Tailoring Supported Palladium Sulfides Catalysts through H_2-Assisted Sulfidation with H_2S

Wei Xu, Jun Ni, Qunfeng Zhang, Feng Feng, Yizhi Xiang† and Xiaonian Li*

State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Industrial Catalysis Institute, Zhejiang University of Technology, Hangzhou, P. O. Box 310014, P.R. China

Supplementary material

1. Sample characterization

X-ray diffraction (XRD) measurements of the samples were performed using an X'Pert PRO diffractometer (PNAlytical Co.) equipped with a Cu Kα radiation source that was operated at 40 kV and 40 mA. Diffraction patterns were collected at a scanning rate of 2^o/min and with a step of 0.02^o. Foil samples were mounted on zero background quartz slides for analysis. The average size of particles was calculated by Scherrer equation.

Transmission electron microscopy (TEM) using a Tecnai G2 F30 S-Twin Microscope (Philips-FEI Co., Netherlands) was carried out to obtain the average size of the palladium sulfide nanoparticle supported activated carbon. At least 500 individual Pd particles were counted for each catalyst and the mean Pd particle size of the catalyst, d_s, was calculated by the following equation: $d_s=\Sigma n_i d_i^3/\Sigma n_i d_i^2$, where visible particle size d_i on the micrographs was measured by a computerized system and n_i is the number of particles of diameter d_i and $\Sigma n_i > 500$. Energy-Dispersive X-ray Spectroscopy (EDS)

using a Thermo Noran Vantage EST instrument was used to obtain the S/Pd atomic ratio of individual particles of each single phase.

The BET surface areas of the Pd-based catalysts was determined by nitrogen physical adsorption at -196 °C. A 0.05 g sample was heated to 110 °C and held at that temperature for 12 h to remove the adsorbed species; nitrogen adsorption isotherm was then performed using a NOVA 1000e surface area analyzer (Quantachrome Instruments Corp.).

The Sample of 0.05 g was purged in He at 140 °C for 2 h in a quartz ampoule, and then weakly bonded H_2S (i.e. physisorbed H_2S) was removed. Then the sample was cooled to room temperature and the H_2-TPR experiments were carried out in the range of 10~850 °C at a heating rate of 10 °C·min^{-1} in 5%-H_2/Ar with a flow rate of 30 mL·min^{-1}. The quantity of H_2S desorbed from the sample was measured every 2.5 min with a mass spectrometry (Omnistar TM). The reduction temperature was monitored by a thermocouple and the signal of H_2S (m/z=34) was collected. The amounts of hydrogen consumption were calibrated using known amounts of CuO. And hydrogenation consumption for the reduction of "Pd_4S", "Pd_3S" and "PdS" phases were calculated as 11.5, 16.2 and 48.1 *u*mol, which were in good agreement with the expected value of 11.8, 15.7 and 47.2 *u*mol, respectively.

XPS measurements were performed on a Thermo ESCALAB 250 Axis Ultra spectrometer using a monochromatic Al Kα radiation ($h\nu$= 1486.6 eV). Slight Ar+ sputtering was employed to remove surface impurities. All binding energy (BE)

values were calibrated by using the value of contaminant carbon (C 1s = 284.8eV) as a reference.

2. Characterization results

"Pd_4S", "Pd_3S", "$Pd_{16}S_7$", "PdS" or mixed Pd-S crystalline phases supported on activated carbon could be selectively produced through the reaction of Pd/C with H_2S/H_2(Ar) at 150-950 °C for 3.5/8 h, and the XRD patterns of all the samples were summarized in Fig. S1-7. The results on the peak area and hydrogenation consumption of Pd_4S/C(150 °C), Pd_3S/C and PdS/C catalysts were shown in Fig. S8 and Table S1. The XRD patters of spent Pd_4S/C(150 °C) and PdS/C were shown in Fig. S9. The XPS results of Pd_4S/C(150 °C) and PdS/C before and after the reaction were shown in Fig. S10-11 and Table S2-3.

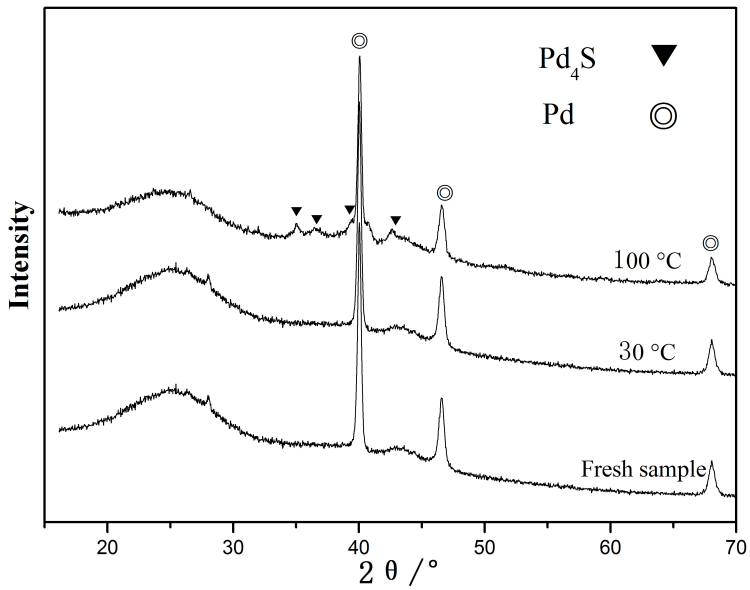

Fig. S1. XRD patterns of Pd/C reacted with H_2S/H_2 at 30～100 °C for 3.5 h

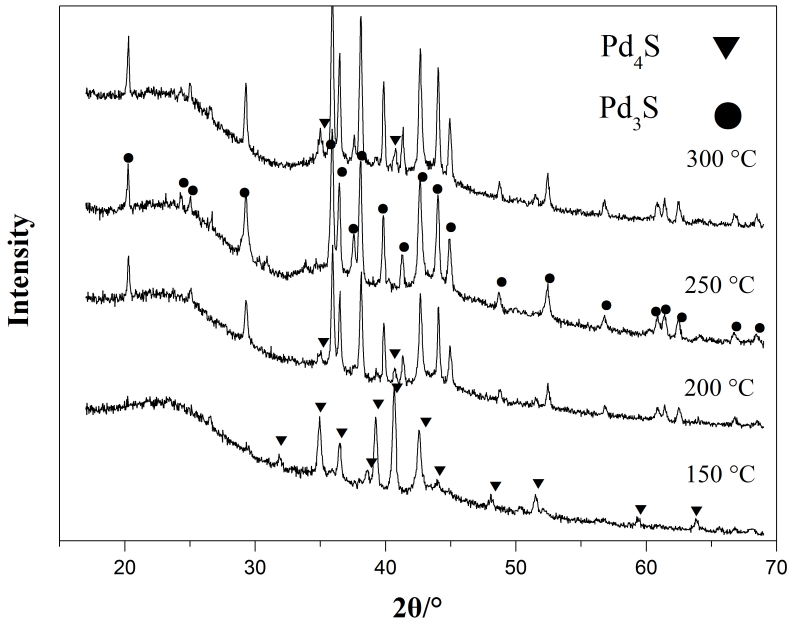

Fig. S2. XRD patterns of Pd/C reacted with H_2S/H_2 at 150～300 °C for 3.5 h

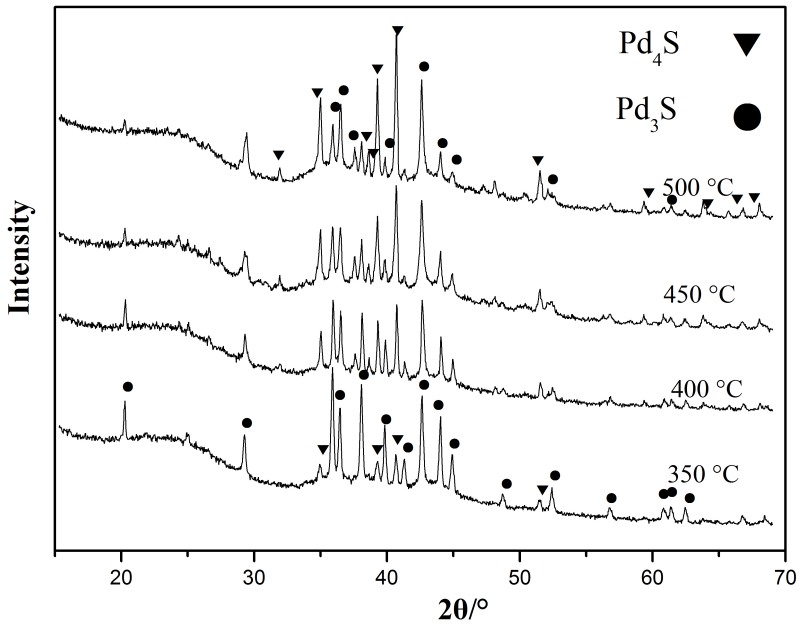

Fig. S3. XRD patterns of Pd/C reacted with H_2S/H_2 at 350～500 °C for 3.5 h

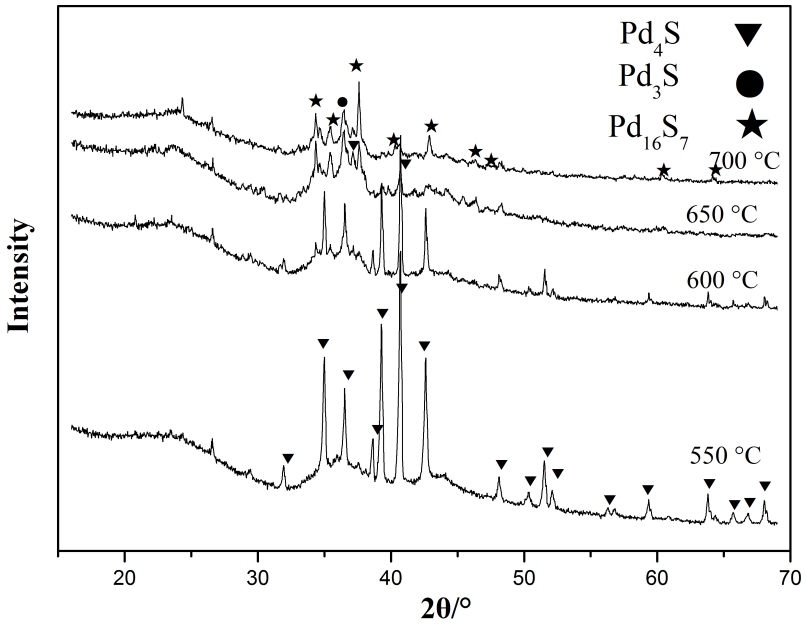

Fig. S4. XRD patterns of Pd/C reacted with H_2S/H_2 at 550～700 °C for 3.5 h

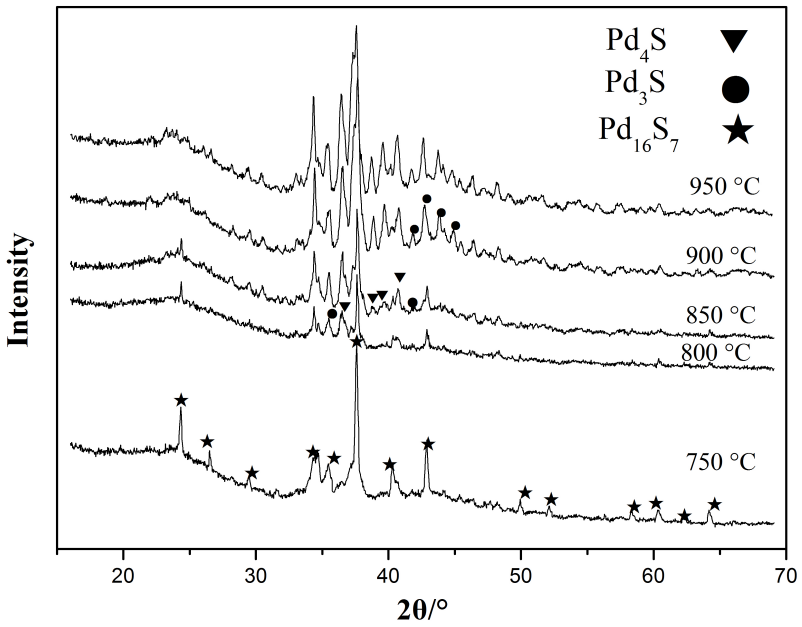

Fig. S5. XRD patterns of Pd/C reacted with H_2S/H_2 at 750～950 °C for 3.5 h

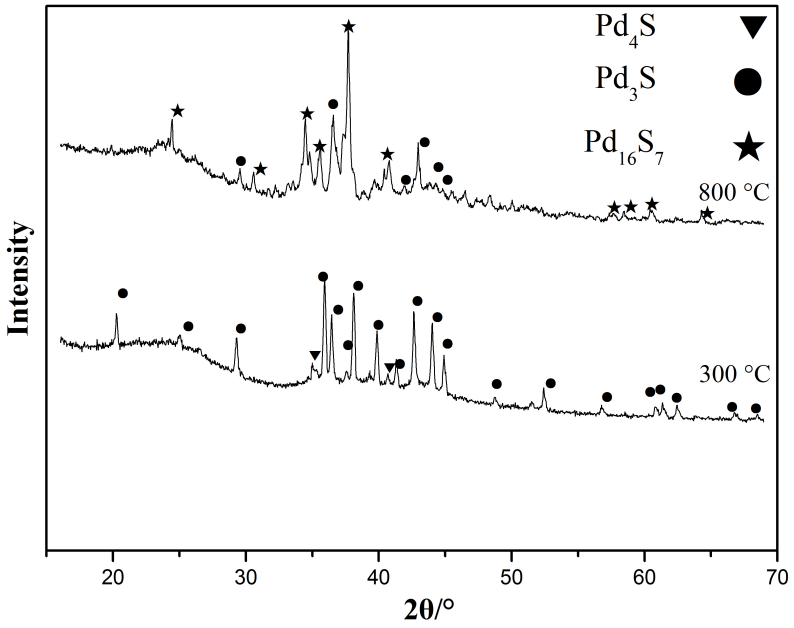

Fig. S6. XRD patterns of Pd/C reacted with H_2S/H_2 at 300 and 800 °C for 8 h

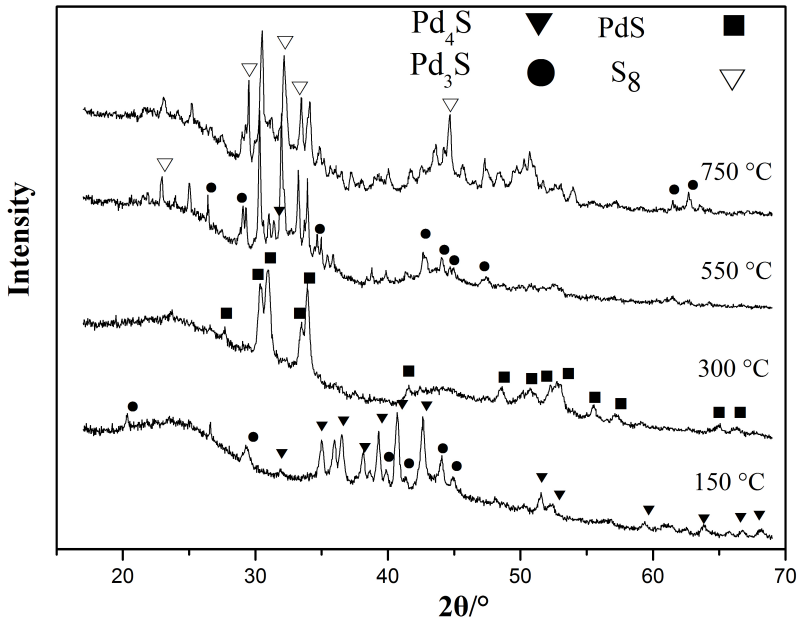

Fig. S7. XRD patterns of Pd/C reacted with H_2S/Ar at 150～750 °C for 3.5 h

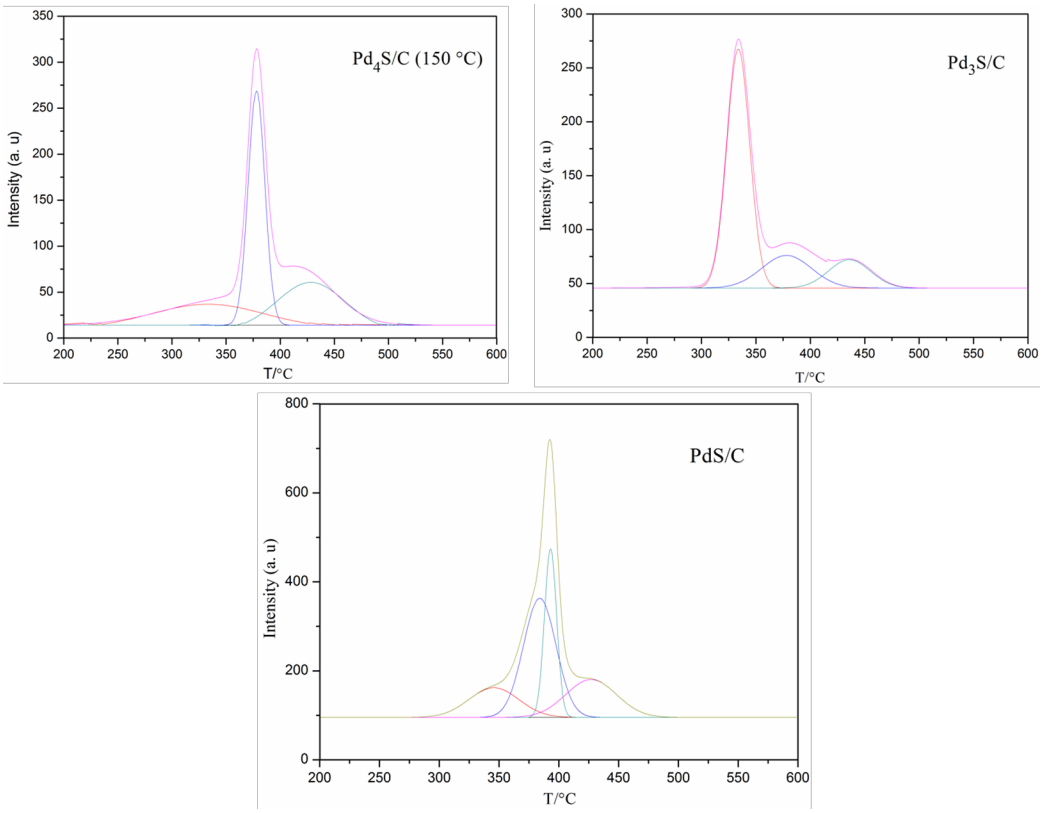

Fig. S8 H_2-TPR analysis of Pd_4S/C (150 °C), Pd_3S/C and PdS/C catalysts

Table S1 The results on the peak area and hydrogenation consumption of Pd_4S (150 °C), Pd_3S and PdS catalysts

Crystal phase		Pd_4S(150 °C)	Pd_3S		PdS		
Peak position/°C		379	338	380	343	384	393
Peak area		4234.90	4512.27	1452.98	3476.48	9289.58	4944.93
Hydrogenation consumption /*u*mol	Calculated value	11.5	16.2		48.1		
	Expected value	11.8	15.7		47.2		

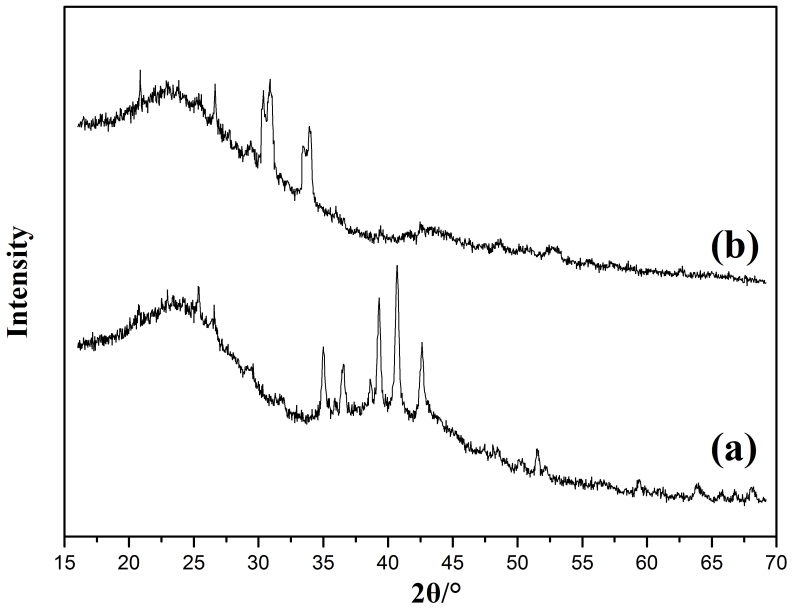

Fig. S9. XRD patterns of spent catalysts (a) Pd_4S/C (150°C) (b) PdS/C

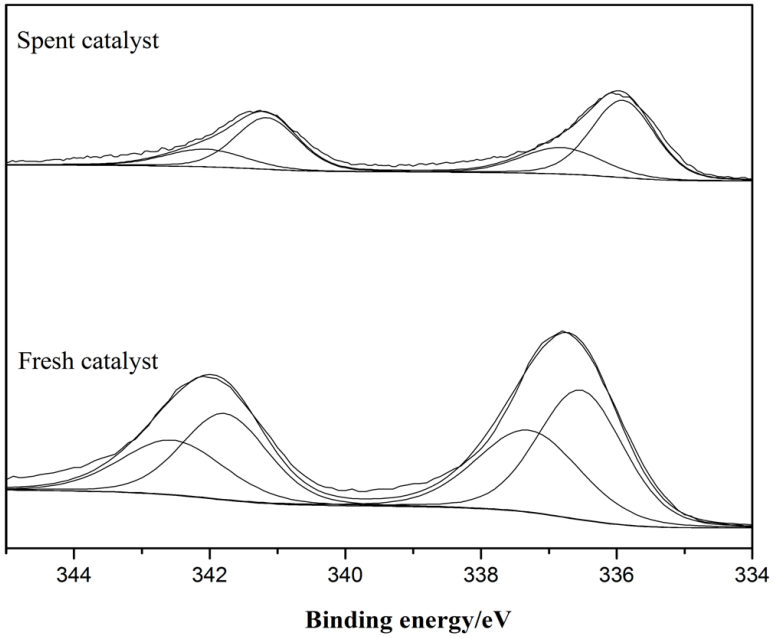

Fig. S10. XPS results of fresh Pd_4S/C(150 °C) and spent Pd_4S/C(150 °C)

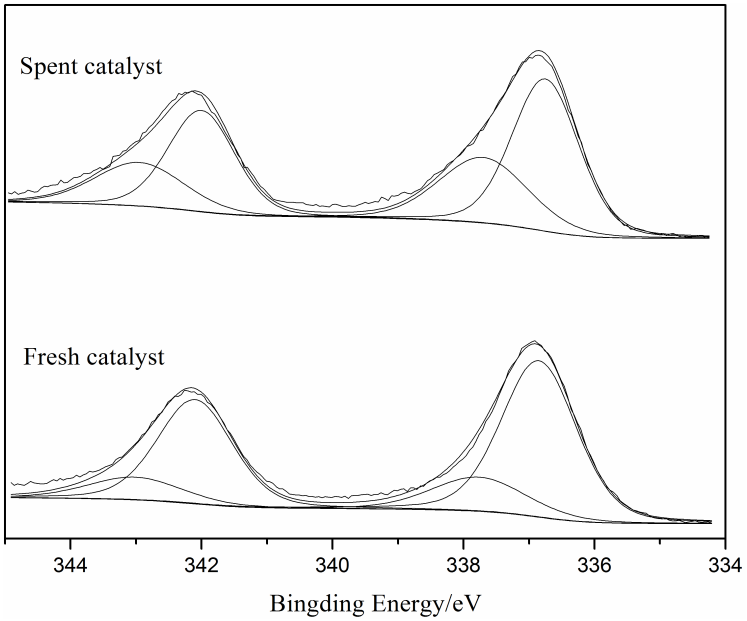

Fig. S11. XPS results of fresh PdS/C and spent PdS/C catalyst

Table S2 The binding energy of Pd $3d_{5/2}$ of Pd_xS_y/C with different phase structures

Catalyst	Lower binding energy (BE)	Higher binding energy (BE)
$Pd_4S/C(150\ ^{\circ}C)$	336.6	337.4
Pd_3S/C	336.3	337.4
$Pd_4S/C(550\ ^{\circ}C)$	336.4	337.7
$Pd_{16}S_7/C$	336	337.2
PdS/C	336.9	337.9

Table S3 The binding energy and Surface S/Pd atomic ratio of fresh and spent catalyst

Catalyst	Lower binding energy (BE)	Higher binding energy (BE)	Surface S/Pd atomic ratio
$Pd_4S/C(150\ ^{\circ}C)$	336.6	337.4	1.02
Spent $Pd_4S/C(150\ ^{\circ}C)$	335.9	336.9	0.28
PdS/C	336.9	337.9	1.12
Spent PdS/C	336.8	337.7	1.08