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Liquid phase selective oxidation of benzyl alcohol over Pd–Ag catalysts supported on pumice

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Abstract

Selective oxidation of benzyl alcohol to benzaldehyde was carried out over pumice supported bimetallic and monometallic Pd and Ag catalysts. Preliminary kinetic studies were performed at 333 K in autoclave, at pressure of 2 atm in pure oxygen. Under these conditions, small amounts of benzoic acid were detected with the monometallic Pd pumice being the most active catalyst. The reaction was also carried out under flowing oxygen at atmospheric pressure and at 348 K. Under these conditions, the selectivity to benzaldehyde was 100%. The catalytic activity of the catalysts was measured after different oxidation and reduction treatments at high temperature. In addition, two mechanical mixtures of pretreated Pd and Ag monometallic samples were tested. The structural data (XRD, XPS, EXAFS) along with the catalytic results would indicate that Ag^0 and Pd^0 species are the catalytic sites acting with certain synergism. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pd–Ag/pumice catalyst; XPS study; Benzyl alcohol oxidation

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1. Introduction

In the past few years, various oxidation reactions in the gas or liquid phases have been studied to synthesize valuable intermediate products or fine chemicals [1]. Catalytic partial oxidation of alcohols is a useful method for the preparation of aldehydes and ketones [2]. Metal catalyzed reactions using molecular oxygen instead of mineral oxidizing agents, are particularly attractive for environmental and economical reasons. Pd and Pt metals supported on alumina are among the mostly used metal catalysts in the selective oxidation of alcohols. Such systems, however, tend to deactivate quickly due to the strongly adsorbed products or by-products formed during the reaction. Addition of a second metal is supposed to improve the lifetime of the catalyst [3,4]. A well established catalyst for such type of reaction is also represented by silver on aluminosilicate or on natural pumice [5]; silver species positively charged are considered the active sites and any additive or particular support which increases the stability of such species would improve the catalytic performance.

Our recent investigations on Pd catalysts supported on pumice had shown a beneficial effect, attributed to a modified electron density on the supported metal, of this type of support in the catalytic performances of the corresponding catalysts [6–8]. Taking advantage

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of the properties of the support and eventually of a bimetallic system, a pumice supported Pd–Ag catalyst was prepared and tested in the selective oxidation of benzyl alcohol. The catalytic behavior of the bimetallic catalyst and of the corresponding monometallic samples was studied after different thermal treatments in oxidizing and reducing atmosphere in an effort to ascertain the active electronic state of palladium and silver as well as to provide some evidence on the reaction mechanism.

2. Experimental

All the used reagents (Aldrich) were of analytical grade. The purity of benzyl alcohol was tested by GC analysis before use. Acetonitrile was purified with molecular sieves, CaH_2 was added, up to H_2 evolution, and then it was distilled under nitrogen just before use.

2.1. Catalysts preparation

The catalysts were prepared via organometallic route. The choice of this procedure was based on previous findings about the attainment of highly dispersed alloy phases in bimetallic system, starting from two organometallic precursors that are reduced in the same temperature range [9,10]. Pumice, extracted from the caves of Lipari, is characterized by a surface area of 5 m^2/g. Its chemical composition is standardized by treatment with boiling 25% HNO_3 [11] before being used as support. The monometallic Pd catalyst, containing 0.27 wt.% of palladium, was prepared from pentane solution of $Pd(C_3H_5)_2$ of known concentration, according to the previous procedure [12]. The solvent was gently evaporated under reduced pressure and a portion of the obtained solid was contacted with the desired amount of dichloromethane solution of $Ag[1,5\text{-}COD]_2BF_4$, at 273 K, under nitrogen and in the absence of light. Following the removal of the solvent, the anchored metals, Pd and Ag were reduced with flowing H_2 at temperature between 273 and 298 K. The monometallic Ag catalyst, with 0.6 wt.% of silver, was prepared from dichloromethane solution of $Ag[1,5\text{-}COD]_2BF_4$ and reduced in the same temperature range as before [9].

Palladium and silver contents were determined by atomic absorption spectroscopy. The weight percentage of each metal in the catalyst is indicated in the adopted notation. Typical catalyst particle sizes were within 30–60 μ. The catalysts along with some structural data are listed in Table 1.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

The X-ray diffraction analyses were performed with a Philips apparatus using nickel filtered Cu Kα radiation. The catalysts were analyzed in the "as prepared" state (reduced at 298 K) and after oxidation and reduction treatments performed before kinetics tests. Metal particle sizes were estimated through the line broadening (LB) of the relevant peaks using the Scherrer equation [13]. Analyses were also performed on the catalysts after the reaction.

2.2.2. X-ray photoelectron spectroscopy (XPS)

Composition, chemical states, as well as electronic structure of the catalysts were investigated by photoelectron spectroscopy using a Kratos ES-300 type electron spectrometer. The Al Kα radiation, the FAT operating mode and the binding energy of Si 2p at 103.5 eV [14] as internal reference line were used. Spectra were taken for the "as prepared", oxidized and reduced samples. The oxidation and reduction treatments at 623 K were performed in a cell directly attached to the spectrometer where air or H_2 was flowing at atmospheric pressure according to the required treatment.

Table 1
Pd and Ag particle sizes *d* (Å) of the pumice supported Pd and Ag catalysts after different treatments

Catalyst	*d* (Å) (as prepared)	*d* (Å) (air 623 K)	*d* (Å) (H_2 623 K)	*d* (Å) (air 773 K)
0.27Pd	Amorphous	Amorphous	Amorphous	120 (PdO)
0.27Pd–0.13Ag	Amorphous	Amorphous	Amorphous	120 (PdO)
0.6Ag	Amorphous	Amorphous	1300 (Ag)	Amorphous

2.2.3. Extended X-ray absorption fine structure (EXAFS) analysis

The EXAFS measurements at the Pd and Ag K edges were performed at the beamline GILDA of the European synchrotron radiation facility (ESRF). The monochromator was operated with Si (3 1 1) crystals in dynamical sagittal focusing mode. The EXAFS spectra were recorded at 77 K to reduce the thermal effects, and due to the very low metal content, in fluorescence geometry.

2.3. Kinetic studies

The catalysts in the "as prepared" state were tested in the high pressure catalytic oxidation of benzyl alcohol, performed in a Berghof autoclave of 50 ml of capacity, equipped with magnetic stirrer. In a typical experiment, the reactor was charged with 0.05 ml of benzyl alcohol dissolved in 20 ml of CH_3CN. All the reactions were carried out using an initial benzyl alcohol/Pd molar ratio equal to 100. The initial benzyl alcohol concentration in CH_3CN was 2.5×10^{-2} M, unless differently stated. The reactions were performed at 333 K, in pure oxygen at 2 atm, at the stirring rate of 1500 rpm. In order to observe any effect on the reaction selectivity, experiments were also performed on the most active Pd catalyst by changing the benzyl alcohol/oxygen molar ratio. The absence of diffusion effects under these operating conditions was adequately checked [15]. The absence of diffusion effects with respect to particle sizes was also checked. During the reaction, samples of the solution were taken periodically and analyzed with a Dani 3800 HRPTV GC equipped with a Supelco capillary column SPB 1701 and with a Dani 68/10 FID detector. This system was linked to a Shimadzu C-R1B Chromatopac integrator.

Catalytic oxidation of benzyl alcohol was also performed in flowing oxygen (160 ml/min) at atmospheric pressure, at 348 K in a pyrex glass reactor, equipped with magnetic stirrer, working in batch conditions. The reactor was connected to a condenser, a vacuum line and a gas introduction system. The reactions were carried out at a stirring rate of 1200 rpm, which allowed conditions of chemical regime, by eliminating any problem of gas diffusion and mass transfer limitations [16]. The benzyl alcohol concentration in CH_3CN was 2.5×10^{-2} M and the benzyl alcohol/Pd molar ratio was equal to 35. This reaction procedure was adopted for all the catalysts in the "as prepared" state and after the different treatments.

3. Results and discussion

The metal content and textural properties, such as particle sizes and phases from X-ray diffraction data, of the three catalysts are reported in Table 1. According to the diffractograms, it is not possible to recognize oxide or metallic palladium diffraction lines for the 0.27Pd catalyst either in the "as prepared" state or after the treatments at 623 K, signifying that the palladium phases are highly dispersed. After calcination at 773 K, PdO particles of approximately 120 Å in size were formed. The bimetallic catalyst shows similar structural behavior. The 0.6Ag catalyst in the "as prepared" state and after oxidation at 623 K is amorphous. After reduction at 623 K only large Ag metal particles were detected. The oxidation at 773 K yields an amorphous diffractogram which may indicate a further dispersion of the silver phases. No changes in the X-ray diffraction data were observed after the catalytic reactions.

In Table 2, the binding energies relative to the Pd $3d_{5/2}$ and Ag $3d_{5/2}$ electron levels along with the XPS derived atomic ratios and the analytical atomic ratios are listed for the untreated and treated catalysts. The samples "as prepared" and after reduction at 623 K were characterized by Pd $3d_{5/2}$ and Ag $3d_{5/2}$ binding energies which in agreement with previous work

Table 2
Pd $3d_{5/2}$ and Ag $3d_{5/2}$ binding energies (eV), XPS derived Ag/Pd atomic ratios and analytical atomic ratios of the catalysts in the "as prepared" state and after different treatments at 623 K

	Pd $3d_{5/2}$	Ag $3d_{5/2}$	Ag/Pd_{XPS}	Ag/Pd_{AAS}
Catalyst (as prepared)				
0.27Pd	334.5, 336.6			
0.27Pd–0.13Ag	334.7	367.0	0.7	0.5
0.6Ag		368.2		
Catalyst (air 623 K)				
0.27Pd	336.6			
0.27Pd–0.13Ag	337.2		0.0	0.5
0.6Ag		368.2		
Catalyst (H_2 623 K)				
0.27Pd	335.1			
0.27Pd–0.13Ag	334.4	367.0	2.5	0.5
0.6Ag		367.7		

Table 3
Specific rate k and selectivity of benzyl alcohol oxidation, of the pumice supported catalysts, run in the "as prepared" state, referred to the experiments carried out in autoclave

Catalyst	k [$\mathrm{mol_{benzaldehyde}/(h\ g_{t\ metal})}$]	Selectivity $(\%)_{\mathrm{benzaldehyde}}$
0.27Pd	95	95
0.27Pd–0.13Ag	9.2	100
0.6Ag	0.8	100

were typical of the Ag^0 and Pd^0 on pumice [10]. The Ag $3d_{5/2}$ binding energy of the bimetallic catalyst 0.27Pd–0.13Ag shifts by −1 eV with respect to the monometallic 0.6Ag. According to the previous XPS study [10] on Pd–Ag pumice supported catalysts, the shift is attributed to the electronic interaction between silver and palladium atoms. After calcination at 623 K of the monometallic and bimetallic catalysts, palladium oxidizes to PdO, whereas silver stays in the metallic state, but, according to the decreased intensity or complete disappearance of the related Ag 3d peak, diffuses into the support. The comparison of the XPS derived atomic ratio Ag/Pd with the analytical ratio $\mathrm{Ag/Pd_{AAS}}$ for the "as prepared" and 623 K reduced sample suggests surface segregation of silver. The EXAFS analysis performed on the bimetallic catalyst in the "as prepared" state had shown the presence of metallic and alloyed phases which, due to the high dispersion were not detected by X-ray diffraction technique.

The specific rate and selectivity for the oxidation of the benzyl alcohol obtained for the three catalysts, run in the "as prepared" state, are reported in Table 3. The data refer to the experiments carried out in autoclave in excess of oxygen. During the activity measurements the concentration of the produced benzaldehyde changed linearly with time. The calculated rates were constant and are denoted by k. The activity of the palladium catalyst decreases by a factor of 10 upon addition of silver. On the contrary, the selectivity to benzaldheyde, calculated at 100% conversion of benzyl alcohol, increases from 95% obtained with the 0.27Pd catalyst to 100% obtained with the bimetallic 0.27–0.13Ag and monometallic 0.6Ag catalysts. The increase by a factor of 10, of the alcohol/oxygen molar ratio did not increase the selectivity of the monometallic Pd catalyst.

The performance of the reaction under flowing oxygen atmospheric pressure gave for all the catalysts a 100% selective conversion of alcohol to aldehyde. The corresponding specific rates calculated with respect to the total grams of metal versus the atomic percentage of silver are plotted in Fig. 1 for the catalysts in the "as prepared" state and after treatments of calcination and reduction at higher temperatures.

In any case, the monometallic palladium catalyst has the highest activity. Different treatments do not affect substantially the catalytic performance, except for a slight improvement after reduction at 623 K. So, palladium appears to be active in both states, Pd^0 and Pd^{2+}. The bi- and monometallic silver catalysts show an increase in activity after each consecutive treatment with the best results obtained after calcination at 773 K. Carbon contamination is not responsible for such behavior, since, as indicated by the XPS results, its amount did not change after the first air treatment at 623 K. On the basis of the X-ray diffractograms and XPS data, the increase in activity of the 0.6Ag catalyst after calcination at 773 K, and the increased activity of the 0.27Pd catalyst after reduction at 623 K, is due to the presence of dispersed metallic palladium and highly dispersed silver atoms which may then be considered the most active species. Since the adopted synthesis procedure did not afford a catalyst with such chemical and structural properties, physical mixtures of the two treated monometallic samples in appropriate relative amounts were tested in the same oxidation reaction under flowing oxygen conditions. The overall results along with those from the most active treated samples of the mono- and bimetallic catalysts are reported in Fig. 2 where the specific rates versus at.%Ag are plotted.

The rates obtained for the physical mixtures are higher than the sum of the weighted rate values of each monometallic component. These results would indicate a certain synergism between the active species, Ag^0 and Pd^0. The lower activity of the 773 K calcined bimetallic catalyst with respect to that of the physical mixtures can be due to extensive presence of PdO. Moreover, the formation of alloyed Ag–Pd, detected by EXAFS, in the "as prepared" state does not seem to be of any relevance, the co-presence of palladium metal and silver metal catalysts, as in the physical mixture, favors the reaction. The synergism observed in the mixture can be explained by invoking

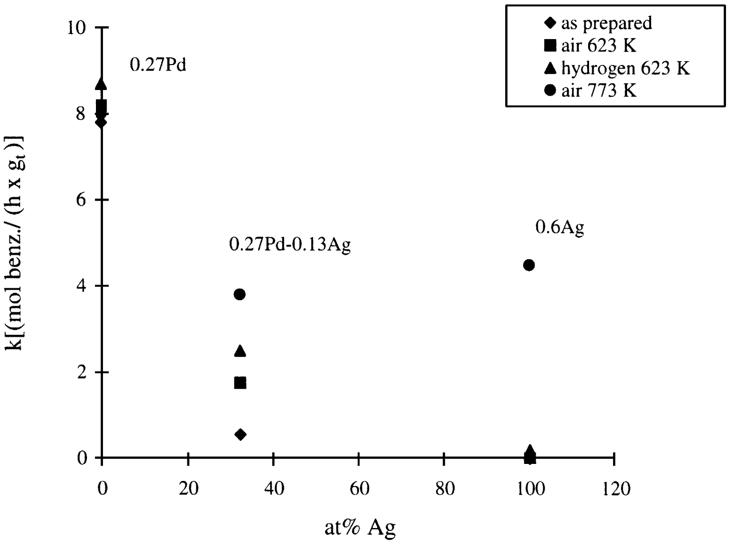

Fig. 1. Specific rates *k* for all the catalysts, calculated for benzyl alcohol oxidation under flowing O_2, versus the atomic percentage of silver.

the oxidative dehydrogenation mechanism proposed for the oxidation of organic molecules [1]. According to such mechanism, the substrate is dehydrogenated, and oxidation of the surface hydrogen by oxygen occurs. The role of palladium could be the activation of the substrate, whereas the highly dispersed silver would be important for the activation of the oxygen molecules, which would migrate, through a "spill over" or "hopping" process, to the near palladium site. The saturation of the Pd sites with the organic molecules would explain a zero order mechanism.

The importance of the role of oxygen was indeed checked by testing the two active monometallic catalysts in the same reaction in the absence of oxygen. In both the cases the reaction was considerably slower than in the presence of O_2.

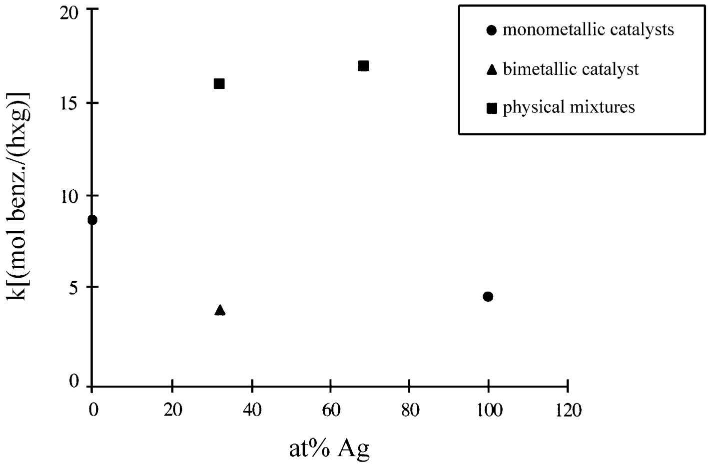

Fig. 2. Specific rates *k* versus at.% Ag for the reaction under flowing oxygen. (●) 0.27Pd catalyst reduced at 623 K and 0.6Ag catalyst calcined at 773 K. (▲) Bimetallic 0.27Pd–0.13Ag calcined at 623 K. (■) Two physical mixtures of the two treated monometallic samples, mixed according to the specific at.% Ag.

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