Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

Simultaneous *in situ* generation of hydrogen peroxide and Fenton reaction over Pd-Fe Catalysts

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Experimental

Materials preparation

The alumina-supported Pd-Fe catalysts were synthesized via co- and successive impregnation. Co-impregnation procedure was firstly to prepare an acidic solution containing certain amount of palladium chloride and iron nitrate 9-hydrate corresponding to 5% Pd and 1% Fe with respect to alumina. The solution was added to slurry solution of γ-Al_2O_3 while stirring vigorously. The slurry was aged stirring for 1 hour at ambient conditions. Water was removed by rotary vapor at 55°C. The precipitate was dried at 110°C and then was calcined at 400°C for 3 hours. Finally, the catalyst was reduced under a flow of pure hydrogen (20 ml min^{-1}) at 200°C for 2 hours. The catalyst is denoted as Pd5FeCI.

Successive-impregnation was performed in two steps. First alumina was impregnated with a solution of iron nitrate or acidic solution of palladium chloride. Similar pretreatment explained above including water removing by rotary vapor, drying at 110 °C and calcination at 400°C for 3 hours was fulfilled. In the second step, the second metal solution (Pd or Fe) was added to the slurry solution of the calcined sample, followed by the above pretreatment program. After final calcination, the samples were reduced under a flow of pure hydrogen (20 ml min^{-1}) at 200°C for 2 hours. The catalyst prepared firstly by Fe is denoted as FePd5 and the one prepared firstly by Pd as Pd5Fe. The Pd and Fe metal contents in the above three samples were 5 and 1 wt%, respectively. A reference Pd5Al sample was also prepared containing 5% Pd on alumina.

Characterization techniques

The catalysts were characterized by XRD, H_2 chemisorption, HRTEM, TPR and XPS. X-ray diffraction of the samples was carried out using a Siemens D5000 diffractometer by nickel-filtered Cu Kα radiation. The patterns were recorded over a range of 2θ angles from 5° to 70°. In all the patterns, the broad peaks corresponding to the structure of γ-Al_2O_3 could be observed. The characteristic reflections of Pd(0) are recognizable clearly only in the pattern of Pd5/Al sample.

Temperature program reduction (TPR) analyses were performed in a ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector (TCD). The sample was purged with argon flow before the analysis. The analysis was carried out using a 3% H_2/Ar gas flowing at 20 ml min^{-1} by heating from room temperature to 900°C with a ramp of 10°C min. Water produced during TPR was trapped in CaO + Na_2O (Soda lime) before reaching the TCD. H_2 consumption was quantified by measuring the peak area and comparing against the standards curve made using CuO known samples.

High-Resolution Transmission Electron Microscopy (HRTEM) on the reduced samples was carried out at 200 kV with a JEOL JEM 2100 instrument equipped with a LaB_6 source and an Energy Dispersive X-ray analyzer (EDX, Oxford Instruments). The point-to-point resolution of the microscope was 0.20 nm. Samples were deposited on holey-carbon-coated Cu grids from alcohol suspensions. For each sample, particle size distribution histograms were obtained over 100-200 individual particles.

X-ray photoelectron spectroscopy (XPS) was performed with a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector. Sample powders were pelleted and fixed mechanically into a special sample holder without glue or tape. Spectra were recorded with pass energy of 25 eV at 0.1 eV steps at a pressure below 5×10^{-9} mbar and binding energies were referred to the C 1s signal. The system was equipped with an HPC-20 reaction chamber. In situ reduction treatments were carried out at 1 bar under an atmosphere of pure hydrogen supplied via a MKS mass flow controller. The temperature was provided with an infrared source and was measured directly on the sample holder with a thermocouple. The temperature was raised smoothly and the sample was maintained at each temperature for 10 minutes. After each treatment, samples were transferred from the reaction cell to the analysis chamber under high vacuum (below 5×10^{-8} mbar). The C 1s peak from the adventitious carbon was used as an internal reference with a binding energy of 284.8 eV. The atomic percentage of each element was determined by dividing the peak area of the most intense XPS signal of each element by the corresponding sensitivity factor and expressing it as a fraction of the sum of all normalized peak areas. High resolution XP spectra were acquired by Gaussian/Lorentzian curve fitting after S-shape background subtraction.

Catalytic tests

The organic pollutants degradation reactions were implemented at ambient conditions (25 °C and atmospheric pressure) in a magnetically stirred three-necked glass reactor with a capacity of 100 ml. The reaction details are as follows unless it is mentioned specifically. The volume of the reaction was always 50 ml containing organic pollutant (phenol, DCP or CFA) (100 ppm), ferrous iron (10 ppm, only added in the tests with Pd5Al) and the catalyst (0.1 g). Formic acid was injected with a concentration of 40 mM. Oxygen was passed bubbling into the reaction medium with a flow rate of 20 ml min^{-1}. The temperature of the reaction was controlled using a water bath. Without any exception, all the reactions were performed at darkness in order to avoid any interfering effect of existing light. Phenol degradation and formic acid decomposition were monitored by sampling at regular time intervals and analysing by high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a SPD-M10A Diode array UV-vis detector). A Varian OmniSpher C18 column and a solution containing Milli-Q H_2O and acetonitrile (60:40) at pH 3.80 adjusted by phosphoric acid as mobile phase were used to analyse phenol, DCP and the aromatic intermediates at wavelength 210 and 254 nm. CFA was analyzed using the same column and a mobile phase containing acetonitirile and a buffer solution (4 ml H_3PO_4 85%, 50 ml MeOH and 1L H_2O Milli-Q) (60:40). An Acclaim OA column and a mobile phase containing 100 mM Na_2SO_4 at pH 2.65 adjusted by methanesulphonic acid as mobile phase were used to analyse formic acid at wavelength 210 nm. TOC for each sample was measured by a Shimadzu TOC-5000A. The reaction solution at the end of each run after filtration was analysed by atomic absorption spectroscopy to detect leached Pd and Fe.

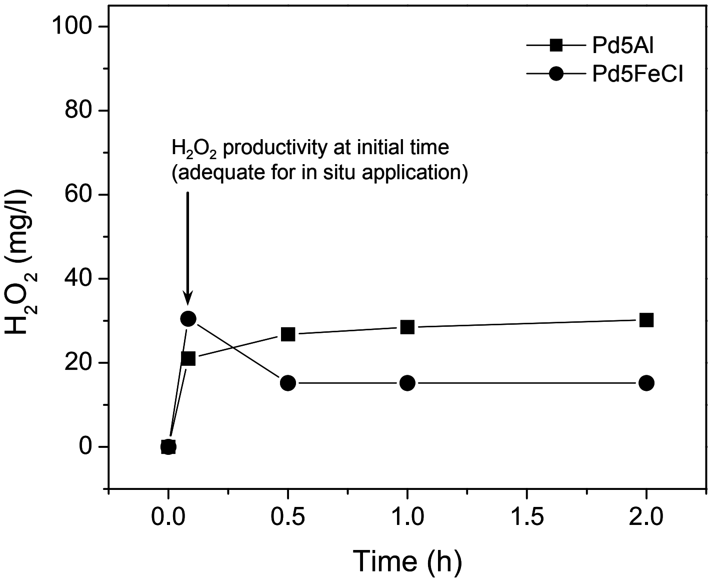

Fig. 1. H_2O_2 generation from formic acid and O_2 over Pd5Al and Pd5FeCl. Reactions were performed at ambient conditions (25°C and atmospheric pressure) in a three necked glass reactor containing 50 ml Milli-Q water, 500 mM formic acid, 100 mg catalyst and O_2 with a flow rate of 20 ml/min. H_2O_2 evolution was measured by iodometric titration and formic acid by HPLC.

Table 1. H_2 consumption during TPR analysis of the Pd-Fe samples.

Catalyst	**H_2 consumption (μmol/g)**					
	PdβH (40-100°C)	**A (80-170°C)**	**B (150-260°C)**	**A/B**	**Pd Theo.**	**Fe Theo.**
Pd5Al	52.3	1.2	1.6	0.75	466	0
Pd5FeCI	T*	315	12.2	25.8	466	268
Pd5Fe	T	263	86	3.1	466	268
FePd5	3.8	37.5	54.8	0.7	466	268

* Trace