydroformylation.

[d] In mmol CO (mol Pd)$^{-1}$ s^{-1}.

It is interesting to note that all catalysts gave 2-methylpropionaldehyde as the main product of the hydroformylation reaction. For $(Pd + Tm)/SiO_2$ catalyst the iso/*n* ratio can reach 4.4 (see table 3). The increase of reaction temperature results in a decreasing iso/*n* ratio. Electron deficiency of supported Pd atoms due to their interaction with lanthanide ions [14] should cause an increasing iso/*n* ratio among oxygenates of propylene hydroformylation and a significant change in the distribution of H_2 adstates to their high temperature mode (fig. 1).

The kinetics of C_3H_7CHO and C_3H_8 formation, as the products of C_3H_6 hydroformylation on $(2.1\%\,Pd + 0.6\%\,Yb)/SiO_2$, $(1.6\%\,Pd + 2.9\%\,Ce)/SiO_2$ and 3.2% Pd/SiO_2 catalysts has been studied. The propylene hydroformylation reaction has a lower hydrogen and propylene reaction order and a less negative CO order compared to that for the propylene hydrogenation reaction. Both reactions of hydroformylation and hydrogenation for all studied catalysts had close kinetics parameters. This suggests that propylene hydroformylation on the catalysts should employ the same mechanism.

FTIR, TPD data and features of methanol synthesis and olefin hydroformylation on $(Pd + Ln)/SiO_2$ and Pd/SiO_2 catalysts suggest that two types of active sites are formed on the surface of $(Pd + Ln)/SiO_2$ catalysts upon $C_3H_5PdC_5H_5$ adsorption on Ln/SiO_2 and reduction: monometallic Pd clusters and mixed bimetallic $Pd\text{–}Ln^{n+}$ centers. The presence of mixed active sites leads to the new forms of CO and H_2 activation which appear as a low-frequency band in CO adsorbed FTIR spectra, high temperature peak in H_2 TPD spectra and H_2 spillover. Olefin hydroformylation on $(Pd + Ln)/SiO_2$ catalysts could occur on monometallic Pd clusters without participation of mixed active sites and CO complexes activated thereon while bimetallic $Pd\text{–}Ln^{n+}$ centers could be responsible for methanol synthesis from CO and H_2. Probably, fast hydrogenolysis of the alkyl–palladium bond (i.e. prior to CO insertion) on Ln-containing Pd catalysts makes them free of hydroformylation activity. The facility of surface migration of Pd atoms at elevated temperature should lead to the consumption of monometallic Pd clusters during high temperature reduction of bimetallic catalysts [32] and, as a consequence, to the decrease of their hydroformylation activity.

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