Sulfated Zirconia-supported Palladium as a Highly Active and Highly Selective Catalyst for the Oxidation of Ethylene in the Vapor Phase

Tomoaki Hamada,[1] Yoshinori Sakamoto,[2] Yasunobu Ooka,[1] Toshio Okuhara,[2] and Yuichi Kamiya*[2]
[1]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810*
[2]*Research Faculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810*

(Received December 19, 2008; CL-081196; E-mail: Kamiya@ees.hokudai.ac.jp)

Pd supported on sulfated zirconia with a S/Zr ratio of 0.077 exhibited high activity and high selectivity for the oxidation of ethylene to partially oxidized products, including acetaldehyde and acetic acid, in the vapor phase.

Catalysts combining a solid acid with a precious metal, such as Pt and Pd, are often called bifunctional catalysts and show an excellent performance for the skeletal isomerization of alkanes.[1] Over this type of catalyst, the metal sites promote dehydrogenation and hydrogenation, and the skeletal isomerization of the corresponding carbenium ion occurs at the acid sites. That is, the precious metal and solid acid separately catalyze the respective reactions. In fact, a catalyst composed of a physical mixture of a solid acid and a precious metal shows a catalytic performance similar to or higher than that of the corresponding solid acid-supported precious metal catalyst.[2]

On the other hand, we have recently proposed a novel catalytic function of the bifunctional catalysts including Pd/WO_3–ZrO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2 that the acid sites promote the reoxidation of metallic Pd sites into the corresponding oxidized Pd sites.[3] In fact, Pd/WO_3–ZrO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2 exhibit high catalytic activities for a Wacker-type reaction involving the transformation of ethylene to acetic acid via an acetaldehyde intermediate in the gas-phase.[3–5] Showa Denko K.K. developed the world's first commercial process employing a highly active and selective Pd–$H_4SiW_{12}O_{40}$/SiO_2 catalyst.[6,7] This process is considered to be environmentally benign because it uses a heterogeneous catalysis.[8] However, in order to improve the yield of the process, a better catalyst is needed. In the present publication, we report that Pd supported on sulfated zirconia (SO_4–ZrO_2), which is known as a solid superacid,[9] is an excellent catalyst for the Wacker-type reaction involving the gas-phase oxidation of ethylene to partially oxidized products, including acetaldehyde and acetic acid.

Sulfated zirconia (SO_4–ZrO_2) samples with different S/Zr ratios were prepared by using an incipient wetness method with dilute sulfuric acid (0.5 mol dm^{-3}, Wako Pure Chem. Co.) and $Zr(OH)_4$ (Dai-ichi Kigenso Kagaku Kogyo Ltd), which was dried overnight at 373 K before use. The resulting solid was dried at 373 K and calcined at 973 K for 3 h at a heating rate of 2 K min^{-1}. The S/Zr ratio of SO_4–ZrO_2 was changed by changing the amount of dilute sulfuric acid added. The amount of sulfur in the calcined SO_4–ZrO_2 was estimated from the amount of $SO_4{}^{2-}$ formed by the combustion of the sample in O_2 by using ion chromatography. Pd/SO_4–ZrO_2 was prepared by impregnating SO_4–ZrO_2 with an aqueous solution (80 mmol dm^{-3}) of $PdCl_2$ (Wako Pure Chem. Co.). The Pd loading was adjusted to 1.0 wt %. After drying at 373 K, the resulting solid was calcined at 673 K for 5 h at a heating rate of 2 K min^{-1}. Other catalysts (Table 1) were prepared according to previously reported methods.[3,4]

The oxidation of ethylene was performed in a fixed-bed flow reactor (stainless steel SUS 317, inner diameter = 10 mm). The catalyst (2 cm^3, 60–80 mesh) was pretreated in the reactor at 573 K for 1 h in a 1:1 mixture of H_2 and He at a flow rate of 60 cm^3 min^{-1}. After cooling in a He flow to the reaction temperature of 423 K, the reactant gas (C_2H_4:O_2:H_2O:He = 50:7:30:13 in vol %) was fed into the reactor at a total flow rate of 100 cm^3 min^{-1} (SV = 3000 h^{-1}) and a total pressure of 0.6 MPa. The effluent gas was introduced into a trap kept at 200 K in order to liquefy and collect the products. The liquefied products were analyzed by using a gas chromatograph with a flame ionization detector (GC-FID, Simadzu 8A) and a Porapak QS column. The gaseous products that passed through the trap were analyzed by using an on-line gas chromatograph (Aera, Micro GC M200).

The results for the different catalysts are summarized in Table 1, in which STY represents the space time yield of the sum of the partially oxidized products (*POxP*), including acetic acid and acetaldehyde. Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, Pd/$MoO_3$–$ZrO_2$, Pd/$Nb_2O_5$, Pd/$SiO_2$–$Al_2O_3$, Pd/H-$\beta$, and Pd/H-mordenite gave only low STYs and/or low selectivities for the reaction. Pd–$H_4SiW_{12}O_{40}$/SiO_2 showed decent selectivity for *POxP* (70%), but the STY was moderate. On the other hand, Pd/SO_4–ZrO_2 gave a significantly high STY per unit volume as well as unit weight of the catalyst. In addition, the formation of CO_x was remarkably suppressed over Pd/SO_4–ZrO_2 (selectivity for CO_x was only 6%), meaning that Pd/SO_4–ZrO_2 exhibited the highest selectivity for *POxP* (94%) among the catalysts examined. Although we have shown that Pd/WO_3–ZrO_2 shows high activity and high selectivity for the gas-phase oxidation of ethylene,[3,4] Pd/SO_4–ZrO_2 was superior in both activity and selectivity to Pd/WO_3–ZrO_2. In addition, even after 9 h, the activity and selectivity of Pd/SO_4–ZrO_2 barely changed (Table 1) and the color change in the catalyst after the reaction was subtle, suggesting that the coke formation was little. Xie et al. have reported that a styrene divinylbenzene copolymer-supported Pd catalyst shows high selectivity for partially oxidized products (85%) in the gas-phase oxidation of ethylene at 393 K.[10] Li and Iglesia have found that a multicomponent catalyst (0.0025 wt % Pd/$Mo_{0.16}V_{0.31}Nb_{0.08}O_x$/$TiO_2$) suppresses the formation of CO_x (selectivity = 11%) and consequently exhibits high selectivity for the partially oxidized products.[11] The results in Table 1 demonstrate that Pd/SO_4–ZrO_2 is superior in selectivity to the previously reported catalysts.

The chemical and physical properties of SO_4–ZrO_2 change depending on the sulfur content.[12] Thus, we investigated the effect of the S/Zr atomic ratio on the STY and selectivity. We

Table 1. Catalytic data for gas-phase oxidation of ethylene over various catalysts[a]

Catalyst[b]	STY[c]	Selectivity[d]/%					Conversion
	$/\mathrm{mol\,h^{-1}\,dm^{-3}}$ $(\mathrm{mol\,h^{-1}\,kg^{-1}})$	*POxP*	AcOH	AcH	EtOH	CO_x	of O_2/%
$Pd/SO_4–ZrO_2$[e]	2.81 (3.02)	94	53	41	0	6	27
$Pd/SO_4–ZrO_2$[e] (at 9 h)[f]	2.61 (2.81)	92	73	19	0	8	37
$Pd/WO_3–ZrO_2$[g]	1.34 (0.76)	82	74	8	0	18	32
$Pd–H_4SiW_{12}O_{40}/SiO_2$[h]	0.88 (1.15)	70	55	15	10	20	21
$Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.62 (0.30)	24	17	7	15	61	68
$Pd/MoO_3–ZrO_2$[i]	0.64 (0.40)	55	36	19	0	45	25
Pd/Nb_2O_5	0.10 (0.10)	76	24	52	1	23	4
$Pd/SiO_2–Al_2O_3$[j]	0.07 (0.15)	72	29	43	0	28	5
Pd/H-β[k]	0.03 (0.06)	48	38	10	4	48	6
Pd/H-mordenite[l]	0.02 (0.02)	40	22	18	4	56	4

[a]Reaction conditions: $C_2H_4:O_2:H_2O:He = 50:7:30:13$, GHSV $= 3000\,h^{-1}$, temperature 423 K, and pressure 0.6 MPa. The data was collected at 3 h. [b]Loading amount of Pd was 1.0 wt % except for 1.5 wt % Pd–40 wt % $H_4SiW_{12}O_{40}/SiO_2$. [c]Space time yield of sum of acetic acid (AcOH) and acetaldehyde (AcH). [d]*POxP*: AcOH + AcH, EtOH: ethanol. [e]S/Zr = 0.077. [f]The data was collected at 9 h. [g]W/Zr = 0.2 and calcination was performed at 1073 K. [h]1.5 wt % Pd–40 wt % $H_4SiW_{12}O_{40}/SiO_2$. [i]Mo/Zr = 0.2 and calcination was performed at 1073 K. [j]Si/Al = 5.3. [k]Si/Al = 12.5. [l]Si/Al = 10.

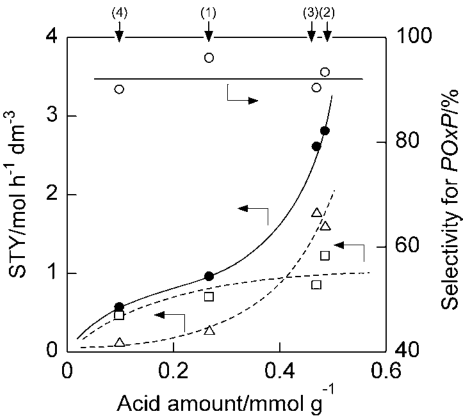

Figure 1. Changes in STY and selectivity over $Pd/SO_4–ZrO_2$ as a function of the acid content of $SO_4–ZrO_2$. STY of (●) *POxP*, (□) acetaldehyde, and (△) acetic acid, and (○) selectivity for *POxP*. *POxP* means partially oxidized products, which included acetaldehyde and acetic acid. S/Zr atomic ratios were (1) 0.035, (2) 0.077, (3) 0.154, and (4) 0.474.

prepared four $SO_4–ZrO_2$ catalysts with S/Zr ratios in the range of 0.035–0.474. The surface areas of the $SO_4–ZrO_2$ catalysts were determined to be 80, 106, 72, and 20 $m^2\,g^{-1}$ for S/Zr ratios of 0.035, 0.077, 0.154, and 0.474, respectively. The acid amount of $SO_4–ZrO_2$ estimated by using temperature-programmed desorption (TPD) of NH_3 also changed depending on the S/Zr ratio (Figure 1). $SO_4–ZrO_2$ (S/Zr = 0.077) and $SO_4–ZrO_2$ (S/Zr = 0.154) possessed large numbers of the acid sites and high surface areas. In Figure 1, STYs of *POxP* (●), acetaldehyde (□), and acetic acid (△), and selectivity for *POxP* (○) are plotted against the acid amount. The catalytic activity changed depending on the S/Zr ratio, whereas the selectivity was independent of the S/Zr ratio. The $Pd/SO_4–ZrO_2$ (S/Zr = 0.077) catalyst with the highest STY of *POxP* possessed the largest number of acid sites.

We believe that the acid sites on the support play an important role in forming the Pd active sites; acid sites play a role in the oxidation of Pd^0 to Pd^{2+} by H^+ with the help of O, as well as accepting H^+ released during the formation of acetaldehyde by the conjugated base of the acid sites.[3,4] The relationship between the STY of *POxP* and the number of acid sites of $SO_4–ZrO_2$ (shown in Figure 1) strongly supports this idea. The acid amount of $SO_4–ZrO_2$ (S/Zr = 0.077) was 0.49 $mmol\,g^{-1}$, which is much larger than those of $WO_3–ZrO_2$ (W/Zr = 0.2, 0.23 $mmol\,g^{-1}$) and 40 wt % $H_4SiW_{12}O_{40}/SiO_2$ (0.07 $mmol\,g^{-1}$, estimated by using benzonitrile-TPD[13]). The large number of acid sites as well as the strong acidity may be one reason for the high activity and high selectivity of $Pd/SO_4–ZrO_2$ toward the oxidation of ethylene.

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