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Reaction path for oxidation of ethylene to acetic acid over Pd/WO_3–ZrO_2 in the presence of water

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Pd-supported on WO_3–ZrO_2 (W/Zr atomic ratio = 0.2) calcined at 1073 K was found to be highly active and selective for gas-phase oxidation of ethylene to acetic acid in the presence of water at 423 K and 0.6 MPa. Contact time dependence demonstrated that acetic acid is formed *via* acetaldehyde formed by a Wacker-type reaction, not through ethanol by hydration of ethylene.

KEY WORDS: ethylene oxidation; acetic acid; acetaldehyde; reaction path; Pd/WO_3–ZrO_2; Wacker-type reaction.

1. Introduction

Approximately 7.8 million tons/year of acetic acid were utilized throughout the world in 1998 for purposes such as a solvent for the production of pure terephthalic acid and as a raw material for acetic anhydride, acetates, and vinyl acetate. The industrial production of acetic acid is accomplished through three main synthetic processes: methanol carbonylation, called the Monsanto process [1,2]; the Hoechst–Wacker process that produces acetaldehyde, which is then oxidized to acetic acid [3,4]; and oxidation of butane in the presence of cobalt acetate [4]. These commercial processes are performed in liquid phase using homogeneous catalysts, but have disadvantages such as the need to separate the catalyst from the product.

Showa Denko K.K. has developed a one-stage process for acetic acid production through the gas-phase oxidation of ethylene [5–8]. This involves a highly selective catalyst based on Pd–$H_4SiW_{12}O_{40}/SiO_2$, and is an environmentally friendly process because of the heterogeneous catalysis. The reaction path for formation of acetic acid is speculated to proceed *via* hydration of ethylene to ethanol on the acid sites, followed by oxidation to acetaldehyde and then to acetic acid [5].

Here, we report that a novel catalyst, Pd supported on WO_3–ZrO_2 with a W/Zr atomic ratio of 0.2, calcined at 1073 K, exhibits high catalytic performance and that the oxidation of ethylene to acetic acid proceeds *via* acetaldehyde formed by a Wacker-type reaction.

2. Experimental

Tungstena–zirconia, WO_3–ZrO_2, with a W/Zr atomic ratio of 0.2 was prepared by an incipient wetness method from an aqueous solution (16 mmol dm^{-3}) of $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (Wako Chemical Co.) and $Zr(OH)_4$ (Daiichi Kigenso Kagaku Kogyo Ltd., dried overnight at 373 K) [9]. The resulting solid was dried overnight at 373 K and calcined at 1073 K in air for 5 h (WO_3–ZrO_2). 1.0wt%Pd/WO_3–ZrO_2 also was prepared by impregnation using an aqueous solution (40 mmol dm^{-3}) of $PdCl_2\cdot H_2O$ (Wako Chemical Co.) and WO_3–ZrO_2. After drying at 373 K, the solid sample was calcined in air at 673 K for 5 h. 1.5wt%Pd–40wt% $H_4SiW_{12}O_{40}/SiO_2$ was prepared by impregnation according to method described previously [10]. This sample was calcined at 523 K in air for 5 h. Examining the effect of Pd loading allowed optimization of the catalytic activity.

Oxidation of ethylene was performed in a fixed-bed flow reactor (stainless-steel SUS 317, 10 mm inside diameter). A catalyst volume of 2 cm^3 (about 60 mesh) was placed in the reactor, which corresponds to 3.12 and 1.56 g for 1.0wt%Pd/WO_3–ZrO_2 and 1.5wt% Pd–40wt%$H_4SiW_{12}O_{40}/SiO_2$, respectively. After pretreatment with 50% H_2 (He balance, total flow rate of 60 cm^3 min^{-1}) at 573 K (for 1.0wt%Pd/WO_3–ZrO_2) or 523 K (for 1.5wt%Pd–40wt%$H_4SiW_{12}O_{40}/SiO_2$) for 1 h, the reactor was cooled to reaction temperature under a He flow (30 cm^3 min^{-1}), and a mixture of the reactant gas (C_2H_4:O_2:H_2O:He = 50:7:30:13 in vol%) was introduced at a total flow rate of 100 cm^3 min^{-1} at 403 or 423 K and total pressure of 0.6 MPa. A trap cooled to dry ice–ethanol temperature (about 200 K) was placed between the reactor outlet and backpressure valve to condense the products, except for CO and CO_2. The condensates collected for 3 h were analyzed using an FID-GC (Shimadzu 8A) equipped with a Porapak QS glass column. A high-speed GC (Aera M200) was connected on-line to analyze CO and CO_2.

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3. Results and discussion

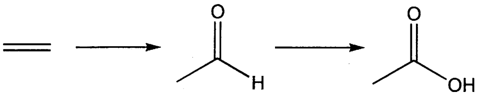
Table 1 shows the activity and selectivity for the oxidation of ethylene over 1.0wt%Pd/WO_3–ZrO_2 and 1.5wt%Pd–40wt%$H_4SiW_{12}O_{40}$/SiO_2. Changes in conversion and selectivity for the time on-stream were not significant and near stationary values were obtained after 3 h of reaction over both catalysts. As table 1 shows, the near stationary activity for 1.0wt%Pd/WO_3–ZrO_2 was approximately 2-fold greater than that for 1.5wt%Pd–40wt%$H_4SiW_{12}O_{40}$/SiO_2, when the space–time–yield (STY) in mol h^{-1} dm $^{-3}$ was employed. Furthermore, selectivity of 1.0wt%Pd/WO_3–ZrO_2 (73% toward acetic acid, 11% toward acetaldehyde) was greater than that of 1.5wt%Pd–40wt%H_4 $SiW_{12}O_{40}$/SiO_2 (52% toward acetic acid, 12% toward acetaldehyde). Notably, ethanol was formed at 5% selectivity over 1.5wt%Pd–40wt%$H_4SiW_{12}O_{40}$/SiO_2, while not detected over 1.0wt%Pd/WO_3–ZrO_2.

Figure 1 shows the dependence of contact time of ethylene conversion to each product over 1.0wt%Pd/WO_3–ZrO_2, when the reaction was conducted at 403 K. Ethanol was not detected under these reaction conditions, while CO_2 increased monotonously with contact time. As shown in figure 1, acetaldehyde was formed predominantly at the low range of contact time. However, the conversion to acetaldehyde decreased with high contact times. Instead of acetaldehyde, acetic acid appeared with an induction period; the conversion to acetic acid increased almost linearly with contact time. These results indicate that the oxidation of ethylene proceeds *via*consecutive reactions through an acetaldehyde intermediate.

Table 2 provides activities and selectivities for reactions related to the oxidation of ethylene over 1.0wt%Pd/WO_3–ZrO_2. For oxidation of acetaldehyde, ethanol, and acetic acid, the concentration of each reactant was adjusted to 1%. The result of hydration of ethylene over 1.0wt%Pd/WO_3–ZrO_2 in the absence of O_2 is also listed in table 2. The oxidation of acetic acid to CO_2 was negligible over this catalyst. Reaction rate for the oxidation of acetaldehyde was approximately 30 times greater than that for ethanol, while both reactants were oxidized to acetic acid with approximately 70% selectivity. As shown in figure 1 and table 1, ethanol was not detected over 1.0wt%Pd/WO_3–ZrO_2 under the reaction conditions, suggesting that the formation of acetic acid proceeds not through ethanol. Hydration of ethylene was very slow under these reaction conditions, compared to the formation of acetic acid from ethylene (table 2).

Figure 2 shows the effects of partial pressure of water on total reaction rate and STY of acetic acid and CO_2 over 1.0wt%Pd/WO_3–ZrO_2. The reaction was extremely slow at the low range of the partial pressure of water. An increase in the partial pressure of water enhanced reaction rate significantly, which indicates that the presence of water is indispensable, indicating that a Wacker-type oxidation operates.

On the basis of these results, we propose that the reaction for oxidation of ethylene to acetic acid over 1.0wt%Pd/WO_3–ZrO_2 occurs *via* acetaldehyde in a Wacker-type reaction, followed by the oxidation of acetaldehyde to acetic acid as shown in equation (1). Analogous to the Wacker reaction over a homogeneous $PdC1_2$ catalyst [11,12], the first step (ethylene → acetaldehyde) is assumed to involve redox of Pd between Pd^{2+} and Pd^0. In contrast, the second step (acetaldehyde oxidation) proceeds on the Pd metallic sites or the WO_3 sites in 1.0wt%Pd/$W0_3$–ZrO_2. WO_3–ZrO_2 (without Pd) was much less active in the oxidation of aldehyde under the reaction conditions, indicating that Pd metallic sites are responsible for the oxidation of acetaldehyde. These results suggest the existence of two types of Pd sites on Pd/WO_3–ZrO_2, Pd^{2+} (reducible to Pd^0) and metallic sites of Pd particle.


(1)

4. Conclusions

1.0wt%Pd/WO_3–ZrO_2 efficiently catalyzed the gas-phase oxidation of ethylene to acetic acid in the presence of water. The composition of the product depended heavily on the contact time of the reaction; acetaldehyde was formed predominantly at low contact times, and acetic acid was the main product at high contact times, while ethanol was not formed throughout the entire contact time range. The oxidation of acetaldehyde occurred more rapidly than the oxidation of ethanol or ethylene and the hydration of ethylene. The presence of

Table 1

Catalytic data for gas-phase oxidation of ethylene over Pd/WO_3–ZrO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2[a]

Catalyst	Conversion of ethylene/%	Selectivity[b]/%				STY of AcOH	
		AcOH	AcH	EtOH	CO_2	Per mol h^{-1} dm^{-3}	Per mol h^{-1} dm^{-3}
1.0wt%Pd/$W0_3$–ZrO_2[c]	2.9	73	11	0	16	1.35	0.87
1.5wt%Pd–40wt%$H_4SiW_{12}O_{40}$/SiO_2	2.0	52	12	5	31	0.63	0.82

[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.

[b] AcOH = acetic acid, AcH = acetaldehyde, EtOH = ethanol.

[c] WO_3–ZrO_2 (W/Zr = 0.2) was calcined at 1073 K before Pd loading.

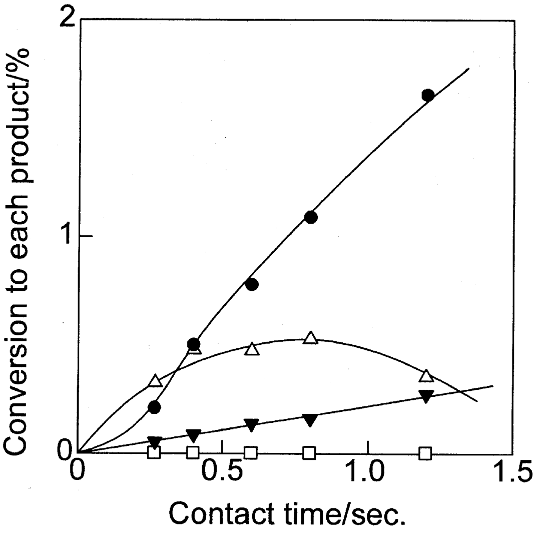


Figure 1. Contact time dependence of ethylene conversion to products over 1.0wt%Pd/WO_3–ZrO_2. (●) acetic acid, (△) acetaldehyde, (□) ethanol, and (▼) CO_2. Reaction conditions: C_2H_4:O_2:H_2O:He = 50:7:30:13, temperature 403 K, and pressure 0.6 MPa.

Table 2
Oxidation of various reactants and hydration of ethylene over Pd/WO_3–ZrO_2

Reaction	Reactant	Selectivity[a]/%				Reaction rate/μmol h^{-1} (g-cat)$^{-1}$
		AcOH	AcH	CO_2	MeOH	
Oxidation	Acetaldehyde[b]	82	–	14	3	
	Ethanol[b]	67	7	26	0	340
	Acetic acid[b]	–	0	100	0	5
	Ethylene[c]	68	6	26	0	1080
Hydration	ethylene[d]					12[e]

[a] Selectivity calculated on the basis of reactant. AcOH = acetic acid, AcH = acetaldehyde, and MeOH = methanol.
[b] Reaction conditions: reactant:O_2:H_2O:He = 1:7:30:62, temperature 423 K, and pressure 0.6 MPa
[c] Reaction conditions: C_2H_4:O_2:H_2O:He = 50:7:30:13, temperature 423 K, and pressure 0.6 MPa.
[d] Reaction conditions: C_2H_4:H_2O:He = 50:30:20, temperature 423 K, and pressure 0.6 MPa.
[e] Selectivity toward ethanol was 100%.

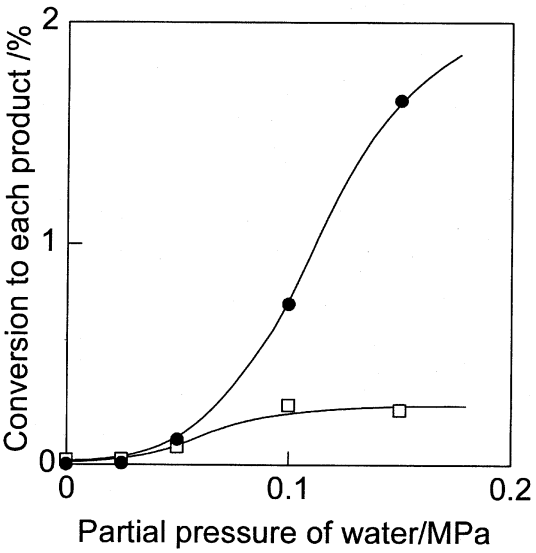


Figure 2. Effect of partial pressure of water on yield of acetic acid and CO_2 over 1.0wt%Pd/WO_3–ZrO_2. (●) yield of acetic acid; (□) yield of CO_2. Reaction conditions: C_2H_4:O_2:H_2O:He = 50:7:0–30:13–43, temperature 423 K, and total pressure 0.6 MPa.

water was indispensable for ethylene oxidation. These results demonstrate that ethylene oxidation proceeded *via* acetaldehyde as an intermediate formed by a Wacker-type reaction, not *via*ethanol formation by hydration of ethylene.

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