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Removal of Adsorbed Organic Impurities from Surface of Spent Catalysts Pd/Activated Carbons

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Abstract. Influence of method and conditions of spent Pd/AC catalyst regeneration on its catalytic activity was studied. It has been stated that supercritical fluid extraction (CO_2) followed by heating in hydrogen atmosphere is an effective method of that catalyst regeneration. The results of FTIR and XPS investigations indicate that regeneration of a spent Pd/AC catalyst, irrespective of the reaction in which it has been used, should be based on the complete removal of by-products and cleaning the catalyst surface as well as on restoring the original form of the palladium. Proposed in this paper procedure i.e. SFE (CO_2) and heating in H_2 fulfils both above mentioned conditions.

Keywords: Pd/activated carbon catalyst, spent catalyst, regeneration

1. Introduction

Owing to their porosity, developed specific surface and capability of modeling both the structure and chemical constitution of a surface, activated carbons are widely used as adsorbents, catalysts and catalysts supports where metals or metal compounds constitute the active phase (Rodriguez-Reinoso, 1995; Radovic and Rodriguez-Reinoso, 1997; Radovic and Sudhaker, 1997; Rodriguez-Reinoso, 1998). The metals most commonly supported on carbon are those of Groups 8–11 of the Periodic System (Fe, Co, Ni and Cu Groups), although the largest volume corresponds to platinum, palladium, rhodium, ruthenium and iridium (Auer et al., 1998), as shown in the brochures of the more important catalyst manufacturers e.g. (Alfa Aesar Johnson Matthey, 2003–2004). Of the great number of catalysts prepared on supports such as activated carbon are those whose active phase consists of palladium scattered over the carbon surface (Pd/AC) (Gurrath et al., 2000; Kang et al., 2002; Köhler et al., 2002; Stiles and Koch, 1995). Catalysts of the palladium-activated carbon type are used commercially in numerous processes (Maulijn et al., 2000; Nagaoasa and Aoyama, 2001; Van de Sand et al., 1998). Among typical examples are the liquid-phase hydrogenation reactions catalyzed by carbon supported palladium catalysts. The aim of the present work was to assess the possibility of regeneration of spent Pd/AC catalysts.

2. Materials and Methods

The following Pd/AC catalyst samples were investigated: a commercial Aldrich 10 wt% Pd catalyst, indicated as CC, a spent catalyst subjected to supercritical fluid (CO_2) extraction (Dabek et al., 2002), indicated as SC/SFE, and a spent catalyst subjected to organic solvents (acetone, methanol, benzene) ultrasonic extraction SC/OSE. The spent Pd/AC catalyst (SC) consists of mixed CC catalyst samples used in the hydrogen reduction of various organic substances. In our previous work (Dabek et al., 2002) the spent Pd/AC catalyst subjected to supercritical extraction was re-used in the

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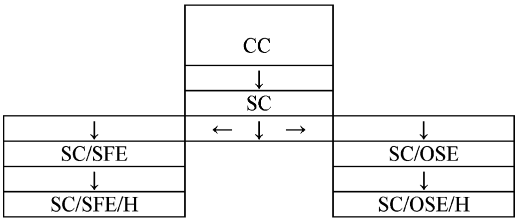

Figure 1. Regeneration processes of spent Pd/AC catalyst: CC–commercial catalyst Pd/AC, SC–spent catalyst, SC/SFE = SC subjected to supercritical extraction, SC/OSE = SC subjected to organic solvents extraction, SC/SFE/H = SC/SFE subjected to heating in hydrogen, SC/OSE/H = SC/OSE subjected to heating in hydrogen.

hydrogen reduction of octanoylbenzene. The activity of catalyst SC/SFE proved to be much lower than that of the commercial catalyst CC. The results of XPS investigations indicate that changes occurred in the form of the palladium present on the catalyst surface (Dabek et al., 2002).

In this work the both samples of spent catalyst after extraction (SC/SFE and SC/OSE) were subjected to heating in hydrogen atmosphere at 410 K for 3 h. The way (methods) of spent Pd/AC catalyst regeneration is shown in Fig. 1.

All Pd/AC catalysts (SC/SFE/H, SC/OSE/H and CC) were tested in the reduction of octanoylbenzene with hydrogen:

$$C_7H_{15}COC_6H_5 + 2H_2 \rightarrow C_8H_{17}C_6H_5 + H_2O$$

Thus, 53 g (0.26 mole) ketone and 2 g Pd/AC catalyst were employed passing hydrogen as the reducer through the system. The activity of the catalyst was assessed by measuring the amount of hydrogen used relative to the theoretical value necessary for the reaction, as well as by measuring the reaction time.

Spectroscopic methods (FTIR and XPS) were used to evaluate changes occurred in the form of palladium present on the Pd/AC catalyst surface during regeneration processes. Transmission FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum 2000 spectrometer using the KBr-pellet technique.

XPS spectra were obtained with an EscaLab 210 (V.G. Scientific) photoelectron spectrometer using non-monochromatized Al K_α radiation (1486.6 eV), the source being operated at 15 kV and 20 mA. Prior to XPS measurement, all the carbon samples were dried for 2 h at 100°C. The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. Survey scans were collected from 0 to 1200 eV with a pass energy of 50 eV. High-resolution scans were performed over the 280–296 eV (C 1s) and 332–346 eV (Pd 3d). Each spectral region was scanned between 10 and 20 times, depending on the signal intensity, in order to obtain an acceptable signal-to-noise ratio at reasonable acquisition times. After subtraction of the base line (Shirley-type), curve-fitting was performed using the non-linear least-squares algorithm and assuming a mixed Gaussian/Lorentzian peak shape of variable proportion (usually around (0.3) (Moulder et al., 1992). This peak-fitting was repeated until an acceptable fit was obtained (error 5%). For calibration purposes, the carbon 1s electron bond energy corresponding to graphitic carbon was referenced at 284.5 eV (Moulder et al., 1992).

3. Results and Discussion

In the case of SC/SFE/H, SC/OSE/H and CC samples the hydrogen consumption in tested reaction was very close to theoretical. The reaction time was about 70 min for CC and SC/SFE/H and about 120 min for SC/OSE/H. An XRF analysis (Canberra Packard-ND Data apparatus) indicated that differences between the palladium content of commercial catalyst (CC) (9.95 wt%) and the spent catalysts subjected to regeneration procedures (SC/SFE/H and SC/OSE/H) are relatively small and may be accounted for the partial removal of palladium with the extraction of organic impurities in the extraction process. Each method of a spent Pd/AC catalyst regeneration should give more or less complete removal of by-products (from reactions in which this catalyst has been used). Connected with "cleaning the catalyst surface" changes observed in FTIR spectra are illustrated in Fig. 2.

In the all recorded FTIR spectra appearance of the band near 1550 cm^{-1} and the overlapping bands in the 1260-1000 cm^{-1} region indicates the presence of different surface oxides (Zawadzki, 1988). The observed differences in the course of all three spectra are relatively small.

XPS investigations were carried out for the Pd/AC catalyst samples in sequence CC → (SC) → SC/SFE → SC/SFE/H. High-resolution XPS spectra of the Pd 3d region are shown in Figs. 3, 4 and 5 for CC, SC/SFE and SC/SFE/H samples, respectively. The spectra measured were subjected to the standard treatment using the ECLIPSE programme which removed any 'satelites' and detached the non-linear background via Shirley's method (Dabek et al., 2002). Next, the spectra in the individual regions were processed by adjusting the

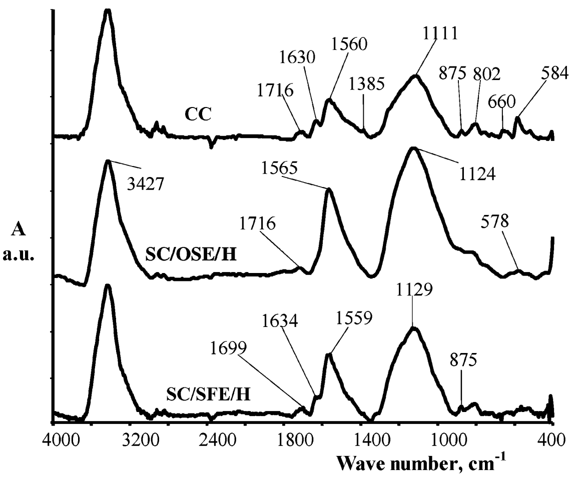

Figure 2. FTIR spectra of Pd/AC catalyst samples (commercial-catalyst and regenerated by different methods).

possible forms of a given element using the different characteristic values of the binding energy BE associated with a given sample. Quantitative analysis was based upon the sensitivity coefficients for individual electron levels and elements according to Scofield (Dabek et al., 2002). The results obtained (for Pd 3d 5/2) are given in Table 1.

Observed differences between XPS spectra Pd 3d recorded for commercial Pd/AC catalyst and spent catalyst after SFE are discussed in our previous paper (Dabek et al., 2002). On the surface of SC/SFE catalyst palladium occurred in three states, i.e. ca. 30% as a metal (large crystallites), ca. 60% as PdO and the remainder of ca. 10% as Pd^{2+} what is represented by peaks 335.31, 336.83 and 338.63 eV, respectively. Result of XPS investigation for SC/SFE/H sample is quite different in comparison with XPS spectrum for SC/SFE

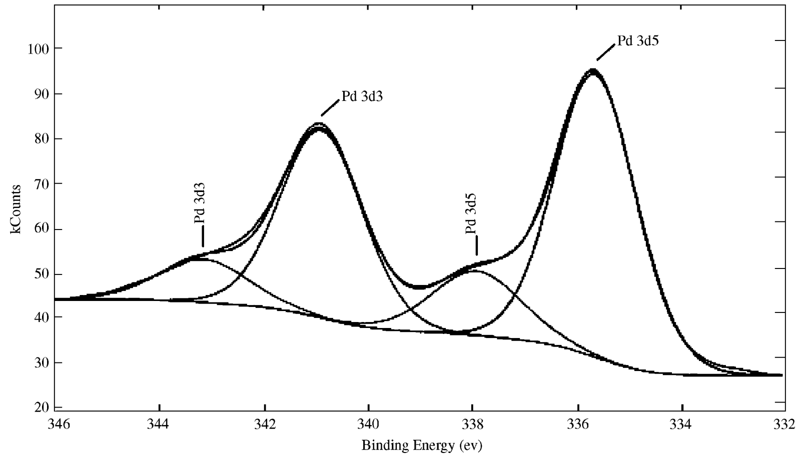

Figure 3. XP spectrum of CC sample.

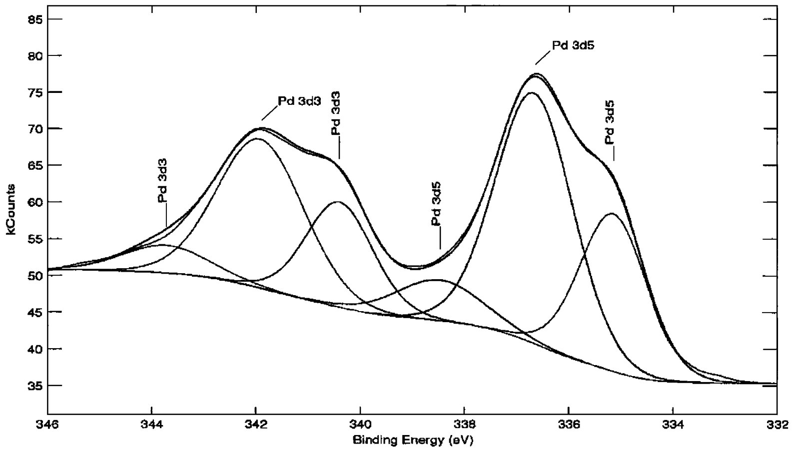

Figure 4. XP spectrum of SC/SFE sample.

Table 1. Fitted Pd 3d 5/2 peaks' parameters deduced from XPS spectra for Pd/AC catalyst samples.

CC			SC/SFE			SC/SFE/H		
BE (eV)	Area (%)	FWHM	BE (eV)	Area (%)	FWHM	BE (eV)	Area (%)	FWHM
335.78	80.16	1.93	335.31	31.65	1.58	335.71	84.94	1.94
–	–	–	336.83	57.86	1.82	–	–	–
338.06	19.84	2.10	338.63	10.49	2.03	337.99	15.06	2.07

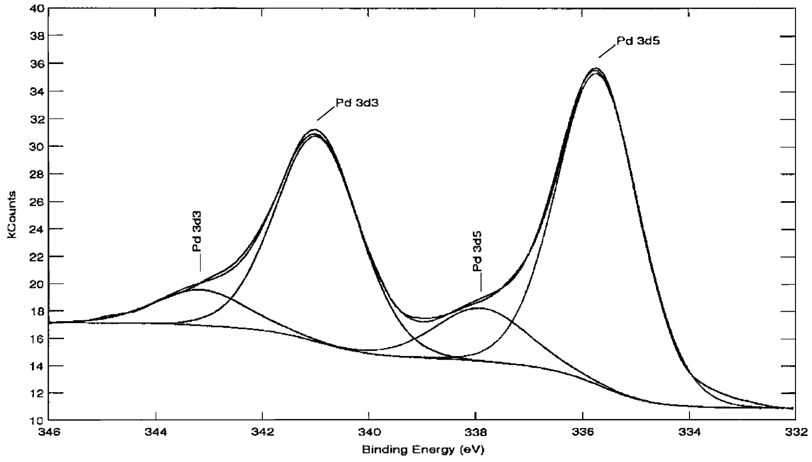

Figure 5. XP spectrum of SC/SFE/H sample.

and very similar to the spectrum recorded for commercial catalyst CC (Figs. 3–5, Table 1). There is no peak representing of PdO (336.83 eV). Observed similarity of parameters describing peaks of XPS spectra recorded for catalyst samples CC and SC/SFE/H indicates high effectiveness of the proposed regeneration method. Obtained XPS spectra of C 1s region confirm above observations.

4. Conclusion

Proposed and used in this work methods of regeneration spent catalyst Pd/AC are effective. A more effective is regeneration by using supercritical fluid extraction (CO_2). The necessary stage after that procedure is heating in hydrogen atmosphere. Obtained in this way regenerated catalyst exhibits catalytic activity comparable with commercial catalyst Pd/AC. However, the spent catalyst subjected to extraction with organic solvents followed by thermal treatment in H_2 atmosphere exhibits lower activity.

Acknowledgments

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