Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 cogelled xerogel catalysts for environmental reactions: hydrodechlorination of 1,2-dichloroethane and volatil organic compounds combustion

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Introduction

Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 xerogel catalysts have been synthesized by cogelation of tetraethoxysilane (TEOS) and chelates of Pd, Ag and Cu with 3-(2-aminoethylamino) propyltrimethoxysilane (EDAS). It appears that, in this cogelled samples, the metal complex acts as a nucleation agent in the formation of silica particles. The resulting catalysts are then composed of completely accessible metallic crystallites with a diameter of about 3 nm located inside silica porous particles with a monodisperse microporous distribution centered on a pore size width of about 0.8 nm. So, Pd, Ag and Cu crystallites cannot migrate because they are trapped in the pores of SiO_2 particles. These catalysts are thus sinterproof during calcination and reduction steps. The gels were dried under vacuum to produce xerogel catalysts while preserving the open structure of the gel.

Results and discussion

In this study, six Pd/SiO_2 catalysts were made from TEOS, EDAS, H_2O, ethanol and NH_3 with various amounts of palladium (0.40, 1.10, 1.60, 2.45, 3.10 and 4.50 wt% Pd), six Ag/SiO_2 catalysts with various amounts of silver (0.25; 0.45; 1.05; 1.50; 2.50 and 3.45 wt% Ag) and four Cu/SiO_2 catalysts with various amounts of copper (1.00; 1.50; 2.15 and 4.50 wt% Cu). The wet gels were then dried under vacuum. All samples were calcined in a flow of dry air at 400°C for 12 h and reduced under flowing H_2 at 350°C for Pd and Ag samples and 400°C for Cu samples for 3 h.

Table 1 gives textural properties of Pd/SiO_2, Ag/SiO_2 and Cu/SiO_2 samples. The specific surface area S_{BET} increases respectively from 315 to 570 m^2/g for samples Pd0.40 to Pd4.50, from 180 to 465 m^2/g for samples Ag0.25 to Ag3.45 and from 285 to 570 m^2/g for samples Cu1.00 to Cu4.50 and the total pore volume V_v decreases respectively from 5.0 to 2.0 cm^3/g for samples Pd0.40 to Pd4.50, from 5.7 to 2.8 cm^3/g for samples Ag0.25 to Ag3.45 and from 3.4 to 1.3 cm^3/g for samples Cu1.00 to Cu4.50. The values of V_v show that the ability of drying under vacuum to retain porosity is high, but do not prove the accessibility of palladium, silver and copper. All samples were examined using a transmission electron microscope to obtain metallic and silica particle sizes. Although TEM gives only a 2D view, a careful examination of cogelled-catalysts TEM pictures shows that Pd, Ag and Cu particles seem to be located inside the microporous silica particles with a mean diameter of about 3 nm. Nevertheless, from samples Pd1.60, samples Ag1.50 and Cu1.50, there are Ag and Cu cristallites located on the external surface of silica particles and these big metallic particles have a mean diameter of 20 to 40 nm. Palladium dispersion was also determined by carbon monoxide (CO) chemisorption, silver dispersion by oxygen chemisorption and copper dispersion by decomposition of N_2O.

Table 1 : Sample textural properties

Sample	V_{Hg} (cm^3/g)	$V_{cum<7.5nm}$ (cm^3/g)	V_m (cm^3/g)	V_v (cm^3/g)	S_{BET} (m^2/g)	d_{SiO2} TEM (nm)
Pd0.40	4.85	0.05	0.07	5.0	315	28.9±2.4
Pd1.10	3.05	0.07	0.13	3.2	365	18.5±1.3
Pd1.60	2.65	0.09	0.15	2.8	370	17.9±1.5
Pd2.45	2.35	0.08	0.17	2.6	475	15.1±1.0
Pd3.10	2.15	0.11	0.20	2.5	495	12.6±1.3
Pd4.50	1.70	0.12	0.20	2.0	570	9.8±1.7
Ag0.25	5.60	0.04	0.07	5.7	180	35.6±1.7
Ag0.45	5.35	0.05	0.08	5.5	200	31.4±1.8
Ag1.05	5.20	0.05	0.10	5.4	260	25.2±1.0
Ag1.50	4.00	0.05	0.10	4.2	280	22.8±1.3
Ag2.50	2.75	0.06	0.15	3.0	375	17.3±1.7
Ag3.45	2.50	0.08	0.17	2.8	465	15.8±1.9
Cu1.00	3.30	0.02	0.11	3.4	285	48.2±4.4
Cu1.50	2.70	0.03	0.15	2.9	395	34.3±3.7
Cu2.15	2.20	0.06	0.17	2.4	460	23.5±2.6
Cu4.50	1.00	0.09	0.23	1.3	570	16.7±1.1

V_{Hg}: specific pore volume measured by mercury porosimetry; $V_{cum<7.5nm}$: cumulative volume pores of diameter between 2 and 7.5 nm determined by Broekhoff-de-Boer theory; V_m: microporous volume; V_v: pore volume obtained by addition of V_{Hg}, $V_{cum<7.5nm}$ and V_m; S_{BET}: specific surface area obtained by BET method; d_{SiO2} : silica particle diameter measured by TEM.

A very important concern about cogelled catalysts is the accessibility of the active centers. Because the palladium, silver and copper is located inside silica particles, there is a risk that it may not be accessible. The specify activity (mol s^{-1} g^{-1}_{metal}) of all Pd/SiO_2 xerogel catalysts for hydrodechlorination of 1,2-dichloroethane has been measured at a pressure of 3 atm and at increasing temperatures from 200°C to 350°C with a mixture containing CH_2Cl-CH_2Cl (1 Nl/h), H_2 (2 Nl/h), and He (37 Nl/h). The specific activity (mol s^{-1} g^{-1}_{metal}) of all Ag/SiO_2 and Cu/SiO_2 xerogel catalysts for benzene combustion has been measured at 1 atm and at increasing temperatures from 160°C to 360°C with a mixture containing 250 ppm benzene in air. It was observed that the specific activity at the same temperature of Pd/SiO_2 catalysts for hydrodechlorination and the specific activity at the same temperature of Ag/SiO_2 and Cu/SiO_2 catalysts for benzene combustion increases when the palladium, silver or copper loading decreases. In fact, visual observations by TEM and chemisorption measurements showed in catalysts with a metal loading < 1.60 wt% of metal, there are not palladium, silver or copper particles located on silica particles external surface and then the metal dispersion values are greater in these samples. So, it is the proof that Pd, Ag and Cu particles located inside the silica particles are accessible for 1,2-dichloroethane and for benzene in these catalytic systems.