Coke deposition on supported palladium catalysts

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Palladium / silica catalysts of varying dispersities were submitted to the coking reaction with cyclopentane at 500°C. Temperature programmed oxidation curves reveal the presence of two peaks for carbon deposition on the metallic function: the first one near 250°C would correspond to coke deposited on palladium atoms of high coordination and the second one near 400°C would involve palladium atoms of low coordination.

Keywords: coke deposition on palladium; palladium catalyzed coking of cyclopentane; coke deposition; palladium catalyst

1. Introduction

Catalytic reforming is an important process for the production of high-octane gasoline and aromatics from naphtas [1]. Most conventional reforming catalysts are based on well-dispersed platinum on a chlorinated alumina [2]. However, since the early introduction of Pt / KL catalysts for the selective aromatization of linear alkanes [3], much work has been devoted to the preparation and characterization of non acidic Pt and Pd catalysts as a possible alternative to the classical bifunctional systems for hydrocarbon reforming [4–6].

An important feature of the catalytic reforming is that the catalyst deactivates in the course of the process, mainly as a result of coke deposition. In the literature, many papers are devoted to the deactivation of platinum based catalysts by carbonaceous deposits. On the other hand, very little is known about the coking reaction on palladium catalysts. The aim of this work was to study the reaction of coke deposition on supported palladium catalysts. Silica was chosen as catalyst support on account of its low acidity in order to avoid or to restrict carbon deposition on the acidic sites of the carrier.

2. Experimental

Catalyst A was prepared by impregnation of silica powder (Shell, 200 m^2/g) with an aqueous solution of $Pd(NH_3)_4(NO_3)_2$. After drying at 120°C overnight, it was calcined in air for 4 h at 300°C and reduced in pure hydrogen for 4 h at 500°C.

Catalysts B and C were obtained by sintering of catalyst A under dry oxidizing atmosphere (1% O_2 in nitrogen) for 10 h at 550 and 600°C, respectively.

Catalyst D was prepared by impregnation of α-alumina powder (SCS 9, Rhône-Poulenc) using bis (acetylacetano) palladium ($Pd(C_5H_7O_2)_2$). After drying at 120°C, it was calcined in air for 4 h at 300°C and reduced in pure hydrogen for 4 h at 500°C.

The metal dispersion was determined by volumetric chemisorption in a conventional glass system equipped with a turbomolecular pump. The system is capable of a dynamic vacuum typically below 10^{-4} Pa. Prereduced samples were reduced again at 500°C, then outgassed at this temperature and cooled to room temperature. Metal accessibilities were obtained by the hydrogen chemisorption method at 70°C [7]. The characteristics of the different catalysts are reported in table 1.

The coking reaction was carried out at 500°C under atmospheric pressure in a classical glass flow reactor. Cyclopentane (Fluka, purum) was employed as a coking agent with a hydrogen : hydrocarbon molar ratio of 2.33 and a WHSV of 2.

The coke deposit was analysed by temperature-programmed oxidation (TPO), the temperature being increased from 25 to 600°C at 7°C min^{-1}. Oxygen, diluted 1 / 100 in helium, was used. The determination of the oxygen consumed and the carbon dioxide produced was carried out at intervals of 1 min by gas chromatography.

The toxicity of coke for the metallic function was defined by its fouling effect on the reaction of cyclohexane dehydrogenation. This reaction was carried out at 270°C under atmospheric pressure with a hydrogen:

Table 1
Characteristics of catalysts

Catalyst	Pt (%)	Pd (%)	*D* (%)
A–Pd/SiO_2	–	1.0	53
B–Pd/SiO_2	–	1.0	37
C–Pd/SiO_2	–	1.0	23
D–Pd/Al_2O_3	–	0.2	42
E–Pt/SiO_2	6.0	–	48

hydrocarbon molar ratio of 33. Cyclohexane dehydrogenation was used also to follow the regeneration of the metallic function after coke burning at various temperatures.

FT-IR experiments of adsorbed CO were carried out on the 1 wt% Pt/SiO_2 catalyst ($D = 53\%$). Samples (30 mg) were pressed into a disk wafer with an 18 mm diameter. The wafer was pretreated in situ in the IR spectrometer. The catalyst was evacuated at room temperature and then reduced under hydrogen at 100°C for 30 min. After cooling and evacuation of hydrogen, the chemisorption of carbon monoxide was performed at room temperature under a pressure of 660 Pa. The IR spectra were recorded with a Nicolet Magna (750) FT-IR spectrometer (resolution 4 cm^{-1}). The spectra presented are obtained by difference between the absorbances of the sample after and before adsorption of the probe molecule.

3. Results and discussion

Catalysts A (1 wt% Pd/SiO_2 ; $D = 53\%$), B (0.2 wt% Pd/α-Al_2O_3 ; $D = 42\%$) and E (Europt 1; 6 wt% Pt/SiO_2; $D = 48\%$) were coked by the cyclopentane reaction at 500°C for 1 h.

Fig. 1 shows that the TPO curves of coked palladium catalysts exhibit three peaks while only two peaks are observed in the case of the platinum/silica catalyst. The recovery of catalyst activity for cyclohexane dehydrogenation after partial coke burning under diluted oxygen points out that the peak of low intensity at 500–600°C corresponds to coke deposited on the support (fig. 2), in accordance with previous work on platinum-alumina catalysts [8,9].

On the other hand, the peaks at low temperature can be attributed mainly to coke deposited on the metallic function and to some coke in interaction with the metal and deposited on the support in the immediate vicinity of the metallic particles. Indeed, the metal activity is wholly recovered before the complete elimination of coke corresponding to the first peak (platinum) or the second peak (palladium). Nevertheless, two TPO peaks corresponding to coke in interaction with the metallic function are observed in the case of palladium catalysts while only one peak appears on supported platinum.

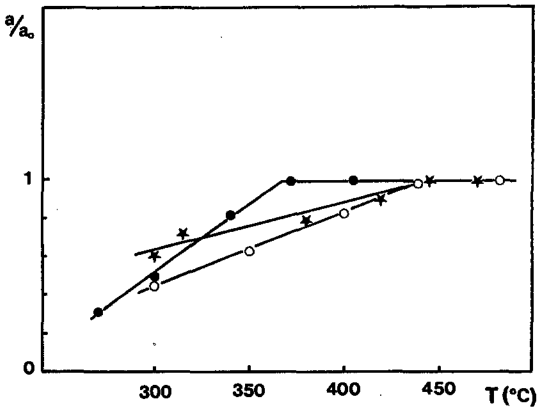

Fig. 2. Relative activity (a/a_0) for cyclohexane dehydrogenation vs. temperature of coke oxidation. (●) 6 wt% Pt/SiO_2, $D = 48\%$; (∗) 1 wt% Pd/SiO_2, $D = 53\%$; (○) 0.2 wt% Pd/α-Al_2O_3, $D = 42\%$.

The same coking reaction was carried out at 500°C on Pd/SiO_2 catalysts of varying dispersities. Fig. 3 compares the TPO curves of catalysts A ($D = 53\%$), B ($D = 37\%$) and C ($D = 23\%$) for the same amount of coked sample. An overall decrease of the TPO areas is observed as palladium particle size increases, this phenomenon being more obvious for the second peak on the metallic function (around 400°C). As for the decrease of the peak corresponding to the coke on the support it can be explained by a lower stabilization of the polymers produced on the acidic sites, through dehydrogenation by a reverse spillover of hydrogen, when palladium accessibility decreases [10].

The activity of the coked samples for cyclohexane dehydrogenation was determined after the burning of the coke corresponding to the first peak at low temperature. The values reported in table 2 show that the regeneration of the metal activity is higher on the less

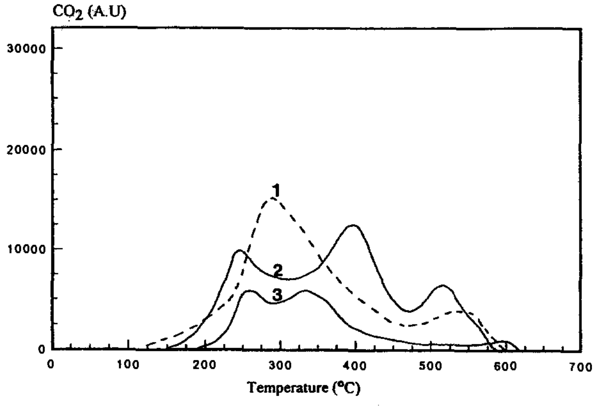

Fig. 1. TPO curves of catalysts coked by the cyclopentane reaction at 500°C: (1) 6 wt% Pt/SiO_2, $D = 48\%$; (2) 1 wt% Pd/SiO_2, $D = 53\%$; (3) 0.2 wt% Pd/α-Al_2O_3, $D = 42\%$.

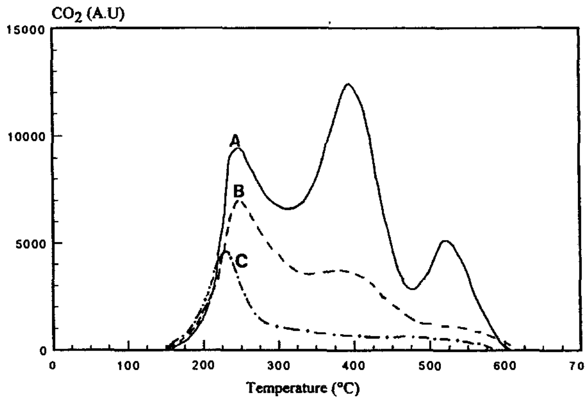

Fig. 3. TPO curves of 1 wt% Pd/SiO_2 catalysts of varying dispersities coked by the cyclopentane reaction at 500°C. (A) $D = 53\%$; (B) $D = 37\%$; (C) $D = 23\%$.

Table 2
Regeneration of the metallic activity for cyclohexane dehydrogenation by oxidation of carbon corresponding to the first TPO peak. (a = activity of the coked catalyst after oxidation of carbon corresponding to the first TPO peak; a_c = activity of the coked catalyst; a_0 = activity of the fresh catalyst)

Catalyst	D(%)	$(a - a_c)/a_0$
A-Pd/SiO_2	53	0.58
B-Pd/SiO_2	37	0.69
C-Pd/SiO_2	23	0.77

dispersed catalyst. This result and the evolution of the TPO curves in function of the metallic dispersion suggest that the carbon which burns at low temperature corresponds to coke deposited on palladium atoms of high coordination, the relative number of which is higher on large particles. On the other hand, the second TPO peak would involve palladium atoms of low coordination like corners or edges which are more numerous on well dispersed catalysts.

Infrared spectroscopy of chemisorbed CO was used in order to bear out such hypothesis by comparing IR spectra of the fresh, the coked and the partially regenerated catalysts. Indeed, the IR spectrum recorded in fig. 4 shows two main peaks of CO adsorbed on the fresh 1 wt% Pd/SiO_2 (D = 53%) catalyst in the 2150–1750 cm^{-1} range. The band at ca. 2085 cm^{-1} corresponds to linearly bound adsorbed CO while the band at ca. 1950 cm^{-1} is attributed to bridging CO [11,12]. In accordance with previous work [13,14], this spectrum can be decomposed into five elementary absorption bands: the A_1 and A_2 bands which might be due to the formation of linear carbonyl (Pd–CO) species adsorbed on the steps, terraces and kinks of the metal crystallites or to CO adsorption on well dispersed palladium metal. The B band is characteristic of the bridged carbonyl (Pd_2CO) species on the (100) planes of the metal crystal. The bridged adsorption of CO on double coordination sites (band C) and on triple coordination sites (band D) are characteristic of the (111) planes.

The comparison of the IR spectra recorded in fig. 5 shows that the different metallic sites are poisoned by the carbon deposited in the course of the coking reaction by cyclopentane at 500°C. Moreover, palladium atoms responsible for the absorption in the lower ν(CO) wavenumbers are regenerated at first by partial coke burning under diluted oxygen while the linearly bound CO are the last regenerated as the oxidation temperature increases. In conclusion, the carbon which burns at low temperature (peak at ca. 250°C) would correspond mainly to coke deposited on the (111) planes whereas the carbon which is oxidized at higher temperature would be deposited on palladium atoms of lower coordination. Further studies are presently in progress to examine the effect of the experimental conditions of the coking reaction (time, temperature) on the relative importance of these two peaks.

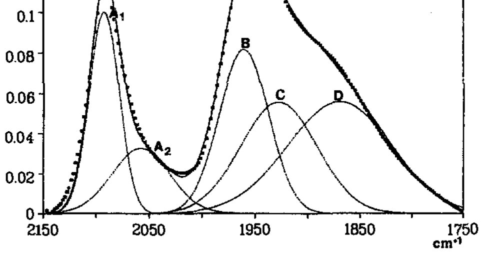

Fig. 4. Infrared spectrum of chemisorbed CO on the fresh 1 wt% Pd/SiO_2 catalyst (D = 53%).

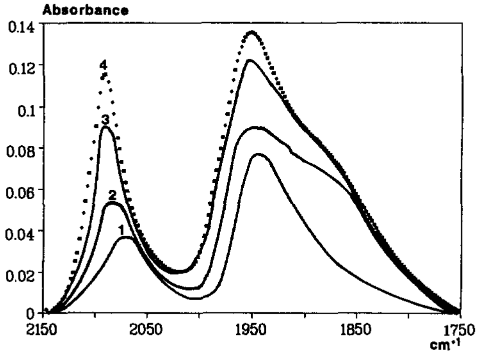

Fig. 5. Infrared spectra of chemisorbed CO on the 1 wt% Pd/SiO_2 catalyst (D = 53%). (1) Coked at 500°C, 1 h; (2) coked at 500°C, 1 h, and partially regenerated by oxidation at 330°C; (3) coked at 500°C, 1 h and partially regenerated by oxidation at 350°C; (4) fresh catalyst.

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