Catalysis Letters Vol. 93, Nos. 3–4, March 2004 (© 2004)

A study of hydrophobic Pd/SDB catalyst for ethylene partial oxidation to acetic acid

Jinhai Xie[a,b,*], Qinglin Zhang[b], and Karl T. Chuang[b]

[a]*Department of Applied Chemistry, Harbin Institute of Technology, Harbin, Heilongjiang, People's Republic of China, 150001*
[b]*Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alta, Canada T6G 2G6*

Received 15 October 2003; accepted 9 January 2004

The performance of 0.2 wt% Pd/SDB catalyst used for partial oxidation of ethylene to acetic acid has been evaluated in a fixed-bed reactor. The catalyst has high activity and selectivity toward acetic acid, but it starts to deactivate after running 84 h at 120 °C and 1200 kPa. BET, XRD, FTIR and XPS have been employed to the characterization of the catalyst. It has been found that the deactivation of the catalyst is mainly due to the partial oxidative degradation of the SDB framework during reaction, particularly, in the presence of oxygen, which results in a decrease in surface area and an increase in hydrophilicity of the catalyst.

KEY WORDS: Pd/SDB catalyst; ethylene; partial oxidation; acetic acid; deactivation; characterization.

1. Introduction

Acetic acid is an important chemical used as the starting materials for the manufacture of vinyl acetate and acetic anhydride. Commercially, it is produced from acetaldehyde oxidation, methanol or methyl acetate carbonylation and light carbon liquid-phase oxidation [1]. Attentions have also been paid to the exploration and development of new processes of acetic acid production such as oxidation of ethylene and oxidation of *n*-butane in vapor phase [1–3].

Recently, a novel hydrophobic Pd/SDB catalyst (SDB: styrene divinylbenzene copolymer) used for single step partial oxidation of ethylene to acetic acid has been developed in our laboratory. Because of the hydrophobicity of the SDB support, Pd/SDB catalyst can be used for the oxidation reactions at low temperatures with water involved as a reactant.

It has been found that the selectivity to acetic acid is more than 85% and the major by-product CO_2 is less than 15%. However, after used at 120 °C and 1200 kPa for about 84 h, the catalyst deactivates to some extent. The stability of the catalyst is thus the key issue for the single step production of acetic acid from partial oxidation of ethylene. In this study, a systematical investigation on the stability of the SDB support and Pd/SDB catalyst has been carried out. BET, XRD, XPS and FTIR techniques have been employed to the characterization of the support and catalyst. The deactivation of the catalyst has been interpreted based on the characterization results.

2. Experimental

SDB supported palladium catalyst with palladium a loading of 0.2 wt% was prepared by using a conventional impregnation method. Methanol was used as a solvent for Pd solution instead of water due to the hydrophobicity of SDB support. The obtained catalyst was dried under infrared light for 8 h and reduced at 240 °C in H_2 flow (100 mL/min) for 16 h. Detailed procedure for the catalyst preparation has been described elsewhere [4].

Activity tests for partial oxidation of ethylene to acetic acid over 0.2 wt% Pd/SDB catalyst was carried out at 120 °C and 1200 kPa in a fix bed reactor made from a stainless steel tubing (1/2″ o.d.) equipped with an electric heater. A cooling coil (7″ in length) made from a stainless steel tubing (1/16″ o.d.) was built inside the reactor to remove the heat released during reaction. Typically, 5 g of the catalyst (20–50 mesh) was loaded into the reactor without using diluting materials. The top and bottom of the reactor were filled with ceramic particles (16–35 mesh). Water was fed by a liquid pump (Model 6000A, Water Associates. Inc) at a rate of 0.5 g/min to a preheater, where it was vaporized and heated to 185 °C. Flow rates of the ethylene and oxygen were controlled by using mass flow controllers and the pressure was maintained by using a back-pressure regulator. The gas phase effluents were analyzed using an online gas chromatograph (Hewlett Packed 5890 Series II) equipped with a TCD detector and a 2 m Porapak R column using helium as carrier gas. The liquid products collected in cold water condensers were analyzed by means of titration method using 0.5 N NaOH as titrant and litmus as indicator.

XPS analyses were performed on a VG Scientific Escalab Mark II spectrometer equipped with a

---

[*] To whom correspondence should be addressed. *Present address*: H2-Tech. Inc, 225 President Kennedy, Montreal, QC, Canada H2X 3Y8. E-mail: j.xie@h2-tech.uqam.ca

1011-372X/04/0300–0181/0

hemispherical analyzer operated in a constant-pass energy mode (20 eV). MgK$_\alpha$ radiation ($h\nu = 1253.6$ eV) eV) operated at 20 mA and 15 kV was used as the X-ray source. The samples were cooled down to −60 °C during measurements and linear lines were used for the background subtraction of the XPS spectra.

FTIR spectra of the SDB support and catalysts were obtained on a Nicolet Magna-750 FTIR spectrometer.

BET specific surface areas and pore volume distributions of the SDB support, fresh and used Pd/SDB catalysts were measured at 77 K on an OMNISORP 360 instrument using nitrogen as sorbate. Prior to the measurements, the sample was treated at 150 °C in vacuum overnight.

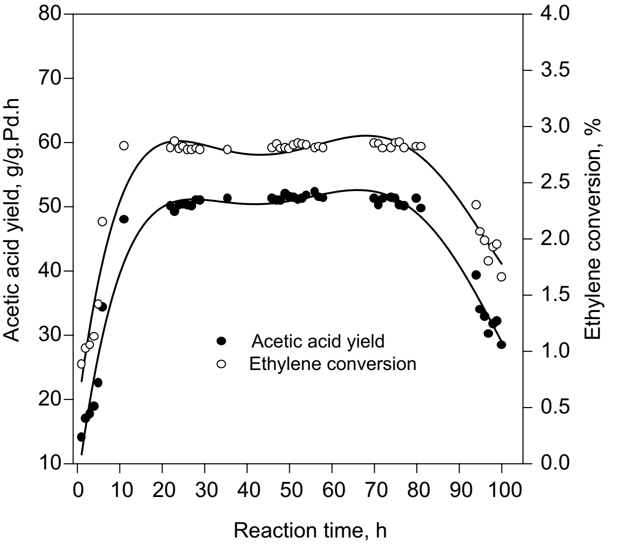

Figure 1. Variation of acetic acid yield and ethylene conversion with time at 120 °C, 1200 kPa, ethylene/oxygen = 200/51, water feed rate = 0.50 g/min.

3. Results and discussion

Figure 1 shows the variation of acetic acid yield and ethylene conversion versus reaction time at 120 °C and 1200 kPa. Note that during the initial 10 h both the conversion and yield increase with time on stream, probably, due to reaction relaxation. The occurrence of the long reaction relaxation remains unclear. After the relaxation period, the reaction gives stable ethylene conversion, high yield and selectivity of acetic acid (ca. 85%). The high activity of the Pd/SDB catalyst can be ascribed to two factors: the high surface area of SDB (767.2 m^2/g), which makes palladium well dispersed on the SDB surface and gives the Pd/SDB catalyst a high surface area (790.9 m^2/g) (the usage of methanol as a solvent in catalyst preparation might clean the micropores of SDB and subsequently increase the surface area after Pd loading and catalyst treatment). The other factor is the hydrophobic property of the catalyst, which prevents the formation of water film on the catalyst surface resulting from the adsorption of water and thus the active sites on catalyst surface cannot be cloaked by water molecules. In contrast, for the hydrophilic Pd-based catalysts, steam fed in the reactant mixture forms water film on the surface of the catalysts and impedes the adsorption of ethylene and subsequently reduces the activities of the catalysts. From figure 1, the hydrophobic Pd/SDB catalyst deactivates after used for about 84 h. In order to identify the factors leading to the catalyst deactivation, both the fresh and used catalysts have been characterized.

Figure 2 presents FTIR spectra of the SDB support, fresh Pd/SDB and used Pd/SDB catalysts. For comparison, the FTIR spectra of Pd(Ac)$_2$/SDB and Pd(Ac)$_2$ are also displayed in this figure. For the SDB support, fresh Pd/SDB and Pd(Ac)$_2$/SDB, three bands located at 1630, 1408 and 989 cm^{-1} are observed and assigned to the stretching vibration of C=C bond conjugated with aryl group [5]. In the case of the used Pd/SDB catalyst, the intensities of the three bands are significantly reduced and new bands appear at about 1727, 1700, 1690, 1360, 1268 and 1170 cm^{-1}. The bands around 1700 cm^{-1} are typical of C=O stretching vibration [5] and their appearance indicates the formation of compounds containing C=O groups in the catalyst. The compounds containing C=O groups could result from the oxidation of SDB and formation of palladium acetate. From figure 2, however, no band around 1700 cm^{-1} is observed for the Pd(Ac)$_2$ sample, suggesting that the compounds containing C=O groups in the used Pd/SDB catalyst does not arise from the formation of palladium acetate, but from the oxidation of SDB. For the SDB support, fresh Pd/SDB and Pd(Ac)$_2$/SDB, minor bands at about 1700 cm^{-1} can be detected, which may arise from the oxidation of SDB during manufacture process. From the intensities of the C=O bands at about 1700 cm^{-1}, it can be derived that the used Pd/SDB catalyst is much more hydrophilic than the fresh one. The bands at 1605 and 1431 cm^{-1} are attributed to the asymmetrical and symmetrical stretching vibrations of COO$^-$ ion, which coincide with those of SDB matrix.

To understand the influence of the reactant mixture on the stability of the catalyst, the SDB support and Pd/SDB catalyst were treated at 120 °C with the mixture of ethylene and water or mixture of oxygen and water. As shown in figure 3, no change is observed in the infrared spectra of SDB and Pd/SDB before and after treatments with ethylene and water. However, for SDB and Pd/SDB treated with the mixture of oxygen and water, the bands at 1630, 1408 and 989 cm^{-1} disappear, which suggests the oxidation of C=C of SDB. The bands at 1727, 1700, 1690, 1360, 1268 and 1170 cm^{-1} are also observed for the support and catalyst treated with the oxygen-containing mixture.

The characteristics of the residual C=C in SDB are the same as those of styrene. It is known that styrene

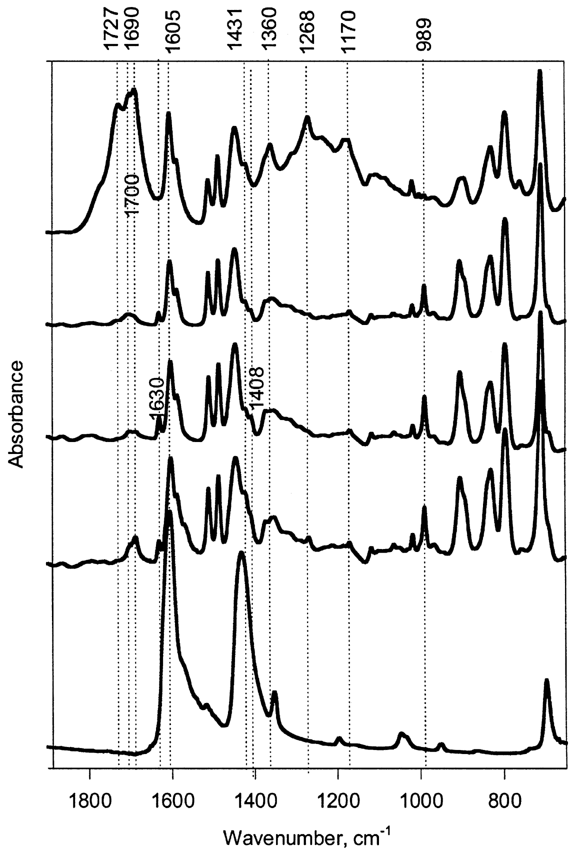

Figure 2. FTIR spectra of fresh Pd/SDB and spent Pd/SDB. From bottom to top: $Pd(Ac)_2$, $Pd(Ac)_2$/SDB, SDB, 0.2 wt%Pd/SDB, and 0.2 wt%Pd/SDB after used at 120 °C 1200 kPa for 100 h.

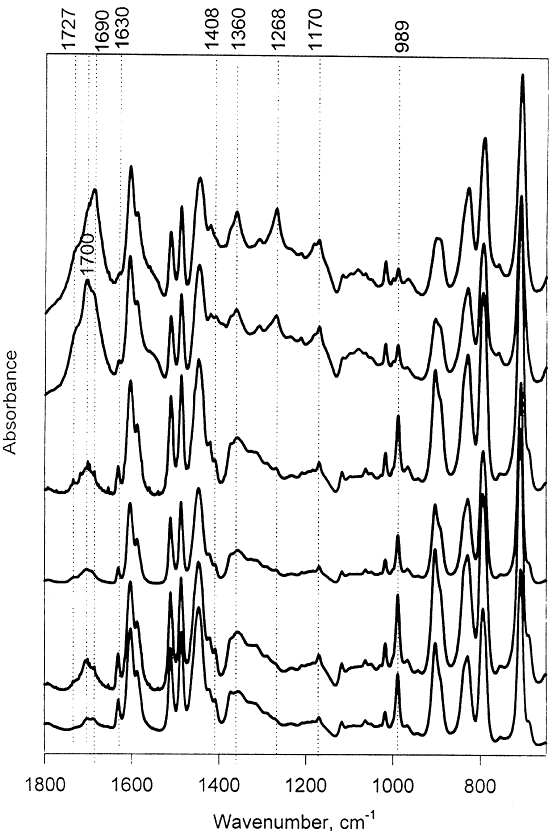

Figure 3. FTIR spectra of SDB, Pd/SDB, treated SDB and Pd/SDB. From bottom to top: SDB and SDB treated with C_2H_4 + H_2O, 0.2 wt%Pd/SDB and 0.2 wt%Pd/SDB treated with C_2H_4 + H_2O, SDB treated with O_2 + H_2O, and 0.2 wt%Pd/SDB treated with O_2 + H_2O (treatment condition: 120 °C, 1200 kPa,100 h).

(containing branch C=C) can be oxidized in air to form peroxides. It can also be oxidized to other compounds such as benzaldehyde, styrene oxide, benzoic acid, etc. [6]. Three bands around 1700 cm^{-1} arising from C=O stretching vibration can be observed for SDB treated with the mixture of oxygen and water, indicating the oxidation of SDB. The simultaneous appearance of the bands at 1700 (C=O stretching vibration), 1270 (C—O stretching vibration), 1360 (C—H symmetrical deformation vibration of O=C—CH_3) and 1170 cm^{-1} (C—C stretching vibration of aromatic ketones) reveals the formation of acetophenone. The absence of the C—H stretching doublet of aldehyde in the region 2870–2695 cm^{-1} excludes the formation of aldehyde on SDB and Pd/SDB treated with oxygen and water. The C=O groups produced in the used Pd/SDB catalyst increase the hydrophilicity of the catalyst and facilitate the adsorption of water. The water adsorbed on the surface of the catalyst impedes the adsorption of ethylene and thus decreases the activity of the catalyst.

BET data are shown in table 1. The surface areas of the SDB support and Pd/SDB catalyst treated with the mixture of ethylene and water are similar to those of the

Table 1
BET surface areas of SDB, fresh and used catalysts

Samples	Surface area (m^2/g)	External surface area (m^2/g)	Total pore volume above 10 Å (cm^3/g)
SDB	767.2	476.1	0.8075
C_2H_4 + H_2O + SDB, 120 °C, 1200 kPa, 100 h	754.7	532.4	0.7209
O_2 + H_2O + SDB at, 120 °C, 1200 kPa, 100 h	652.3	466.7	0.7333
0.2 wt%Pd/SDB	790.9	548.5	0.8673
C_2H_4 + H_2O + 0.2 wt%Pd/SDB, 120 °C, 1200 kPa, 100 h	762.1	541.3	0.8546
Used 0.2 wt%Pd/SDB at 120 °C, 1200 kPa, 100 h	539.5	436.9	0.7357
O_2 + H_2O + 0.2 wt%Pd/SDB, 120 °C, 1200 kPa, 100 h	685.1	481.4	0.7648

Table 2
Variation of O1s binding energy of fresh SDB, Pd/SDB and spent SDB, Pd/SDB

Sample	O1s (eV)	FWHM (eV)
SDB	532.7	2.8
SDB treated with reaction mixture at 120 °C, 1200 kpa	532.4	2.9
0.2 wt%Pd/SDB	532.8	2.9
0.2 wt%Pd/SDB used at 120 °C, 1200 kPa	532.5	3.3

samples prior to the treatments. After treated with the oxygen-containing mixture, the surface areas of the samples are reduced. This is in agreement with the FTIR results as mentioned above. The decrease in surface area may cause the deactivation of the catalysts. It is interesting to note that no significant decrease is observed in external surface area and pore volume of the pores with their diameters larger than 10 Å for the SDB support, used Pd/SDB catalyst and the catalyst treated with the mixture of oxygen and water. The surface areas of the samples are very close to their corresponding external surface areas. This indicates that the reduction in surface area arises mainly from the reduction of the micropores in SDB because of the oxidation of C=C bond in SDB that induces the partial collapse of polymer framework. It is worthwhile to note that no CO_2 has been detected during the treatment of SDB and Pd/SDB with oxygen and water, indicating that the decrease in surface area cannot be attributed to the combustion of the SDB support. Compared with the fresh catalyst, the surface area of the used Pd/SDB catalyst (539.5 m^2/g) is reduced by about 32%. However, the acetic acid yield and ethylene conversion are reduced by about 45%. Therefore, the reduction in activity may not be only due to the decrease of the surface area but also due to the increase of hydrophilicity of the used catalyst.

Pd(0) in Pd-based catalyst is considered as the active center for partial oxidation reactions [7]. In order to identify the oxidation state of the palladium species, the SDB support, fresh and used Pd/SDB catalysts and SDB treated with reaction mixture were characterized by using XRD and XPS techniques. The palladium signals are hardly detected because of the low loading and high dispersion of palladium. The recorded O1s XPS spectra of the samples indicate that the O1s binding energy and peak width expressed as FWHM (full width at half maximum) vary with the samples as shown in table 2. The O1s binding energies of the SDB and Pd/SDB samples treated with reaction mixture are decreased compared with the samples prior to the treatment, indicating the change of oxidation state of the oxygen species in SDB. The peak widths of O1s for the used Pd/SDB and SDB treated with reaction mixture are also larger than those for the fresh Pd/SDB and non-treated SDB. The increase in O1s peak width reveals the presence of oxygen species with different oxidation states. This is in agreement with the FTIR results, i.e., SDB is oxidized to some extent in the presence of oxygen.

4. Conclusion

0.2 wt%Pd/SDB catalyst shows high activity and selectivity for partial oxidation of ethylene to acetic acid at a temperature of 120 °C. The catalyst deactivates after run on stream for about 84 h. Two factors are responsible for the deactivation of the catalyst, i.e., the decrease of Pd/SDB surface area, which is probably caused by the partial collapse of the framework leading to a reduction of the micropores in SDB, and the oxidation of SDB under reaction conditions, which produces more hydrophilic C=O groups on the surface of SDB. The existence of residual branch C=C double bonds in SDB facilitates the oxidation of SDB and production of C=O groups. The modification of the SDB support to eliminate residual branch C=C double bonds could prevent the catalyst from deactivation.

References

[1] A. Aguilo, C.C. Hobbs and E.G. Zey, in: *Ullman's Encyclopedia of Industrial Chemistry*, Vol. A1, 1985, p. 45.

[2] H.J. Hagemeyer, in: *Encyclopedia of Chemical Technology*, Vol. 1, 1991, p. 121.

[3] K.S. McMahon, in: *Encyclopedia of Chemical Processing and Design*, Vol. 1, 1976, p. 216.

[4] S. Sood, One-step Oxidation of Propylene to Acrylic Acid, Master Thesis at University of Alberta, 1995.

[5] D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules* Chapters 6, 9, Appendix 3.

[6] Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25, p. 331; *Encyclopedia of Chemical Technology*, Fourth ed., Vol. 22, p. 957.

[7] J.E. Lyons, Catal. Today 3 (1988) 205.