Journal of Catalysis 333 (2016) 71–77

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Impact of alkali acetate promoters on the dynamic ordering of PdAu catalysts during vinyl acetate synthesis

Elisabeth K. Hanrieder, Andreas Jentys *, Johannes A. Lercher *

Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

ARTICLE INFO

Article history:
Received 31 August 2015
Revised 22 October 2015
Accepted 24 October 2015
Available online 19 November 2015

Keywords:
Dynamic reordering of silica supported Pd–Au alloy particles
In situ IR spectroscopy
CO adsorption
Absorption/extinction coefficient
EXAFS

ABSTRACT

Fresh and used alkali acetate (MOAc with $M^+ = Li^+, Na^+, K^+, Cs^+$) promoted bimetallic PdAu catalysts were studied to investigate the impact of the alkali metal cations on the deactivation of the catalysts during vinyl acetate (VA) synthesis from ethene and acetic acid. Dynamic reordering of PdAu toward an active Pd_1Au_1 phase, a less active $M_2Pd_2(OAc)_6$ and inactive $Pd_3(OAc)_6$ complexes determines the overall activity. Decreasing deactivation from LiOAc to CsOAc promoted PdAu can be associated with the lower concentration of inactive $Pd_3(OAc)_6$ leached from the active PdAu particles and with the lower loss of Cs^+ compared to Li^+ during reaction. CsOAc binds most efficiently to $Pd_3(OAc)_6$ and forms active $Cs_2Pd_2(OAc)_6$, lowering the tendency to leach Cs^+. Reduction of Pd in $M_2Pd_2(OAc)_6$ to a mixed "Pd/M^+–O" adlayer on the bimetallic PdAu particles stabilized active Pd^0 on the PdAu surface maintaining the catalyst activity. Thus, increasing "Pd/M^+–O" concentrations from LiOAc to CsOAc lower long-term deactivation of PdAu.

1. Introduction

The complex interaction between Pd and Au in PdAu alloys leads to superior catalytic performance in many reactions. This is attributed to ligand (electronic) as well as ensemble (geometric) effects of the constituent alloy elements [1,2]. The ligand effect summarizes electronic effects between Pd and Au atoms that alter the strength of Pd-adsorbate bonds [3]. Ligand effects can, therefore, be viewed as electronic perturbations of Pd by Au, which generally increases the electron density in the Pd d-band [4]. The ensemble or dilution effect refers to structural modifications in the surface atom geometry to create hetero-nuclear bonds [3,5,6]. Dilution of surface Pd atoms by the more weakly interacting Au modifies the arrangement of multi-atom sites required to better enable sorption in structure-sensitive reactions such as vinyl acetate synthesis (VAS) [3,7,8].

The catalytically active sites for VAS were identified as two Pd^0 atoms isolated by inactive Au atoms [6,9–11], such as Pd^+ [12–14] and/or Pd^{2+} species [13,15–19]. The presence of solid Pd^0 and Pd^+/Pd^{2+} complexes was hypothesized to simultaneously contribute to the reaction within a supported liquid phase mechanism [20,21]. Oxidized Pd species (e.g. $K_2Pd_2(OAc)_6$ [21]) may form during the dynamic reorganization of the PdAu bulk and surface structure [18,19,21,22] being at least partly covered by a condensed liquid-like film of acetic acid/potassium acetate (KOAc) under operating conditions (150 °C, 9 bar) [16,23]. The presence of $K_2Pd_2(OAc)_6$ points to a pathway catalyzed by a molecular organometallic species in addition to the reaction on the solid bimetallic PdAu particles. The overall activity is controlled by the concentration of Pd sites on the solid surface. The way the promoter interacts especially with the heterogeneous PdAu particles and its impact on the formation of less active Pd acetate species is crucial in order to understand the reordering and, thus, the deactivation of the catalysts.

Deactivation of supported Pd catalysts limits the lifetime of industrial catalysts (typically 8 months to 2 years) [24]. Deactivation was found to depend on the temperature as well as on the O_2 and acetic acid concentration [14,15], while both ethylene concentration and initial GHSV have almost no influence [14]. PdC_x formation from acetate and/or ethylene may also contribute to deactivation [25–31]. Diffusion of Au from the surface into the particle bulk [14] and formation of deposits on the catalyst surface [32] have been invoked as additional reasons for the deactivation. Abel et al. [15] had associated the formation of highly dispersed Pd acetate as transport species with sintering. In contrast, Han et al. [30,31] and Pohl et al. [18] observed hardly any sintering of the Pd particles during VAS. Thus, deactivation was explained by the

---

* Corresponding authors. Fax: +49 89 289 13544.
E-mail addresses: jentys@mytum.de (A. Jentys), johannes.lercher@mytum.de (J.A. Lercher).

http://dx.doi.org/10.1016/j.jcat.2015.10.019

Pd surface enrichment on PdAu particles and by the formation of water-soluble Pd acetate [13,15,17,18].

In accordance with Samanos et al. [16] dispersed Pd particles have a significantly lower activity compared to Pd within the bimetallic PdAu particles, because the highly dispersed particles are completely embedded in the liquid AcOH layer and interact as consequence very weakly with ethene [16]. It is known that KOAc promoted PdAu catalysts suffer from gradual loss of KOAc, which is compensated by adding small amounts of KOAc to the feed stream in the industrial process [33]. As the rate crucially depends on the presence of KOAc [21,34] the loss of the alkali ions is likely one of the reason for deactivation. Additionally, we have recently shown that the catalytic restructuring and, thus, the activity of PdAu catalysts strongly depend on the presence of the KOAc [21]. However, the effect of the different alkali acetate promoters on the PdAu reordering and on deactivation is not understood. The present contribution addresses this gap and resolves the discrepancies regarding deactivation of PdAu in the literature by systematically exploring the location and the interaction of the different alkali metal acetates with the active site Pd by elemental analysis, X-ray diffraction, X-ray absorption spectroscopy, and infrared spectroscopy on fresh and used samples.

2. Experimental section

2.1. Synthesis

$PdAu/SiO_2$ with a Pd/Au ratio of 2.0 was prepared via incipient wetness impregnation as described in patent DE102006058800A1 [35]. $HAuCl_4$ and $PdCl_2$ were dissolved in bidistilled water (1 mL/1 g support) and impregnated on SiO_2. Precipitation with sodium carbonate and washing with ammonia solution (pH 8) were carried out to remove chloride ions from the precipitated metal salts. The $PdAu/SiO_2$ precursor catalysts were reduced in flowing H_2 (100 mL/min) at 300 °C for 1 h (5 °C/min). The catalyst powder was freeze-dried under reduced pressure between the synthesis steps. The total noble metal loading was 1.5 wt% for Pd and Au. Portions of $PdAu/SiO_2$ were impregnated with equimolar amounts of Li-, Na-, K- or Cs-acetate (1.28 mmol/g catalyst) (“$PdAu/MOAc/SiO_2$”). The average particle size of as synthesized PdAu catalyst, determined by TEM, was ~3.5 nm [21].

2.2. Catalytic reactions

Activity tests were performed in a 6-fold reactor setup at a temperature of 150 °C and a gas composition of 60 vol.% C_2H_4, 13 vol.% AcOH, 4.5 vol.% O_2 in N_2 at 9 bar total pressure. The diluent SiC/catalyst ratio was 10/1 to maintain a constant temperature over the whole catalyst bed. The product stream was analyzed using a GC (model 2014 from Shimadzu) equipped with a Haysep Q and a molecular sieve column and a TCD detector. As Pd species are the active sites in vinyl acetate synthesis, the formation rate of vinyl acetate was normalized to the concentration of Pd. Deactivation was calculated from the maximum activity (~15 h time on stream) and the average activity level after 4500 min on stream.

2.3. Elemental analysis

Contents of Pd and Au were determined by atomic absorption spectroscopy (AAS) using a Solaar M5 Dual Flame graphite furnace AAS (ThermoFisher). 50 mg of catalyst was dissolved in a mixture containing 48% hydrofluoric acid and nitrohydrochloric acid.

The measured Pd concentration of washed samples after reaction is the sum of Pd in the PdAu bimetallic phase and Pd in the $Pd/M^+–O$ layer (Eq. (1)). The concentration of “Pd in the AcOH” layer (solved Pd acetate species [17] or dispersed Pd^0) was calculated from the difference between the initial and measured Pd loading (Eq. (2)).

$$\mathrm{Pd}_{\text{measured by AAS}} = \mathrm{Pd}_{(\mathrm{PdAu})} + \mathrm{Pd}_{(\mathrm{Pd/M+–O})} \tag{1}$$

$$\mathrm{Pd}_{\text{total}} = \mathrm{Pd}_{\text{measured by AAS}} + \mathrm{Pd}_{(\text{acetic acid layer})} \tag{2}$$

$$\mathrm{Pd}_{(\text{total})} = 1.30\ \mathrm{wt\%}$$

2.4. IR spectroscopy of adsorbed CO

The IR spectra were recorded on a Vertex 70 spectrometer from Bruker Optics at a resolution of 4 cm^{-1} collecting at least 100 scans. Samples were washed with bidistilled water (20 mL/100 mg catalyst) for 20 min to remove KOAc, AcOH and solved Pd^{2+} species from the PdAu surface. Additionally, water-soluble $Pd/M^+–O$ compounds formed on the bimetallic particles were removed by washing with H_2O for 24 h. Samples were pressed into self-supporting wafers (~10 mg/cm^2), activated in vacuum (~1.0×10^{-7} mbar) at 300 °C for 1 h (heating rate of 5 °C/min), reduced in static H_2 (1000 mbar) and outgassed at 300 °C in vacuum for 30 min. The system was cooled to −150 °C with liquid N_2 and a spectrum of the activated sample was taken in 5 mbar He. After the removal of He, 1.0 mbar CO was adsorbed at −150 °C. Spectra were recorded every minute until the CO adsorption–desorption equilibrium was established.

Analysis of the spectra was carried out using the software Grams AI. Spectra were background corrected and subtracted from the background corrected spectrum of the activated sample to obtain the CO absorption bands. These difference spectra were normalized to the integrated area of Si–O overtones between 2107 and 1741 cm^{-1} of the activated sample. Absorption bands were evaluated by band fitting applying a mixed 50/50 Gaussian–Lorentzian function.

2.5. X-ray absorption spectroscopy

2.5.1. Pd–K and Au–L_3 edges

X-ray absorption spectroscopy was measured at HASYLAB, DESY, Hamburg/Germany, on the beamlines X1 and C. During the experiments, the storage ring operated at an electron energy of 4.5 GeV and an average current of 100 mA. Spectra were recorded in transmission mode at the Pd–K edge (E_0 = 24,350 eV, Si(3 1 1) crystals) and Au–L_3 edge (E_0 = 11,919 eV, Si(1 1 1) crystals). The alignment of the second monochromator crystal was set to 60% of the maximum intensity to minimize the intensity of higher order reflections. The samples were pressed into self-supporting wafers with weights of a total absorbance of 2.0 to optimize the signal to noise ratio. The samples were heated to 300 °C with 5 °C/min in H_2 (100 mL/min), reduced at 300 °C for 1 h and flushed with 150 mL/min He before cooling to −150 °C to record 2–3 XAS spectra per sample.

EXAFS data were processed and analyzed with IFEFFIT, Athena and Artemis [36]. The scattering contributions of the pre- and post-edge were removed from the X-ray absorption spectra by a third-order polynomial function. The oscillations were weighted by k^2 and Fourier transformed within the limits $k = 2.1–12$ Å^{-1} for the Pd K edge and $k = 2.8–12$ Å^{-1} for the Au L_3 edge. The amplitude S_o^2, was derived from EXAFS data analysis of known references with known coordination numbers and was fixed during analysis (S_o^2 was found to be 0.9 for Au and 1.0 for Pd). The multiple-edge fitting was carried out with following constraints.

$$N_{\mathrm{AuPd}} = N_{\mathrm{PdAu}} x_{\mathrm{Pd}} / x_{\mathrm{Au}} \tag{3}$$