DOI: 10.1002/cctc.201600153

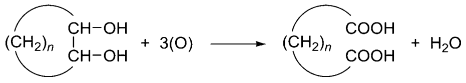
Oxidative Cleavage of Vicinal Diols with the Combination of Platinum and Vanadium Catalysts and Molecular Oxygen

Naoyuki Obara, Shota Hirasawa, Masazumi Tamura, Yoshinao Nakagawa,* and Keiichi Tomishige*[a]

The combination of Pt/C and V_2O_5 catalysts gave good performance for the oxidative cleavage of *trans*-1,2-cyclohexanediol into adipic acid via 2-hydroxycyclohexanone. The yield of adipic acid reached 90 % in the one-pot oxidative cleavage of *trans*-1,2-cyclohexanediol. The yield was higher than that obtained in the oxidation of 2-hydroxycyclohexanone with V catalyst, and the higher yield was due to the low 2-hydroxycyclohexanone concentration during the one-pot oxidation of *trans*-1,2-cyclohexanediol. Cyclic vicinal diols having a six-membered ring and linear vicinal diols having two secondary OH groups were converted into dicarboxylic acids and two carboxylic acids, respectively. The activity of the Pt catalyst decreased during the reaction, and the activity was partially restored by treating the used catalyst with H_2 at 573 K. Even without regeneration, the turnover number based on total Pt could reach ≈1000 in a long reaction with an increased amount of *trans*-1,2-cyclohexanediol.

Introduction

Oxidative cleavage of vicinal diols selectively dissociates one C–C bond in the substrate. In particular, oxidative cleavage of cyclic vicinal diols to the corresponding dicarboxylic acids proceeds without decrease in the length of the carbon chain (Scheme 1).



Scheme 1. Oxidative cleavage of cyclic vicinal diols to the corresponding dicarboxylic acid.

Oxidative cleavage of the C–C bonds of diols is also one of the methods to convert large compounds to smaller ones.[1] This reaction can be applied to biomass conversion, because biomass generally has many oxygen atoms, especially as hydroxy groups.[2] This reaction is traditionally performed with stoichiometric oxidants, such as lead tetraacetate, periodic acid and its salts.[1] However, these oxidants are expensive and their reactions result in the formation of toxic inorganic waste compounds. The use of a catalyst and a clean oxidant such as molecular oxygen is desired from the viewpoint of green and atom-economical chemistry.[3] A typical substrate is *trans*-1,2-cyclohexanediol (*trans*-1,2-CHD), and the target product is adipic acid, which is industrially one of the most important dicarboxylic acids.[4] Systems using molecular oxygen as an oxidant for oxidation of 1,2-CHD to adipic acid are limited (see the Supporting Information, Table S1).[5–10] Ru catalysts (e.g., ruthenium pyrochlore oxides, $A_{2+x}Ru_{2-x}O_{7-y}$ (A = Pb or Bi; $0<x<1$; $0<y\leq 0.5$)) were reported to be effective;[5,6] however, bases such as NaOH and KOH were necessary for high activity and the product was adipate instead of adipic acid. In addition, the turnover number (TON) of adipate formation was not very high (≤44; based on total Ru). To the best of our knowledge, high yields of free adipic acid in the oxidation of 1,2-CHD with O_2 have not been reported. On the other hand, good (≤90 %) yields of adipate or adipic acid have been reported for oxidation of 2-hydroxycyclohexanone (2-HCO) with P/Mo/V polyoxometalate catalysts and molecular oxygen.[11] It was hypothesized that the reaction begins with the formation of a catalytically active oxovanadium(V) species, and the oxidation reaction is catalyzed by the V^V/V^{IV} redox system.[11–13] Some vanadium compounds are also known as effective catalysts for oxidative cleavage of lignin model compounds.[14–20] In addition, it is well known that noble metal catalysts are active in alcohol oxidation with molecular oxygen,[21–25] and 2-HCO is the oxidation product of 1,2-CHD at one of the two OH groups. Various noble metal catalysts including conventional carbon-supported ones have been tested for alcohol oxidation. For example, propylene glycol oxidation to hydroxyacetone proceeds over conventional Pt/C and Pd/C catalysts.[26,27] Although typical systems including these[26,27] also use homogeneous bases such as NaOH or basic supports,[5,6,28–31] there are some reports showing that Pt catalysts have higher activity in the oxidative

---

[a] N. Obara, S. Hirasawa, Dr. M. Tamura, Dr. Y. Nakagawa,
Prof. Dr. K. Tomishige
Department of Applied Chemistry, School of Engineering
Tohoku University
6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579 (Japan)
E-mail: yoshinao@erec.che.tohoku.ac.jp
tomi@erec.che.tohoku.ac.jp

Supporting information for this article can be found under http://dx.doi.org/10.1002/cctc.201600153.

or oxidant-free dehydrogenation of alcohol than other noble metal catalysts in base-free conditions.[32,33] In this report, we conducted the one-pot oxidation of vicinal diols including 1,2-CHD to the corresponding carboxylic acids with the combination of Pt and V catalysts. Very high yields (83–92 %) of acids and high TON values were obtained in the oxidation of 1,2-CHD and linear diols.

Results and Discussion

First of all, various combinations of catalysts were tested for the oxidation of aqueous *trans*-1,2-CHD in a 190 mL stainless-steel autoclave with 0.3 MPa O_2 at 353 K (Table 1). The metal dispersion of catalysts is shown in the Supporting Information, Table S2. The HPLC charts of the standard materials (Figure S1 a) and typical reaction mixture (Figure S1 b) are also shown in the Supporting Information. The combination of Pt/C + V_2O_5 showed high selectivity for adipic acid (Table 1, entry 1). We found that *trans*-1,2-CHD was converted to 2-HCO over Pt/C alone, whereas *trans*-1,2-CHD was not converted over V_2O_5 alone (entries 2 and 3). Although some systems with V catalysts have been reported to be active in alcohol oxidation,[34–40] water is generally unfavorable as the solvent.[34–37] All the Pt/C + vanadium compound systems showed high selectivity (81–92 %) for adipic acid (entries 1 and 4–7), although the activity of Pt, which was reflected in the *trans*-1,2-CHD conversion, was more or less decreased by addition of vanadium compounds. The Pt/C + $NaVO_3$ system (entry 7) showed much lower activity than Pt/C + V_2O_5; however, when the pH value of the reaction mixture was adjusted by addition of H_2SO_4 to a similar value to that of the Pt/C + V_2O_5 system (pH 6–7), the system gave a similar performance to that of the Pt/C + V_2O_5 system (entries 1 and 8). The combinations of other noble metal catalysts and V_2O_5 gave much lower conversions of 1,2-CHD than in the case of Pt/C (entries 9–11). The low activity of Pd/C and Ru/C catalysts was in contrast to the reported high performance of Pd- and Ru-based catalysts in basic conditions.[5,6,28–31] The neutral or acidic conditions in this system can be related to the higher performance of Pt/C than other noble metal catalysts.[32,33] We selected the combination of Pt/C + V_2O_5 because of the simplicity and high performance.

When 2-HCO was used as the substrate, adipic acid was produced with the V_2O_5 catalyst (entry 12), similarly to previous studies.[11–13] Over Pt/C alone, both the conversion of 2-HCO and selectivity to adipic acid were very low (entry 13). These data suggest that the conversion of *trans*-1,2-CHD to adipic acid proceeded by Pt-catalyzed oxidative dehydrogenation of *trans*-1,2-CHD to 2-HCO and V-catalyzed oxidative cleavage of 2-HCO to adipic acid.

Although the conversion of 2-HCO with the V_2O_5 catalyst (entry 12) was ≈2 times higher than that of *trans*-1,2-CHD over Pt/C (entry 1), the rate ratio cannot explain the result that 2-HCO was hardly observed in the *trans*-1,2-CHD oxidation with Pt/C + V_2O_5 catalysts (< 1 % selectivity; entry 1). In addition, it should be noted that the adipic acid selectivity of 2-HCO oxidation (entry 12) was lower than that of *trans*-1,2-CHD oxidation with Pt/C + V_2O_5 (entry 1). More than twenty kinds of byproducts were formed in the 2-HCO oxidation (entry 12). According to the GC-MS spectra, most byproducts were oxygenates with C4 or C5 carbon chains, including esters. Then, we tested the effect of co-existing activated carbon in the oxidation of 2-HCO with a V catalyst. Addition of activated carbon to the V_2O_5 solution increased the activity in the oxidation of 2-HCO (entry 14). The high activity of V_2O_5 + C agrees with the absence of 2-HCO in the *trans*-1,2-CHD oxidation in the Pt/C + V_2O_5 system; that is, Pt/C-catalyzed oxidation of *trans*-1,2-CHD

Table 1. Oxidation of *trans*-1,2-CHD, 2-HCO, or adipic acid over various catalysts with molecular oxygen.

Entry	Substrate	Catalyst	Conversion [%]	Selectivity [%] Adipic acid	2-HCO	Glutaric acid	Succinic acid	CO_x	Others
1	*trans*-1,2-CHD	Pt/C + V_2O_5	40	92	< 1	2	< 1	1	4
2	*trans*-1,2-CHD	Pt/C	53	6	84	3	2	2	3
3	*trans*-1,2-CHD	V_2O_5	< 1	–	–	–	–	–	–
4	*trans*-1,2-CHD	Pt/C + VCl_3	22	88	< 1	3	< 1	4	5
5	*trans*-1,2-CHD	Pt/C + $VOSO_4{\cdot}6\,H_2O$	25	82	< 1	5	2	2	8
6	*trans*-1,2-CHD	Pt/C + NH_4VO_3	8	86	4	2	< 1	3	6
7	*trans*-1,2-CHD	Pt/C + $NaVO_3$	27	86	2	3	1	4	3
8	*trans*-1,2-CHD	Pt/C + $NaVO_3$ + H_2SO_4[a]	38	92	1	2	< 1	2	2
9	*trans*-1,2-CHD	Pd/C + V_2O_5	10	90	2	1	< 1	1	6
10	*trans*-1,2-CHD	Ru/C + V_2O_5	1[b]	≈70	< 1	< 1	< 1	< 1	≈30
11	*trans*-1,2-CHD	Rh/C + V_2O_5	< 1	–	–	–	–	–	–
12	2-HCO	V_2O_5	82	63	–	3	2	6	25
13	2-HCO	Pt/C	17	2	–	17	4	14	63
14	2-HCO	V_2O_5 + C[c]	98	62	–	3	2	6	27
15	2-HCO[d]	V_2O_5 + C[c]	> 99	82	–	2	2	5	8
16	2-HCO[e]	V_2O_5 + C[c]	> 99	84	–	1	2	5	7
17	2-HCO	none	< 1	–	–	–	–	–	–
18	adipic acid	Pt/C + V_2O_5	< 1	–	–	–	–	–	–

Reaction conditions: Substrate, 4.3 mmol; 5 wt % metal/C, 26 µmol or 0 µmol metal; vanadium compound, 110 µmol or 0 µmol V; water, 10 g; O_2, 0.3 MPa; 353 K; 4 h. CHD = Cyclohexanediol. HCO = Hydroxycyclohexanone. [a] H_2SO_4, 5 µmol; pH before the reaction, 6.8. [b] Selectivities in the entry are nominal ones as the low conversion precludes the obtained data from being comparable with other entries. [c] Activated carbon (Shirasagi FAC-10), 0.1 g. [d] 2-HCO, 2.2 mmol. [e] 2-HCO, 1.1 mmol.

to 2-HCO is much slower than the V_2O_5+C catalyzed oxidation of 2-HCO to adipic acid. However, the selectivity to adipic acid in entry 14 was still lower than the *trans*-1,2-CHD oxidation with Pt/C+V_2O_5. Then, we focused on the concentration of 2-HCO as it was kept extremely low in the one-pot reaction. In fact, the selectivity to adipic acid increased with decreasing 2-HCO concentration in the V_2O_5+C system (entries 14–16). We also conducted the reaction of 2-HCO over V_2O_5+C at short reaction times (see the Supporting Information, Table S3). The reaction can proceed without significant decrease in the rate under the conditions of lower 2-HCO concentration. The rate ratio of the Pt-catalyzed oxidation of *trans*-1,2-CHD (see the Supporting Information, Table S3, entry 5) to (V_2O_5+C)-catalyzed oxidation of 2-HCO was estimated to be around 4. Therefore, the key to high adipic acid selectivity is the low concentration of the 2-HCO intermediate during the one-pot conversion of *trans*-1,2-CHD to adipic acid because of the high reaction rate of 2-HCO oxidation.

The time course of the *trans*-1,2-CHD oxidation over Pt/C+V_2O_5 is shown in Figure 1. The numerical data are shown in the Supporting Information, Table S4. The reaction proceeded to some extent during the initial heating to the reaction temperature. The conversion reached higher than 99%, and 90% yield of adipic acid was obtained at 48 h. The selectivity to adipic acid remained at about 90% after 4 h. 2-HCO was detected at short reaction times, and it almost disappeared after 4 h. This behavior agreed with the idea that 2-HCO is the intermediate of adipic acid formation. The selectivities to glutaric acid and succinic acid as well as adipic acid hardly changed, indicating that the acids are stable under the reaction conditions. The low reactivity of adipic acid under the reaction conditions was also confirmed (Table 1, entry 18).

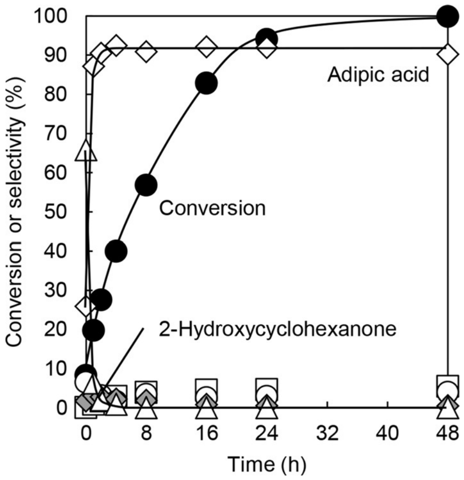


Figure 1. Time course of the *trans*-1,2-cyclohexanediol oxidation over Pt/C+V_2O_5. Conversion (●), selectivity to adipic acid (◇), 2-hydroxycyclohexanone (△), glutaric acid+succinic acid (□), CO+CO_2 (○), and others (◆). Reaction conditions: Substrate, 0.5 g (4.3 mmol); 5 wt% Pt/C, 0.1 g (26 μmol Pt); V_2O_5, 0.01 g (110 μmol V); water, 10 g; O_2, 0.3 MPa; 353 K. Numerical data are shown in Table S4 in the Supporting Information.

The Pt/C+V_2O_5 system was applied to various related substrates (Table 2). The data for shorter reaction times are shown in the Supporting Information, Table S5. Both *cis*- and *trans*-1,2-CHD were converted to adipic acid in good yields (83–90%; entries 1–3). Among the linear diols, 2,3-butanediol, 3,4-hexanediol, and *meso*-hydrobenzoin, which have two secondary OH groups, were converted to acetic acid, propionic acid, and benzoic acid, respectively, in good yields (≥84%; entries 4–6). Propylene glycol, which has one primary OH group and one secondary OH group, was converted to acetic acid and CO_2 (entry 7). The carbon-based yield of acetic acid (55%) corresponds to 83% of the theoretical value [(carbon number of acetic acid)/(carbon number of propylene glycol)=66.7%]. Sugar alcohols (ethylene glycol and glycerol) were almost completely converted to CO_2 (entries 8 and 9). For the substrates with primary OH group(s), formic acid was probably formed in the initial stage, and the formic acid would be rapidly oxidized to CO_2 over the Pt catalyst.[41] We confirmed that CO_2 was formed from formic acid under the reaction conditions (entry 10). Five-membered-ring diols are unsuitable substrates for this system. 1,2-Cyclopentanediols were converted to glutaric acid in lower yields (≤48%; entries 11 and 12). Large

Table 2. Oxidation of various substrates over Pt/C+V_2O_5.

Entry	Substrate	*t* [h]	Conversion [%]	Product (carbon-based selectivity [%])
1	*trans*-1,2-CHD	48	>99	adipic acid (90), glutaric acid (3), succinic acid (2), CO_2 (4), others (1)
2	*cis*-1,2-CHD	48	99	adipic acid (83), glutaric acid (4), succinic acid (4), CO_2 (7), others (1)
3	1,2-CHD (*cis*/*trans*-mixture, *cis*/*trans*=4:1)	48	>99	adipic acid (87), glutaric acid (3), succinic acid (3), CO_2 (5), others (1)
4	2,3-butanediol	24	>99	acetic acid (92), CO_2 (6), others (2)
5[a]	3,4-hexanediol	72	98	propionic acid (86), acetic acid (4), CO_2 (4), others (5)
6	*meso*-hydrobenzoin	48	>99	benzoic acid (92), benzaldehyde (3), CO_2 (4), others (2)
7	propylene glycol	4	>99	acetic acid (55), CO_2 (42), others (2)
8	ethylene glycol	4	>99	CO_2 (98), others (0.8)
9	glycerol	4	>99	CO_2 (98), others (1)
10	formic acid	4	>99	CO_2 (99), others (1)
11	*trans*-1,2-cyclopentanediol	48	>99	glutaric acid (35), succinic acid (28), CO_2 (28), others (7)
12	*cis*-1,2-cyclopentanediol	48	>99	glutaric acid (48), succinic acid (15), CO_2 (18), others (18)
13	1,4-anhydroerythritol	8	98	diglycolic acid (69), glycolic acid (0.7), CO_2 (28), others (3)

Reaction conditions: Substrate, 4.3 mmol; 5 wt% Pt/C, 0.1 g (26 μmol Pt); V_2O_5, 0.01 g (110 μmol V); water, 10 g; O_2, 0.3 MPa; 353 K. [a] 333 K. CHD=Cyclohexanediol.

amounts of smaller dicarboxylic acid (succinic acid) and CO_2 were formed than in the cases of 1,2-CHDs. The selectivity to glutaric acid was even lower at short reaction times (see the Supporting Information, Table S5, entries 8 and 9). When 1,2-cyclopentanediols were oxidized over the Pt/C catalyst alone, more than ten kinds of byproducts with a combined selectivity of $\geq 50\%$ were formed in addition to the corresponding α-ketol. The lower glutaric acid yield in Table 2, entries 11 and 12 was due to this low α-ketol selectivity in the Pt-catalyzed reaction. 1,4-Anhydroerythritol (*cis*-3,4-tetrahydrofurandiol) was converted to diglycolic acid and CO_2 in 69% and 28% yields, respectively (Table 2, entry 13). Unlike cyclopentanediols, at low conversion the selectivity to diglycolic acid was higher (89% at 69% conversion; see the Supporting Information, Table S5, entry 10).

The reuse experiment was conducted to see the stability of the catalyst (Figure 2). The used Pt/C with or without V_2O_5 was collected by filtration, dried in the air, and reused for another catalytic run. When Pt/C + V_2O_5 catalyst was reused without regeneration, the catalyst showed good selectivity to adipic acid (Figure 2A), although the selectivity to 2-HCO was a little increased. The amount of eluted metal into the reaction solution was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). ICP analysis of the filtrate showed that about half of the vanadium still remained in the solid catalyst in each run (the percentage of dissolved V: 45%→19%→9%, in the order of fresh, reuse 1, and reuse 2). It is indicated that the remaining vanadium species had enough catalytic activity to oxidize most of the 2-HCO. The leaching of dissolved Pt was very small (the percentage of dissolved Pt: 0.3%→0.1%→<0.1%, in the order of fresh, reuse 1, and reuse 2), however, the conversion of *trans*-1,2-CHD, which reflects the activity of Pt, was decreased in each reuse. Over Pt/C alone, the conversion was also decreased in each reuse (Figure 2B), which is similar to the case of Pt/C + V_2O_5, suggesting that Pt/C was deactivated. The XRD analyses (Figure 3) indicated that the Pt particle aggregation was not a cause of deactivation. Peaks for vanadium species were not observed in the XRD pattern of Pt/C + V_2O_5 after the catalytic use without reduction and replenishment with fresh V_2O_5 (Figure 3d), suggesting that the vanadium species in the recovered solid catalyst were highly dispersed or amorphous. Poisoning with CO or organic molecules can cause deactivation of the Pt catalyst. We tried to remove the adsorbed species by treating the used catalysts with a flow of hot H_2, as calcination treatments cannot be applied to this carbon-supported catalyst. Davis et al. reported the regeneration of Pt catalysts by reduction with H_2 at 473 K after use in the oxidation of alcohols.[42] We reused the Pt/C + V_2O_5 catalyst with H_2 treatment at 473 K before each reuse (Figure 2C). The activity of the catalyst was slightly recovered by H_2 treatment. The XRD analysis (Figure 3e) showed that the linewidth of Pt peaks was almost unchanged (4.8 nm to 5.4 nm). The adsorbed poisonous species was probably not removed. To complete the regeneration, we increased the H_2 treatment temperature

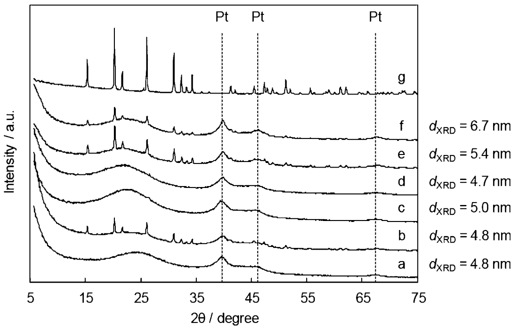


Figure 3. XRD patterns of Pt/C, Pt/C + V_2O_5, and V_2O_5. (a) Pt/C before the reaction, (b) Pt/C + V_2O_5 before the reaction (mixed with a Pt/V = 26:110 molar ratio) (c) Pt/C after the catalytic use three times (Figure 2B), (d) Pt/C + V_2O_5 after catalytic use three times (not reduced; Figure 2A), (e) Pt/C + V_2O_5 after catalytic use three times (reduced at 473 K before the catalytic use; Figure 2C), (f) Pt/C + V_2O_5 after catalytic use three times (reduced at 573 K before the catalytic use; Figure 2D), (g) V_2O_5 before the reaction. d_{XRD} was calculated by Scherrer's equation and the width of the Pt (111) peak at 39.2°.

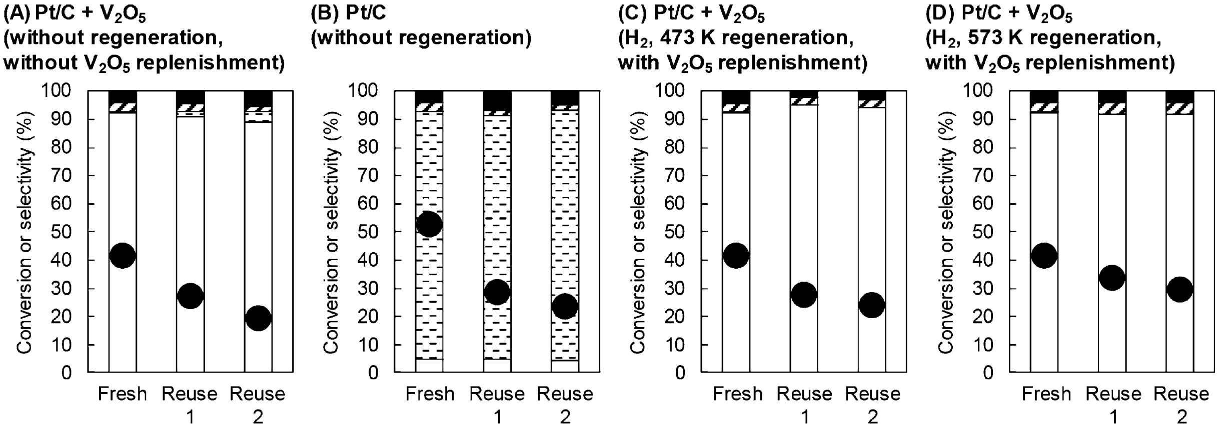


Figure 2. Reuse experiments of Pt/C + V_2O_5 or Pt/C. (A) Pt/C + V_2O_5 without regeneration and replenishment with fresh V_2O_5. (B) Pt/C without regeneration. (C) Pt/C + V_2O_5 with H_2 treatment at 473 K before each reuse. Reduction conditions: H_2 flow, 473 K, 2 h. Fresh V_2O_5 (4.5 mg) was added for each reuse. (D) Pt/C + V_2O_5 with H_2 treatment at 573 K before each reuse. Reduction conditions: H_2 flow, 573 K, 1 h. Fresh (4.5 mg) V_2O_5 was added for each reuse. Conversion (●), adipic acid (□), 2-hydroxycyclohexanone (▤), glutaric acid + succinic acid (▨), others (■). Reaction conditions: *trans*-1,2-Cyclohexanediol, 0.5 g (4.3 mmol); 5 wt% Pt/C, 0.1 g (26 μmol Pt); V_2O_5, 0.01 g (110 μmol V); water, 10 g; O_2, 0.3 MPa; 353 K; 4 h.

from 473 K to 573 K (Figure 2D). The activity of the used catalyst was much improved by treating at 573 K. However, the Pt particle size was significantly increased (Figure 3 f, 4.8 nm to 6.7 nm). The increase in Pt particle size can explain the remaining activity loss. Fine optimization of the reductive regeneration conditions may further improve the catalyst life.

We tested a long reaction with a larger substrate amount to evaluate the limit of the catalyst life without regeneration. In this experiment, higher O_2 pressure (0.3→2 MPa) and a higher reaction temperature (353→363 K) were applied to increase the reaction rate. The vanadium amount was decreased to try to increase the V-based turnover number. The results are shown in Figure 4 and the numerical data are shown in the Supporting Information, Table S6. The selectivity to adipic acid was low at short reaction times, however, it increased with decreasing selectivity to 2-HCO during the reaction's progress. The high selectivity to adipic acid (≈80%) was maintained after 24 h. Although the conversion was not completed at 168 h, the turnover number (TON) in adipic acid formation reached up to 920 (based on total Pt) and 1100 (based on total V). These values were approximately 20 times as large as the highest one in the literature for 1,2-CHD oxidation to adipic acid (see the Supporting Information, Table S1). Therefore, even without regeneration the catalyst can give much higher TON values for 1,2-CHD oxidation to adipic acid than literature systems. However, the selectivity to adipic acid was slightly lower than the case of the standard reaction conditions (Figure 1 and Table 2). One of the reasons could be the higher 2-HCO concentration caused by the small amount of solvent and V_2O_5 catalyst (Figure 4). We checked the dependence on the amount of V_2O_5 catalyst in the oxidation of *trans*-1,2-CHD under the same conditions as those used for Figure 4. In fact, increasing the V_2O_5 amount (2 mg→10 mg) increased the selectivity to adipic acid from 81% (at 24 h) to 85%, although the conversion was almost the same (data shown in the Supporting Information, Figure S2). Considering the lower cost of V than Pt, a higher V/Pt ratio such as 10 mg V_2O_5 with 0.1 g Pt/C is a better choice than 2 mg V_2O_5 from the view of organic synthesis. We carried out an activity test of the catalyst after the run for 168 h in Figure 4. The result showed that the catalyst after the run was almost totally deactivated (see the Supporting Information, Table S7, entry 2), indicating that the recycling procedure was not the cause of deactivation. The deactivation was significantly suppressed by treatment with flowing H_2 at 573 K (see the Supporting Information, Table S7, entry 3), as in the case of the reuse experiment of Pt/C+V_2O_5 under standard reaction conditions (Figure 2). These data agreed with the idea that the poisoned Pt surface was regenerated by the reductive heat treatment.

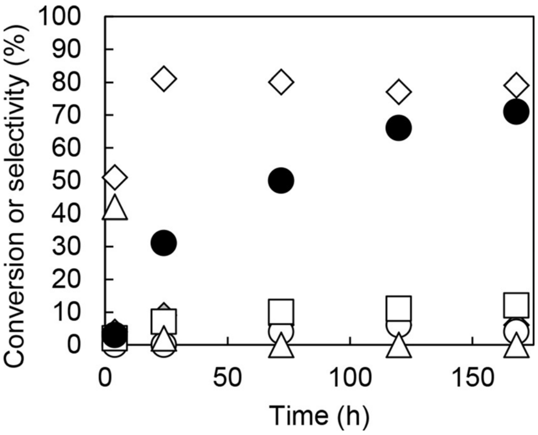


Figure 4. Time course of the *trans*-1,2-cyclohexanediol (*trans*-1,2-CHD) oxidation over Pt/C+V_2O_5 in the case of a large amount of substrate. Conversion (●), selectivity to adipic acid (◇), 2-hydroxycyclohexanone (△), glutaric acid+succinic acid (□), CO+CO_2 (○), and others (◆). Reaction conditions: *trans*-1,2-CHD, 6 g (52 mmol); 5 wt% Pt/C, 0.1 g (26 μmol Pt); V_2O_5, 2 mg (22 μmol V); water, 40 g; O_2, 2 MPa; 363 K.

Conclusions

Pt/C combined with V_2O_5 can selectively convert vicinal diols into the corresponding carboxylic acids with molecular oxygen. The yield of adipic acid from *trans*-1,2-cyclohexanediol reached 90% over Pt/C+V_2O_5. This value was higher than the yield obtained in the α-ketol (2-hydroxycyclohexanone) oxidation conducted separately. The turnover number for adipic acid formation based on total Pt can reach ≈1000. The Pt catalyst was gradually deactivated, and the activity was partially restored by treating the used Pt catalyst with H_2 at 573 K. The V-catalyzed α-ketol oxidation gave higher selectivity to carboxylic acids when the concentration of α-ketol was lower. The combination with Pt-catalyzed diol oxidation can keep the concentration of α-ketol low enough to obtain good selectivity to carboxylic acids. Linear vicinal diols having two secondary OH groups were converted into two carboxylic acids in good yields. For substrates with a primary group, CO_2 was formed instead of formic acid from the $-CH_2OH$ unit.

Experimental Section

Catalyst

Carbon-supported noble metal catalysts (5 wt% loading, metal dispersion is shown in the Supporting Information, Table S2) and V_2O_5 were purchased from Wako Pure Chemical Industries, Ltd. The vanadium compounds used were commercial V_2O_5, VCl_3, $VOSO_4{\cdot}n\,H_2O$ ($n=6$ as determined by thermogravimetric and differential thermal analysis (TG-DTA)), $NaVO_3$, and NH_4VO_3.

Activity tests

The oxidation of vicinal diols was performed in a 190 mL stainless-steel autoclave with an inserted glass vessel. The noble metal catalyst, vanadium compound, substrate, and water (solvent) were put into the autoclave together with a spinner. The pH was measured with a pH meter when necessary. After sealing, the reactor was filled with 0.3 MPa oxygen. The autoclave was then heated to 353 K, and the temperature was monitored by using a thermocouple inserted in the autoclave. The heating took about 20 min. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag. The autoclave contents were diluted with 2-propanol and transferred to a vial, while the catalyst was separated by filtration. The standard conditions for the reaction were as follows: 4.3 mmol *trans*-1,2-cyclohexanediol (substrate), 0.1 g carbon-supported Pt catalyst (26 μmol Pt), 0.01 g V_2O_5 (110 μmol V), 10 g water (solvent), 0.3 MPa initial oxygen pressure, 353 K reaction temperature, and 4 h reaction time. Under these conditions, the solubility limit of adipic acid in water at 293 K corresponds to 30% yield. For the runs with higher adipic acid yield, crystalline adipic acid was formed, and dilution is essential for correct analysis. Details of the reaction conditions are described for each result. Analyses were conducted by means of FID-GC, GC-MS, and HPLC. The FID-GC (Shimadzu GC-2014) for analysis of liquids and GC-MS (Shimadzu GCMS-QP2010 Ultra) were equipped with a CP-Sil 5 CB or HP-FFAP capillary column. They were mainly used when the linear vicinal diols were used as substrates. A Porapak N packed column and a methanator were used for the separation of products in the gas phase such as CO_2, CO, and CH_4. The HPLC (Shimadzu Prominence) was equipped with a UV/Vis detector (wavelength 210 nm), refractive index detector, and an Aminex HPX-87H column (Bio-Rad). Diluted H_2SO_4 (0.01 M) was employed as eluent. The HPLC charts of the standard materials (Figure S1 a) and a typical reaction mixture (Figure S1 b) are shown in the Supporting Information. HPLC analysis was used when cyclic vicinal diols were used as substrates. The conversion and the selectivity were calculated based on carbon and defined as follows: Conversion (%) = {(mol of consumed substrate)/(mol of substrate)} × 100. Selectivity (%) = [{(mol of product) × (number of carbon atoms in a product molecule)}/{(mol of consumed substrate) × (number of carbon atoms in a substrate molecule)}] × 100. Turnover number (TON) was calculated by the following equation for each metal (Pt or V): TON = (mol of adipic acid)/(mol of metal). The carbon balance was also confirmed for each result, and the difference in the carbon balance was always in the range of 100 ± 10% unless noted. The amount of metal eluted into the reaction solution was analyzed by ICP-OES (Thermo Fisher Scientific Inc., iCAP6500). Cold water was used as the washing solvent instead of 2-propanol for the reuse experiments and determination of eluted metal. In the reuse experiments, the adipic acid yield was not very high in comparison with the solubility limit of adipic acid, and washing with water can totally dissolve the formed adipic acid. Metal dissolution was calculated as follows: Metal dissolution (%) = (mol of metal in the recovered reaction solution)/(mol of metal initially put into the autoclave).

Catalyst characterization

X-ray diffraction (XRD) patterns were measured by using a Rigaku MiniFlex600 diffractometer. $Cu_{K\alpha}$ ($\lambda = 0.154$ nm, 40 kV, 15 mA) radiation was used as an X-ray source. The particle size on Pt/C was calculated by the Scherrer's equation.[43] The amount of CO chemisorption was measured in a high-vacuum system by using a volumetric method. Before adsorption measurements, the catalysts were treated with H_2 at 373 K for 1 h. Subsequently, the adsorption was performed at room temperature. The gas pressure at adsorption equilibrium was about 1.2 kPa. The sample weight was about 0.1 g. The dead volume of the apparatus was about 60 cm^3. The adsorption amount of CO is represented as the molar ratio to the amount of noble metal.

Acknowledgments

Part of this work is supported by the JSPS KAKENHI "Grant-in-Aid for Scientific Research (C)" (10436545).

Keywords: molecular oxygen · oxidative cleavage · platinum · vanadium · vicinal diols

[1] T. K. M. Shing in *Comprehensive Organic Synthesis Vol. 7* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1993**, pp. 703.
[2] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411 – 2502.
[3] P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson, *Catal. Today* **2000**, *55*, 11 – 22.
[4] S. Van de Vyver, Y. Román-Leshkov, *Catal. Sci. Technol.* **2013**, *3*, 1465 – 1479.
[5] a) T. R. Felthouse, P. B. Fraundorf, R. M. Friedman, C. L. Schosser, *J. Catal.* **1991**, *127*, 393 – 420; b) T. R. Felthouse, *J. Am. Chem. Soc.* **1987**, *109*, 7566 – 7568.
[6] S. J. H. F. Arts, F. van Rantwijk, R. A. Sheldon, *J. Carbohydr. Chem.* **1996**, *15*, 317 – 329.
[7] J.-M. Brégeault, B. ElAli, J. Mercier, J. Martin, C. Martin, *C. R. Acad. Sci. Ser. II* **1989**, *309*, 459 – 462.
[8] E. Takezawa, S. Sakaguchi, Y. Ishii, *Org. Lett.* **1999**, *1*, 713 – 715.
[9] T. Iwahama, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2000**, *65*, 6502 – 6507.
[10] E. Rozhko, K. Raabova, F. Macchia, A. Malmusi, P. Righi, P. Accorinti, S. Alini, P. Babini, G. Cerrato, M. Manzoli, F. Cavani, *ChemCatChem* **2013**, *5*, 1998 – 2008.
[11] M. Vennat, P. Herson, J.-M. Brégeault, G. B. Shul'pin, *Eur. J. Inorg. Chem.* **2003**, 908 – 917.
[12] J.-M. Brégeault, *Dalton Trans.* **2003**, 3289 – 3302.
[13] J.-M. Brégeault, M. Vennat, L. Salles, J.-Y. Piquemal, Y. Mahha, E. Briot, P. C. Bakala, A. Atlamsani, R. Thouvenot, *J. Mol. Catal. A* **2006**, *250*, 177 – 189.
[14] I. A. Weinstock, E. M. G. Barbuzzi, M. W. Wemple, J. J. Cowan, R. S. Reiner, D. M. Sonnen, R. A. Heintz, J. S. Bond, C. L. Hill, *Nature* **2001**, *414*, 191 – 195.
[15] S. K. Hanson, R. T. Baker, J. C. Gordon, B. L. Scott, D. L. Thorn, *Inorg. Chem.* **2010**, *49*, 5611 – 5618.
[16] S. Son, F. D. Toste, *Angew. Chem. Int. Ed.* **2010**, *49*, 3791 – 3794; *Angew. Chem.* **2010**, *122*, 3879 – 3882.
[17] B. Sedai, C. Díaz-Urrutia, R. T. Baker, R. Wu, L. A. Silks, S. K. Hanson, *ACS Catal.* **2011**, *1*, 794 – 804.
[18] S. K. Hanson, R. Wu, L. A. Silks, *Angew. Chem. Int. Ed.* **2012**, *51*, 3410 – 3413; *Angew. Chem.* **2012**, *124*, 3466 – 3469.
[19] R. Ma, Y. Xu, X. Zhang, *ChemSusChem* **2015**, *8*, 24 – 51.
[20] J. Mottweiler, M. Puche, C. Räuber, T. Schmidt, P. Concepción, A. Corma, C. Bolm, *ChemSusChem* **2015**, *8*, 2106 – 2113.
[21] T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037 – 3058.
[22] T. Mallat, A. Baiker, *Catal. Today* **1994**, *19*, 247 – 284.
[23] P. Gallezot, *Catal. Today* **1997**, *37*, 405 – 418.
[24] M. Besson, P. Gallezot, *Catal. Today* **2000**, *57*, 127 – 141.
[25] C. Parmeggiani, F. Cardona, *Green Chem.* **2012**, *14*, 547 – 564.
[26] L. Prati, M. Rossi, *J. Catal.* **1998**, *176*, 552 – 560.
[27] H. H. C. M. Pinxt, B. F. M. Kuster, G. B. Marin, *Appl. Catal. A* **2000**, *191*, 45 – 54.
[28] G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636 – 1639.
[29] K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2002**, *41*, 4538 – 4542; *Angew. Chem.* **2002**, *114*, 4720 – 4724.
[30] Y. Uozumi, R. Nakao, *Angew. Chem. Int. Ed.* **2003**, *42*, 194 – 197; *Angew. Chem.* **2003**, *115*, 204 – 207.
[31] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657 – 10666.
[32] T. Wang, H. Shou, Y. Kou, H. Liu, *Green Chem.* **2009**, *11*, 562 – 568.
[33] K. Kon, S. M. A. H. Siddiki, K. Shimizu, *J. Catal.* **2013**, *304*, 63 – 71.
[34] S. Velusamy, T. Punniyamurthy, *Org. Lett.* **2004**, *6*, 217 – 219.

[35] Z. Du, J. Ma, H. Ma, M. Wang, Y. Huang, J. Xu, *Catal. Commun.* **2010**, *11*, 732–735.
[36] A. Dewan, T. Sarma, U. Bora, D. K. Kakati, *Tetrahedron Lett.* **2011**, *52*, 2563–2565.
[37] G. Sarmah, S. K. Bharadwaj, A. Dewan, A. Gogoi, U. Bora, *Tetrahedron Lett.* **2014**, *55*, 5029–5032.
[38] M. Kirihara, Y. Ochiai, S. Takizawa, H. Takahata, H. Nemoto, *Chem. Commun.* **1999**, 1387–1388.
[39] Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, T. Kawamura, S. Uemura, *J. Org. Chem.* **2002**, *67*, 6718–6724.
[40] N. Jiang, A. J. Ragauskas, *J. Org. Chem.* **2007**, *72*, 7030–7033.
[41] J. M. A. Harmsen, L. Jelemensky, P. J. M. Van Andel-Scheffer, B. F. M. Kuster, G. B. Marin, *Appl. Catal. A* **1997**, *165*, 499–509.
[42] M. S. Ide, D. D. Falcone, R. J. Davis, *J. Catal.* **2014**, *311*, 295–305.
[43] Z. Hu, H. Nakamura, K. Kunimori, H. Asano, T. Uchijima, *J. Catal.* **1988**, *112*, 478–488.

Received: February 8, 2016