Pd/WO_3–ZrO_2 as an Efficient Catalyst for the Selective Oxidation of Ethylene to Acetic Acid in the Vapor Phase

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Pd supported on WO_3–ZrO_2 calcined at temperatures of 973–1073 K exhibits a high activity and selectivity for the oxidation of ethylene to acetic acid in the vapor phase. The space time yield (STY) per unit volume of catalyst is higher for Pd/WO_3–ZrO_2 than for Pd/$H_4SiW_{12}O_{40}$–SiO_2, the best catalyst reported to date.

Recently, it was reported that a catalyst composed of Pd and a heteropoly acid exhibited a high yield of acetic acid in the one-step gas-phase oxidation of ethylene.[1] Among the heteropoly acids, silicotungstic acid ($H_4SiW_{12}O_{40}$) exhibited the highest space time yield (STY) of acetic acid. Sano et al. suggested that the acidic nature of $H_4SiW_{12}O_{40}$ contributed to its high activity in the oxidation of ethylene.[1] They also reported that the addition of Se and Te to the catalyst increased the STY of acetic acid, due to the suppression of CO_2 formation.[1] A plant for the production of acetic acid based on the catalyst Pd/$H_4SiW_{12}O_{40}$–SiO_2 was commercialized in 1998. In the present publication we present Pd/WO_3–ZrO_2 as an efficient catalyst for the production of acetic acid from ethylene. Pd/WO_3–ZrO_2 is a more efficient catalyst than a number of other catalysts, including Pd/$H_4SiW_{12}O_{40}$–SiO_2.

WO_3–ZrO_2 with different W/Zr ratios was prepared by an incipient wetness method from an aqueous solution (16 mmol dm^{-3}) of $(NH_4)_{10}W_{12}O_{41}$ (Wako Chemical Co.) and $Zr(OH)_4$ (Dai-ich Kigenso Kagaku Kogyo Ltd., dried overnight at 373 K).[2] The resulting solid was dried at 373 K and calcined at a pre-determined temperature for 3 h, with the temperature being gradually increased at a rate of 10 K min^{-1}. Pd/WO_3–ZrO_2 was prepared by the impregnation of WO_3–ZrO_2 with an aqueous solution (40 mmol dm^{-3}) of $PdCl_2 \cdot H_2O$ (Wako Chemical 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, with the temperature being raised at a rate of 2 K min^{-1}. 1.5 wt % Pd/40 wt % $H_4SiW_{12}O_{40}$–SiO_2 was prepared by impregnation according to a method described previously.[3] The solid was calcined at 523 K in air for 5 h. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and MoO_3–ZrO_2 (Mo/Zr = 0.2, calcined at 1073 K) were prepared according to literature procedures.[4,5] SiO_2–Al_2O_3 (JRC-SAL-2), H-β (Zeolist, Si/Al = 12.5), H–mordenite (Zeolist, Si/Al = 10) were used after calcination at 773 K. Nb_2O_5 (CBMM, HY-340) calcined at 573 K was also used. Pd was loaded onto these supports by the method described for Pd/WO_3–ZrO_2.

The oxidation of ethylene was performed in a fixed-bed flow reactor (stainless steel SUS 317, 10 mm inside diameter). Catalyst (2 cm^3, 60–80 mesh) was placed in the reactor and pretreated at 573 K for 1 h under a stream of H_2–He (1:1 mixture) at a flow rate of 60 cm^3 min^{-1}. After cooling under the He flow to a reaction temperature of 423 K, a mixture of 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 total pressure of 0.6 MPa. The effluent gas was introduced to a trap kept at 200 K in order to collect the liquefied products. The liquefied components were analyzed by gas chromatography (Simadzu 8A, FID with Porapak QS column). The gaseous products passing through the trap were directly injected into a gas chromatograph (Aera, Micro GC M200).

The results of catalytic reactions with different types of catalysts are summarized in Table 1. It is noted that Pd/WO_3–ZrO_2 gave the highest STY of acetic acid per unit volume of catalyst. In addition, Pd/WO_3–ZrO_2 exhibited high selectivity for acetic

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

Catalyst[b]	STY of AcOH[c] /mol h^{-1} dm^{-3} (mol h^{-1} kg^{-1})	Selectivity/%				Conversion of O_2/%
		AcOH[d]	AcH[d]	EtOH[d]	CO_x	
Pd/WO_3–ZrO_2[e]	1.21 (0.69)	74	8	0	18	32
Pd–Te/WO_3–ZrO_2[f]	0.91 (0.56)	81	10	0	9	27
Pd/$H_4SiW_{12}O_{40}$–SiO_2[g]	0.69 (0.90)	55	15	10	20	21
Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.44 (0.21)	17	7	15	61	68
Pd/MoO_3–ZrO_2[h]	0.42 (0.26)	36	19	0	45	25
Pd/SiO_2–Al_2O_3	0.03 (0.06)	29	43	0	28	5
Pd/H–β[i]	0.02 (0.05)	38	10	4	48	6
Pd/H–mordenite[j]	0.01 (0.01)	22	18	4	56	4
Pd/Nb_2O_5	0.03 (0.03)	24	52	1	23	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 acetic acid; [d]AcOH: acetic acid, AcH: acetaldehyde, EtOH: ethanol; [e]W/Zr = 0.2 and calcined at 1073 K; [f]Te/Pd atomic ratio was 0.1; [g]1.5 wt %Pd/40 wt %$H_4SiW_{12}O_{40}$–SiO_2; [h]Mo/Zr = 0.2 and calcined at 1073 K; [i]Si/Al = 12.5; [j]Si/Al = 10.

acid among the catalysts examined. As reported by Sano et al.,[1] although Pd/$H_4SiW_{12}O_{40}$–SiO_2 was a highly active catalyst for the reaction, its selectivity for acetic acid was moderate. Thus, Table 1 demonstrates that Pd/WO_3–ZrO_2 has potential for practical use. As a matter of fact, the addition of Te to Pd/WO_3–ZrO_2 greatly enhanced its selectivity for acetic acid, producing 81% acetic acid and 10% acetaldehyde. Time courses for this reaction over Pd/WO_3–ZrO_2 and Pd/$H_4SiW_{12}O_{40}$–SiO_2 showed that changes in the activity and selectivity were small for a period up to at least 9 h for both catalysts.

Pd/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Pd/MoO_3–ZrO_2 also exhibited high activities, comparable to that of Pd/$H_4SiW_{12}O_{40}$–SiO_2, however the selectivity of this catalyst was very low. Both Pd/H-β and Pd/H-mordenite were less active and less selective. Pd/SiO_2–Al_2O_3 and Pd/Nb_2O_5 were inferior to the other catalysts.

To optimize the conditions for Pd/WO_3–ZrO_2, the effect of the Pd starting material, the Pd loading, the calcination temperature of the WO_3–ZrO_2 support, the W/Zr ratio and the pretreatment of Pd/WO_3–ZrO_2 (calcination and reduction temperatures) were investigated. The Pd starting material affected the catalytic activity of the resulting catalysts. The catalyst prepared using $PdCl_2$ exhibited a higher STY than those prepared using $(NH_4)_2PdCl_4$ and $Pd(NO_3)_2$. In particular, the use of the latter two catalysts generated significant amount of CO_2. $PdCl_2$ is therefore the preferred source of Pd. Although the Pd loading did not greatly affect the STY, the catalyst loaded with 1 wt % Pd showed the highest STY.

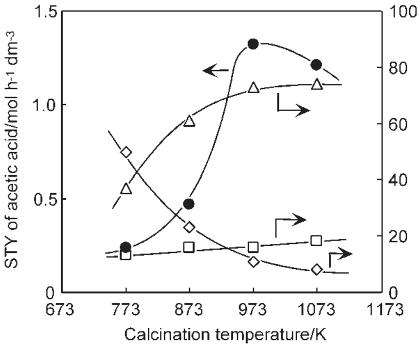

Figure 1. Effect of calcination temperature of WO_3–ZrO_2 on STY of acetic acid and selectivity for oxidation of ethylene over 1 wt %Pd/WO_3–ZrO_2(W/Zr = 0.2). (●) STY and selectivity to (△) acetic acid, (◇) acetaldehyde, and (□) CO_2.

Figure 1 shows the influence of the calcination temperature of the WO_3–ZrO_2 support on the activity and selectivity. The optimum temperatures were 1073 K for the greatest selectivity for acetic acid and 973 K for the highest activity. It is remarkable that the selectivity for acetic acid increases instead of decrease of the selectivity for acetaldehyde as the calcination temperature increased. The surface area of the catalyst decreased monotonically as the calcination temperature increased (124, 109, 82, and 72 $m^2\ g^{-1}$ for 773, 873, 973, and 1073 K, respectively). Thus, the observed change in activity (Figure 1) probably relates to the change in acidity of WO_3–ZrO_2, since the activities for acid-catalyzed reactions were higher at higher WO_3–ZrO_2 calcination temperatures.[6,7]

Figure 2 shows effect of the W/Zr atomic ratio on the STY and selectivity. Pd/WO_3–ZrO_2 exhibited the highest STY with W/Zr = 0.2 and the highest selectivity for acetic acid with W/Zr = 0.05. The surface areas of WO_3–ZrO_2 were measured to be 46, 72, 63, 61, and 45 $m^2\ g^{-1}$ for 0.05, 0.1, 0.2, 0.3, and 0.4 of W/Zr ratio, respectively. The surface densities of WO_3 were 5.1, 5.7, 11.2, 15.4, and 24.8 W-atom nm^{-2} for 0.05, 0.1, 0.2, 0.3, and 0.4 of W/Zr ratio, respectively, calculated using the surface areas and the W/Zr loadings. Since, in theory, 7 W-atom nm^{-2} is just sufficient to cover the ZrO_2 surface with a monolayer WO_3,[8] it is considered that monolayer WO_3 species and/or three-dimensional WO_3 clusters[9] would be formed on Pd/WO_3–ZrO_2 with the W/Zr range of 0.05–0.3, the catalysts which showed the high STY and high selectivity for acetic acid. Since WO_3–ZrO_2 with a WO_3-surface density of 7–15 W-atom nm^{-2} shows the highest activity for acid catalyzed reactions such as the benzoylation of toluene,[6] and isomerizations of pentane[6] and *o*-xylene,[7] acidity of WO_3–ZrO_2 would much contribute to the formation of the active sites. From contact time dependencies and indispensableness of water to the reaction we have previously demonstrated that ethylene is oxidized to acetaldehyde over Pd/WO_3–ZrO_2 through a Wacker-type reaction, with acetaldehyde being further oxidized to acetic acid.[10] Considering the similarity to the Wacker oxidation using homogeneous $PdCl_2$–$CuCl_2$ catalyst, the acidity of WO_3–ZrO_2 thus may play an important role in forming active sites such as Pd^{2+}.[10]

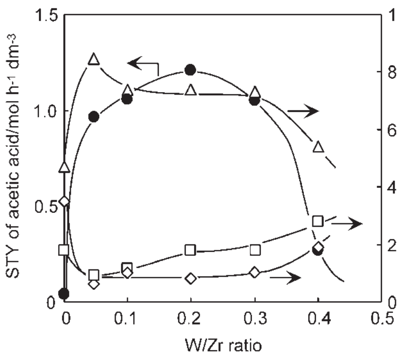

Figure 2. Effect of atomic ratio of W/Zr for WO_3–ZrO_2 on STY of acetic acid and selectivity for oxidation of ethylene over 1 wt %Pd/WO_3–ZrO_2. WO_3–ZrO_2 was calcined at 1073 K. (●) STY and selectivity to (△) acetic acid, (◇) acetaldehyde, and (□) CO_2.

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References

1 K. Sano, H. Uchida, and S. Wakabayashi, *Catal. Surv. Jpn.*, **3**, 55 (1999).
2 W. Chu, T. Echizen, Y. Kamiya, and T. Okuhara, *Appl. Catal., A*, **259**, 199 (2004).
3 A. Miyaji, T. Echizen, K. Nagata, Y. Yoshinaga, and T. Okuhara, *J. Mol. Catal. A: Chem.*, **201**, 145 (2003).
4 T. Okuhara, T. Nishimura, and M. Misono, *J. Mol. Catal.*, **74**, 247 (1992).
5 L. Li, Y. Yoshinaga, and T. Okuhara, *Phys. Chem. Chem. Phys.*, **1**, 4913 (1999).
6 M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, **1988**, 1259.
7 D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes, and E. Iglesia, *J. Catal.*, **181**, 57 (1999).
8 K. C. Pratt, J. V. Sanders, and V. Christov, *J. Catal.*, **124**, 416 (1990).
9 A. Satsuma, H. Yokoi, H. Nishiyama, S. Kakimoto, S. Sugaya, T. Oshima, and T. Hattori, *Chem. Lett.*, **33**, 1250 (2004).
10 W. Chu, Y. Ooka, Y. Kamiya, and T. Okuhara, *Catal. Lett.*, in press.

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