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Kinetic Studies on the Promotional Effect of Te in Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ for Direct Oxidation of Ethylene to Acetic Acid

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Abstract The role of Te in Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$, a highly active and selective catalyst for direct oxidation of ethylene to acetic acid, was investigated. Kinetic studies of ethylene oxidation over Pd–$H_4SiW_{12}O_{40}/SiO_2$ and Te-promoted Pd-$H_4SiW_{12}O_{40}/SiO_2$ demonstrated that doping with Te enhanced the rate of reaction of ethylene to acetaldehyde but reduced direct formation of CO_2 from ethylene. In contrast, the successive reaction of acetaldehyde to acetic acid was not influenced to a significant extent by the addition of Te.

Keywords Acetic acid · Kinetic study · Te · Heteropolyacid · Wacker-type reaction

1 Introduction

Approximately 8.3 million tons of acetic acid were used throughout the world in 2006, mainly as a solvent for the production of pure terephthalic acid and as a raw material for acetic anhydride, acetate, and vinyl acetate production. Methanol carbonylation, known as the Monsanto process [1, 2], the Hoechst–Wacker process (which produces acetaldehyde, which is then oxidized to acetic acid) [3, 4], and oxidation of butane in the presence of cobalt acetate [4] are the major industrial processes in which acetic acid is produced. These commercial processes are performed in the liquid phase using homogeneous catalysts, but have some disadvantages, such as difficulty in separating the catalyst from the product.

Gas-phase oxidation of ethylene over a catalyst consisting Pd and solid acid has recently attracted attention as a new and environmentally benign process that generates little waste due to its use of heterogeneous catalysis. In 1998, Showa Denko K.K. succeeded in developing the world's first commercial process employing this reaction [5–8]. The process involves a highly active and selective catalyst with the formula Pd–$H_4SiW_{12}O_{40}/SiO_2$. Its catalytic activity and selectivity in the formation of acetic acid are significantly enhanced by the addition of Te as a promoter [5]. In fact, Te-promoted Pd–$H_4SiW_{12}O_{40}/SiO_2$ is utilized as the main industrial catalyst [5]. However, the role played by Te in the catalyst is still unclear. Thus, we investigated the role of Te by conducting kinetic studies of ethylene oxidation over non-Te-promoted and Te-promoted Pd–$H_4SiW_{12}O_{40}/SiO_2$.

2 Experimental

Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ was prepared according to the patent literature [9]. First, Pd was supported on SiO_2 (Shanghai Haiyuan Chemical Industry Science and Technology Co., Ltd.; S.A. = 148 $m^2\,g^{-1}$) by an incipient wetness method using an aqueous acidic solution of Na_2PdCl_4 (N.E. Chemcat K.K.) in which Pd loading was adjusted to 1.5 wt%. The resulting solid was dispersed in an aqueous solution containing $Na_2SiO_3{\cdot}9H_2O$ (0.61 wt%

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Si, Wako Pure Chemical Industries, Ltd.) and Na_2TeO_3 (Te/Pd molar ratio 0.067, Wako Pure Chemical Industries, Ltd.), and stirred at room temperature for 20 h. To the resulting suspension, an appropriate amount of hydrazine monohydrate (Wako Pure Chemical Industries, Ltd.) was added, and this was allowed to stand for 4 h. After washing with running water for 40 h, the resulting Pd–Te/SiO_2 was dried in air at 373 K for 4 h. The supporting of 40 wt% $H_4SiW_{12}O_{40}$ on Pd–Te/SiO_2 was conducted by an incipient wetness method using an aqueous solution of $H_4SiW_{12}O_{40}$ (Nippon Inorganic Color and Chemical Co., Ltd.). Finally, the resulting solid was dried in air at 373 K for 4 h.

Pd–$H_4SiW_{12}O_{40}$/SiO_2 was prepared using a similar procedure to that for Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2, but without addition of Na_2TeO_3. In order to allow analysis by XPS analysis, Pd/SiO_2 and Pd–Te/SiO_2 were also prepared by a similar method, but without supporting $H_4SiW_{12}O_{40}$.

Oxidation of ethylene was performed in a fixed-bed flow reactor. The *W*/*F* dependencies, where *W* is the catalyst weight (g) and *F* the flow rate of ethylene (mol h^{-1}), were obtained by changing the catalyst weight from 0.25 to 5.0 g at a fixed total flow rate. The catalyst was pretreated under a H_2/He flow (H_2/He = 1, total flow rate 60 cm^3 min^{-1}) at 523 K for 1 h, and then cooled to 423 K under a He flow (30 cm^3 min^{-1}). Next, a mixture of the reactant gas (C_2H_4:O_2:H_2O:He = 50:7:30:13, vol%) was introduced at a total flow rate of 100 cm^3 min^{-1}, at a temperature of 423 K and a total pressure of 0.5 MPaG. A trap cooled to dry-ice-ethanol temperature (about 200 K) was placed between the reactor outlet and back-pressure valve to collect the products (acetic acid, acetaldehyde, and ethanol), which were analyzed using an FID-GC (Shimadzu 8A) equipped with a Porapak QS glass column. For CO and CO_2 analysis, a high-speed GC (Aera M200) was utilized.

The Pd dispersion was measured by a CO-pulse adsorption method using an automatic apparatus (R6015, Ohkura Riken Inc.) at room temperature. In order to calculate the dispersion, the CO/Pd stoichiometry was assumed to be 1:1. The catalyst (1.0 g) was placed into a cell (i.d. 6 mm) and then reduced under a H_2 flow at 313 K. After reduction, pulses of CO (1 cm^3) were intermittently introduced to the cell under a He flow until no further adsorption of CO on the catalyst was observed.

X-ray photoelectron spectroscopy (XPS) studies were then performed using an AXIS-NOVA (KRATOS) spectrometer with Mg Kα irradiation. In order to highlight the effect of Te, Pd–Te/SiO_2 with Te/Pd = 0.83 was used for XPS measurement.

3 Results and Discussion

Table 1 summarizes the activity and selectivity of Pd–$H_4SiW_{12}O_{40}$/SiO_2 and Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 catalysts in the oxidation of ethylene under the same reaction conditions. It is notable that the activity (conversion) for Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 was higher than that for Pd–$H_4SiW_{12}O_{40}$/SiO_2. Apart from the effect on activity, the addition of Te to Pd-$H_4SiW_{12}O_{40}$/SiO_2 caused a significant reduction in selectivity to CO_2. In fact, Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 was found to be a highly selective catalyst for the formation of products including acetic acid and acetaldehyde. The sum of the space-time yields (STY) of acetic acid and acetaldehyde over Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 was about 2.3 times greater than that for Pd–$H_4SiW_{12}O_{40}$/SiO_2.

Next, we investigated in detail, via a kinetic study, the cause of the different results obtained using Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2. Figure 1 shows the *W*/*F* dependencies of conversion for the oxidation of ethylene over Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2. The total reaction rates were estimated from the initial slope of the conversion. The reaction rate for Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 was 2.8 mol kg^{-1} h^{-1}, which was two times greater than that for Pd–$H_4SiW_{12}O_{40}$/SiO_2 (1.4 mol kg^{-1} h^{-1}), as shown in Table 2.

In Fig. 2, selectivity to acetic acid, acetaldehyde, and CO_2 are plotted as a function of ethylene conversion. It should be emphasized that selectivity to CO_2 was independent of conversion for both Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 and Pd–$H_4SiW_{12}O_{40}$/SiO_2, indicating that CO_2 was predominantly formed from ethylene, and its formation by consecutive reaction of intermediates such as acetaldehyde and acetic acid was negligible. When selectivity was extrapolated to 0% conversion, the selectivities to CO_2 were 5% and 23% for Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 and

Table 1 Catalytic performance of Pd–$H_4SiW_{12}O_{40}$/SiO_2 and Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 in gas-phase oxidation of ethylene to acetic acid[a]

Catalyst	Selectivity[b]/%				STY/mmol g^{-1} h^{-1}		
	AcOH	AcH	EtOH	CO_2	AcOH	AcH	Sum
Pd–$H_4SiW_{12}O_{40}$/SiO_2	49	29	5	17	0.76	0.44	1.2
Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2	52	41	1	6	1.8	1.4	3.2

[a] Reaction conditions: C_2H_4:O_2:H_2O:He = 50:7:30:13, W/F = 7.4 g h mol^{-1}, temperature 423 K, pressure 0.5 MPaG

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

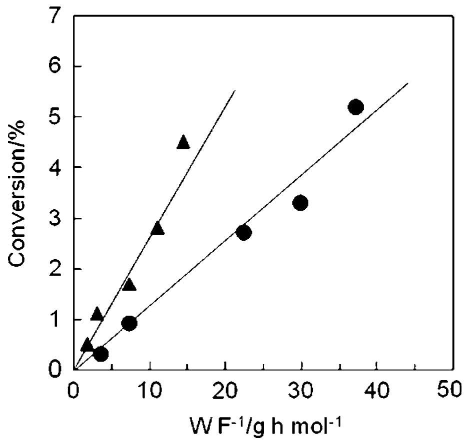


Fig. 1 *W/F* dependence of conversion of ethylene over Pd–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$. (●) Pd–$H_4SiW_{12}O_{40}/SiO_2$; (▲) Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$. Reaction conditions: gas composition, $C_2H_4:O_2:H_2O:He = 50:7:30:13$; total flow rate, 100 cm^3 min^{-1}; reaction temperature, 423 K; pressure, 0.50 MPaG

Pd–$H_4SiW_{12}O_{40}/SiO_2$, respectively (Table 2). Acetaldehyde was formed predominantly at low conversion, especially for Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$; however, selectivity to acetaldehyde decreased with increasing conversion, and selectivity to acetic acid increased. At conversion near 5%, acetic acid was main product for both catalysts.

In previous work, we demonstrated, based on the contact time dependency and the requirement for the presence of water in the reaction, that oxidation of ethylene to acetaldehyde over Pd/WO_3–ZrO_2 takes place via a Wacker-type reaction, with the acetaldehyde being further oxidized to acetic acid [10]. In light of the similarity between the current catalyst and Pd/WO_3–ZrO_2, it is likely that ethylene oxidation over Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ or Pd–$H_4SiW_{12}O_{40}/SiO_2$ proceeds via the same reaction pathway; that is, acetic acid is formed by a consecutive reaction with acetaldehyde as an intermediate. In addition, as mentioned above, CO_2 is predominantly formed directly from ethylene. Based on these findings, we propose a reaction pathway as shown in Scheme 1.

Table 2 Selectivity toward CO_2 and reaction rates for Pd–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$[a]

Catalyst	CO_2 selectivity[b]/%	Reaction rate/mmol g^{-1} h^{-1}		
		Total[c]	r_1[d]	r_3[e]
Pd–$H_4SiW_{12}O_{40}/SiO_2$	23	1.4	1.1	0.3
Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$	5	2.8	2.7	0.1

[a] Reaction conditions: $C_2H_4:O_2:H_2O:He = 50:7:30:13$, total flow rate 100 cm^3 min^{-1}, temperature 423 K, pressure 0.5 MPaG

[b] Selectivity to CO_2 at 0% conversion

[c] Calculated from the slope of *W/F* dependency of conversion of ethylene (Fig. 1)

[d] Reaction rate for oxidation of ethylene to acetaldehyde calculated from the total rate and selectivity to CO_2

[e] Reaction rate for oxidation of ethylene to CO_2 calculated from the total rate and selectivity to CO_2

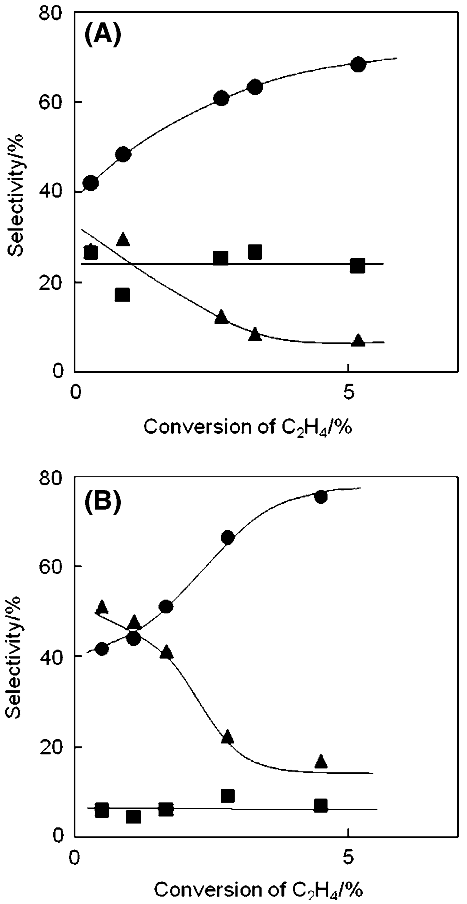
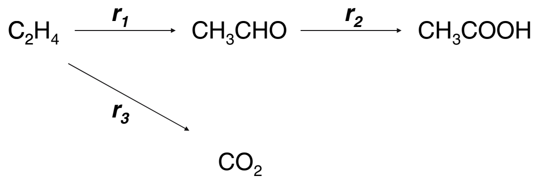


Fig. 2 Relationship between selectivity and conversion for (**A**) Pd-$H_4SiW_{12}O_{40}/SiO_2$ and (**B**) Pd-Te-$H_4SiW_{12}O_{40}/SiO_2$. (●) acetic acid; (▲) acetaldehyde; (■) CO_2

As shown in this scheme, the total rate is the sum of $\boldsymbol{r}_1$ (ethylene → acetaldehyde) and $\boldsymbol{r}_3$ (ethylene → CO_2). In addition, selectivity to CO_2 at 0% conversion is expressed as shown in Eq. 1.

$$\text{Selectivity to } CO_2(\%) = \frac{\boldsymbol{r}_3}{\boldsymbol{r}_1 + \boldsymbol{r}_3} \times 100 \quad (1)$$



Scheme 1 Reaction pathway for oxidation of ethylene over Pd–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$

Based on the total rate and the selectivity to CO_2 at 0% conversion, $\boldsymbol{r}_1$ and $\boldsymbol{r}_3$ for Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–$H_4SiW_{12}O_{40}/SiO_2$ can be calculated (Table 2). It is obvious from Table 2 that the addition of Te enhances $\boldsymbol{r_1}$ by a factor of about 2.5, but lowers $\boldsymbol{r_3}$ by about one third.

In order to estimate the contribution of Te to $\boldsymbol{r}_2$, we assumed that both reactions (ethylene → acetaldehyde and acetaldehyde → acetic acid) were first-order reactions. Thus, the yields of acetaldehyde and acetic acid can be written as follows:

$$Yield(CH_3CHO) = [C_2H_4]0\frac{k_1}{k_2 - k_1}(e^{-k_{1t}} - e^{-k_{2t}})$$

$$Yield(CH_3COOH) = [C_2H_4]0\left(1 - \frac{k_2e^{-k_{1t}} - k_1e^{-k_{2t}}}{k_2 - k_1}\right)$$

Here, $[C_2H_4]_0$ is the concentration of ethylene in the inlet of the reactor, k_1 and k_2 are the first-order reaction constants for the reactions ethylene → acetaldehyde and acetaldehyde → acetic acid, respectively, and t is the *W/F* value. As fitted to the catalytic data, k_2/k_1 ratios were optimized for Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–$H_4SiW_{12}O_{40}/SiO_2$. The calculated curves using the optimized k_2/k_1 are shown in Fig. 3, and the optimized k_2/k_1 ratios are listed in Table 3. It was found that the k_3/k_1 ratio for Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ was 2.5 times larger than that for Pd–$H_4SiW_{12}O_{40}/SiO_2$. However, based on the fact that the ratio $\boldsymbol{r}_1$(Te promoted)/$\boldsymbol{r}_1$(un-promoted) was 2.4, the ratio k_2(Te-promoted)/k_2(un-promoted) was estimated to be 1.1, indicating that addition of Te does not influence the reaction from acetaldehyde to acetic acid. To summarize these findings, the addition of Te to Pd–$H_4SiW_{12}O_{40}/SiO_2$ enhanced the reaction rate of ethylene to acetaldehyde, but reduced the rate of direct formation of CO_2 from ethylene. However, the successive reaction of acetaldehyde to acetic acid was not influenced to a significant extent by the addition of Te.

The next matter for investigation was the reason for enhancement of the reaction rate of ethylene to acetaldehyde by addition of Te. As mentioned above, ethylene is oxidized to acetaldehyde via a Wacker-type reaction, with reduction and oxidation of Pd. Therefore, we can consider two possible reasons for enhancement of the reaction rate by Te. The first is that the dispersion of Pd may be increased by addition of Te. However, CO-pulse adsorption measurements indicated that the dispersion of Pd on Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ was decreased somewhat compared with Pd–$H_4SiW_{12}O_{40}/SiO_2$ (9.2 and 10.0%, respectively). Therefore, the difference between the two catalysts cannot be explained in terms of Pd dispersion.

The second possible reason is that the redox ability of Pd is enhanced by the addition of Te. Comparing this reaction with Wacker oxidation using homogeneous $PdCl_2$–$CuCl_2$ catalyst [11, 12], it may be concluded that the re-oxidation of Pd^0 to Pd^{2+} is possibly a rate-determining step over Pd–$H_4SiW_{12}O_{40}/SiO_2$ as well as Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$. As demonstrated by XPS measurement (Fig. 4), Pd was oxidized to a much greater extent on Pd–Te/SiO_2 than on Pd/SiO_2, because in the Pd–Te/SiO_2 spectrum, the Pd 3d peak was shifted towards the higher-binding-energy side. This suggests that Pd was also oxidized to a greater extent on Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$ than on Pd-$H_4SiW_{12}O_{40}/SiO_2$. It

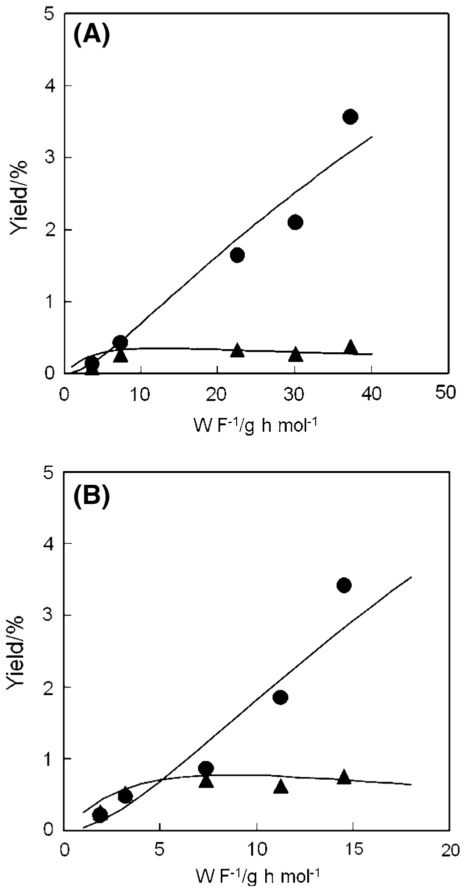


Fig. 3 Actual measured yields and calculated curves using optimized reaction constants for (**A**) Pd–$H_4SiW_{12}O_{40}/SiO_2$ and (**B**) Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$. Actual measured yields: (●) acetic acid; (▲) acetaldehyde. Solid lines are the curves calculated using the optimized reaction constants (k_2/k_1) shown in Table 3

Table 3 Reaction constants for ethylene oxidation over Pd–$H_4SiW_{12}O_{40}/SiO_2$ and Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$.[a]

Catalyst	Reaction constants		k_2/k_1
	k_1	k_2	
Pd–$H_4SiW_{12}O_{40}/SiO_2$	0.011	0.28	25
Pd–Te–$H_4SiW_{12}O_{40}/SiO_2$	0.030	0.30	10

[a] Reaction conditions: C_2H_4:O_2:H_2O:He = 50:7:30:13, total flow rate 100 cm^3 min^{-1}, temperature 423 K, pressure 0.5 MPaG

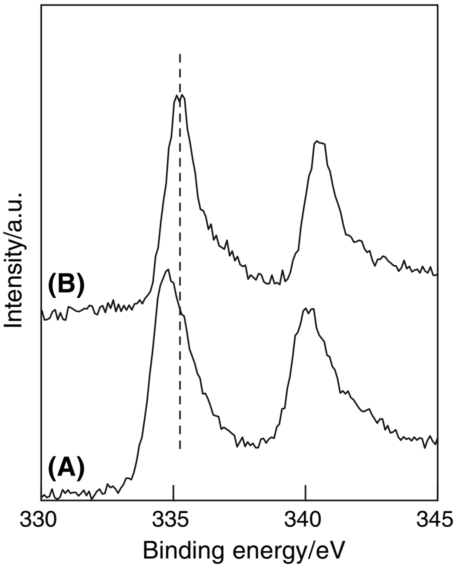


Fig. 4 XPS spectra of (**a**) Pd/SiO_2 and (**b**) Pd–Te/SiO_2 after pretreatment

appears that this is the reason for the high activity of Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2 in the conversion of ethylene to acetaldehyde.

4 Conclusion

In the gas-phase oxidation of ethylene to acetic acid in the presence of water, Te-promoted Pd–$H_4SiW_{12}O_{40}$/SiO_2 catalyst was found to be superior, in terms of activity and selectivity, to un-promoted Pd–$H_4SiW_{12}O_{40}$/SiO_2. Kinetic studies of ethylene oxidation over Te-promoted and un-promoted Pd–$H_4SiW_{12}O_{40}$/SiO_2 clearly demonstrated that the addition of Te enhanced the rate of reaction of ethylene to acetaldehyde, but reduced the rate of direct formation of CO_2 from ethylene. The subsequent reactions of acetaldehyde to acetic acid and to CO_2 were not significantly influenced by the addition of Te. It is thought that the reason for the high activity of the Te-promoted catalyst was increased redox ability of Pd in Pd–Te–$H_4SiW_{12}O_{40}$/SiO_2.

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