Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: Oxidative C-C Cleavage of Ketols over Vanadium-Carbon Catalysts

Authors: Yoshinao Nakagawa, Dai Sekine, Naoyuki Obara, Masazumi Tamura, and Keiichi Tomishige

To be cited as: *ChemCatChem* 10.1002/cctc.201700566

Link to VoR: http://dx.doi.org/10.1002/cctc.201700566

A Journal of
ChemPubSoc Europe

WILEY-VCH www.chemcatchem.org

Oxidative C-C Cleavage of Ketols over Vanadium-Carbon Catalysts

Yoshinao Nakagawa,*[a,b] Dai Sekine,[a] Naoyuki Obara,[a] Masazumi Tamura,[a,b] Keiichi Tomishige*[a,b]

[a] Dr. Y. Nakagawa, D. Sekine, N. Obara, Dr. M. Tamura and Prof. K. Tomishige: Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

[b] Dr. Y. Nakagawa, Dr. M. Tamura and Prof. K. Tomishige: Research Center for Rare Metal and Green Innovation, Tohoku University, 468-1, Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan

*Corresponding author: Yoshinao Nakagawa and Keiichi Tomishige

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

Abstract

Oxidation of 2-hydroxycyclohexanone and carbohydrates to adipic acid and formic acid, respectively, was carried out with combination of vanadium catalyst, carbon as co-catalyst and molecular oxygen in water under mild conditions (353 K, 0.1-0.3 MPa). The catalytic activity of aqueous V_2O_5 was significantly increased by addition of activated carbon (C), while addition of carbon black, graphene oxide and carbon nanotube has much smaller effect. The UV-vis and ICP analyses showed that most vanadium(V) species is adsorbed on C at least at short reaction time. Vanadium(IV) species (VO^{2+}) was not adsorbed on C. The order of activity of vanadium species was vanadium(V) on C > dissolved free vanadium(V) >> dissolved free vanadium(IV). In order to help oxidation of vanadium(IV), further addition of phosphomolybdate ($PMo_{12}O_{40}^{3-}$; PMo) was also tested, and the activity was actually improved. The selectivity and yield of adipic acid from 2-hydroxycyclohexanone was also slightly improved by addition of PMo. However, in the oxidation of glucose, the addition of PMo did not improve the final formic acid yield. Oxidation of glucose with vanadium + C system gave 42% yield of formic acid, which was comparable to the values reported with more expensive P-V-Mo polyoxometalate catalyst. A reaction mechanism is proposed where reversibly formed “biradical” state of vanadium-ketol complex reacts with molecular oxygen, and accompanying rearrangement dissociates the C-C bond.

Keywords

Vanadium; oxidation; carboxylic acid; activated carbon

1. Introduction

Selective oxidative C-C cleavage of poly-functionalized compounds to aldehydes or carboxylic acids attracts growing interest, especially in the research area of biomass conversions.[1-3] Oxidative C-C cleavage of vicinal diols or ketols (hydroxyketones) is typically performed with stoichiometric oxidants such as lead tetraacetate and periodates.[1,4,5] Because of the non-green nature of such oxidants, catalytic systems using molecular oxygen as an oxidant have been searched. Typical catalysts for oxidative C-C cleavage with molecular oxygen are ruthenium-,[6-10] manganese-,[11] copper,[12-14] and vanadium-based ones.[10,13,15-22] Ruthenium and manganese catalysts can convert aromatic vicinal diol to aldehydes in good yields, and they are less effective for aliphatic substrates, especially in neutral or acidic conditions. Substrates for Cu-catalyzed C-C oxidation are also aromatic compounds, typically those with benzoyl group. On the other hand, homogeneous vanadium catalysts are active in oxidative C-C cleavage of aliphatic ketols such as 2-hydroxycyclohexanone[10,15,16] and sugars[17-22] to adipic acid and formic acid, respectively (Scheme 1). As related systems, oxidations of catechols[23,24] and lignin-model compounds[25-28] with homogeneous vanadium catalysts have been also intensively investigated. The most investigated vanadium-based catalyst in oxidative C-C cleavage of ketols is Keggin-type polyoxometalate, $H_{3+n}PV_nMo_{12-n}O_{40}$ (denoted as PVMo).[10,15a,16-18,20,22,29,30] PVMo polyoxometalates are redox-active: vanadium(V) in PVMo is easily reduced to tetravalent, and the vanadium(IV) in reduced PVMo is easily re-oxidized by molecular oxygen.[31] On the other hand, oxidation of simple dissolved vanadium(IV) species such as VO^{2+} to vanadium(V) is slow with molecular oxygen. The reactivity of reduced PVMo with molecular oxygen enables PVMo to be good oxidation catalysts in various reactions.[31,32] However, aqueous solution of PVMo is a mixture of polyoxometalates with different V/Mo ratio and monomeric metal-oxo species in equilibrium.[31] Because of the variety of vanadium species in PVMo solution, the amount of active vanadium species at one time should be much lower than the total vanadium amount in the system, and there can be vanadium catalysts with more activity. Very recently, we have developed a catalytic system with combination of Pt/C + V_2O_5 solution for oxidation of vicinal diols to two carboxylic acids.[33] Platinum works as the oxidation catalyst for vicinal diols to ketols, and vanadium works as the oxidation catalyst for ketols to carboxylic acids. During this research, we found that the catalytic activity of vanadium in the latter reaction is enhanced by the presence of carbon, which has been added to the system as a support of Pt. However, in that paper[33] we did not further investigate the effect of carbon because the ketol oxidation is not the rate-determining step in vicinal diol oxidation to carboxylic acids. In this study, we focus on the vanadium-catalyzed ketol oxidation, which itself is a valuable reaction, in the presence of carbon. We found that pentavalent vanadium species adsorbed on the activated carbon have high activity. The effect of further addition of polyoxometalate salt to vanadium-carbon system has been also evaluated.

2. Results and discussion

2.1. Effect of carbon on vanadium-catalyzed oxidation of 2-hydroxycyclohexanone

Oxidation of 2-hydroxycyclohexanone to adipic acid (AA) was selected as a model reaction, since this substrate has been one of the most tested ones for ketol oxidation.[10,15,16] In addition, the product, adipic acid, has high importance in chemical industry.[34] The results of 2-hydroxycyclohexanone oxidation with V_2O_5 catalyst and various carbon additives are shown in Table 1. The amount of V_2O_5 (<0.01 g/ 10 mL) was below the solubility in water solvent (0.8 g/ 100 mL at 293 K, according to the safety data sheet by the supplier); no V_2O_5 powder was left in the reaction media of all runs. V_2O_5 solution has some catalytic ability (Table 1, entry 2). The addition of activated carbon (FAC-10 and

Carboraffin) increases the catalytic activity (entries 3 and 4), and FAC-10 showed the best promotional effect. On the other hand, carbon black (XC-72), graphene oxide (entry 6) and carbon nanotube (entry 7) have almost no promotional effect. It is well known that activated carbon have various types of functional groups such as carboxylic acids, phenols, ketones and so on. On the other hand, typical functional groups in graphene oxide are alcoholic OH and epoxide.[35] Carbon black has smaller amount of oxygen-containing functional groups and carbon nanotubes have very few functional groups. Functional groups which are not major in graphene oxide such as phenolic OH and aromatic carboxyl may be the ligands for active vanadium species. Without V_2O_5, the carbon materials hardly enhanced the formation rate of adipic acid (entries 8-12), indicating that vanadium is essential in the catalysis. Activated carbon FAC-10 was selected as the additive in the following studies because of the highest promotional effect.

The selectivity to adipic acid with V_2O_5 + carbon (FAC-10) catalysts (63%) was not higher than V_2O_5 alone catalyst system (80%) in Table 1. However, at higher conversion level the selectivity of V_2O_5 alone catalyst system was decreased and the selectivity order was reversed, as discussed later. The main by-products in Table 1 were glutaric acid (C5 dicarboxylic acid; GA), CO_2 and several unidentified compounds detected by RID-HPLC. Succinic acid (C4 dicarboxylic acid; SA) was sometimes produced; however the formation was negligible in the case of V_2O_5 + FAC-10 catalyst system.

Next, the effect of pH value was checked (Table 2). Carbon materials with many functional groups have some acidity and make buffer solution when they are added to water. It is well known that the structure of vanadium(V) species much depends on the pH value.[36] The purpose of this experiment is to check whether the promotional effect by carbon addition is only due to the pH control or not. The aqueous V_2O_5 solution had a pH value of 3.7 (Table 2, entry 1), and the value was increased to

5.0 when carbon (FAC-10) was added (entry 2). When NaOH was added to V_2O_5 solution to control similar pH value of V_2O_5 + carbon system (entry 3), the change of activity was much smaller than the case of carbon addition. Conversely, when H_2SO_4 was added to the V_2O_5 + C system to decrease the pH values (entries 4 and 5), the reaction rate was almost unchanged, although the selectivity to adipic acid was slightly decreased. These data show that the addition of carbon has more effect than pH control.

The catalytic performance of V_2O_5 + C was further compared with that of $H_5PV_2Mo_{10}O_{40}$, which is a typical PVMo polyoxometalate (Table 2, entry 6). While the conversion rate was similar between $H_5PV_2Mo_{10}O_{40}$ and V_2O_5 + C catalysts, the selectivity to adipic acid was very low (34%) with $H_5PV_2Mo_{10}O_{40}$. Low selectivity (<35%) to adipic acid from aqueous 2-hydroxycyclohexanone with PVMo catalyst has been also reported in the literature.[10] The V_2O_5 + C catalyst system is superior to PVMo catalyst for simple ketol in water solvent, while in methanol solvent PVMo catalyst has been reported to give good selectivity to dimethyl adipate.[15a,16]

2.2. The state of vanadium during the reaction

The state of vanadium species during the reaction was investigated. As a preliminary experiment, hot filtration at 353 K and ICP-OES analysis of the filtrate was conducted for the mixture of V_2O_5 + C + water (2 mg + 20 mg + 10 g) system. It has been known that main species of acidic aqueous V_2O_5 solution are decavanadate ($V_{10}O_{28}^{6-}$) and VO_2^+, both of which have yellow~orange color.[36] The yellow color of dissolved vanadium(V) almost disappeared by carbon addition and filtration, and only 3% of vanadium was dissolved in the filtrate. Then we determined the state of vanadium in the reaction mixture for 2-hydroxycyclohexanone oxidation after hot filtration. In order to conduct the hot filtration, the reaction was carried out in a test tube under 0.1 MPa O_2. The results were summarized in Table 3. The reaction time was set as 10 and 60 min, and for all cases (V_2O_5, $V^{IV}OSO_4$ and V_2O_5 + C catalysts) the conversion at 60 min was higher than that at 10 min, indicating that the catalyst was active at least at 10 min. In the case of V_2O_5 alone system with low activity (Table 3, entries 1 and 2), the amount of dissolved vanadium(V) species was gradually decreased, and the amount of dissolved vanadium(IV) species increased. In addition, significant amount of black solid was formed which probably contained the rest of vanadium species. However, significant amount of dissolved vanadium(V) species was still present at 10 min (34% of initial amount), indicating that dissolved vanadium(V) species as well as the black solid have low activity. In the case of $VOSO_4$ (entries 3 and 4), most vanadium(IV) species remained in the homogeneous phase during the reaction. The activity of $VOSO_4$ was even lower than that of V_2O_5. In the cases of V_2O_5 + C systems with higher activity (entries 5-7), vanadium was present as adsorbed species on carbon support and homogeneous (dissolved) vanadium(IV) species. The combination of vanadium(IV) species + C (entry 9) gave lower activity than V_2O_5 + C, and the most vanadium species was dissolved vanadium(IV) with very low activity. The activity of vanadium(IV) species + C (entry 8) can be explained by the small amount of carbon-adsorbed vanadium(V) species produced by oxidation of vanadium(IV), since dissolved vanadium(IV) was indeed decreased during the reaction (entries 8 and 9). Based on these results, we concluded that adsorbed vanadium(V) species on activated carbon have much higher activity in ketol oxidation than homogeneous (dissolved) vanadium(V) and vanadium(IV) species.

Yao Fu et al. and Ye Wang et al. reported that $VOSO_4$ has good activity in sugar oxidation to formic acid;[18,19] however, the oxygen pressure was much higher (2 MPa) than our case (0.1-0.3 MPa), and the vanadium(IV) species can be readily oxidized in the literature systems.

10.1002/cctc.201700566

2.3. Effect of addition of polyoxometalate

As described in the previous section, formation of vanadium(IV) species will decrease the catalytic activity. To assist the oxidation of vanadium(IV) species to vanadium(V), we conducted the reaction tests with addition of polyoxometalate (phosphomolybdate), although the system became more complex due to the complexity and the reactions of polyoxomealate. As well as acid-type phosphomolybdate ($H_3PMo_{12}O_{40}$; HPMo), cesium phosphomolybdate ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$; CsPMo) was used because of the low solubility in water and large surface area of cesium phosphomolybdate.[32,37] The reaction results are summarized in Table 4. The addition of CsPMo or HPMo slightly increases the activity of V_2O_5 + C system (entries 3, 5 and 6), and the selectivity to adipic acid was also increased. The promotional effect of CsPMo was larger than that of HPMo. Without carbon, the addition of CsPMo or HPMo also increased the activity of V_2O_5; however, the order was opposite: V_2O_5 + HPMo system has higher activity than V_2O_5 + CsPMo (entries 7 and 8). It is well known that dissolved vanadium(V) and phosphomolybdate quickly react each other to form phophomolybdovanadates (PVMo),[31] and the activity increase can be explained by the formation of PVMo with higher activity than V_2O_5 (cf. Table 2). In V_2O_5 + C + HPMo system, the formation of PVMo in homogeneous phase may decrease the amount of carbon-adsorbed vanadium(V) species, limiting the promotional effect of phosphomolybdate addition (Table 4, entries 3 and 6; conversion +7%) in comparison with that of CsPMo addition (entries 3 and 5; conversion +11%) and that of HPMo addition to carbon-free system (entries 2 and 8; conversion +14%). The homogeneous phase after the reaction showed yellow color which is indicative of fully oxidized vanadium and/or polyoxometalate species for all entries 5-8, and the UV-Vis spectrum has negligible band for vanadium(IV) species (Figure S2). However, significant amount of vanadium species was still present in the homogeneous phase after the reactions with V_2O_5 + C + CsPMo or HPMo (entries 5 and 6). At higher conversion level, some products may coordinate the vanadium species and desorb the vanadium(V) from carbon surface. In addition, vanadium-containing polyoxometalates produced by the reaction of phosphomolybdate with vanadium species were likely to be present in the homogeneous phase, especially in the case using HPMo (entries 6 and 8).

According to Table 4, V_2O_5 + C system has good performance, and V_2O_5 + C + CsPMo system has slightly higher performance. The reaction tests at longer reaction time were carried out to complete the reaction for both systems (Scheme 2). The selectivity was almost unchanged until the total conversion of 2-hydroxycyclohexanone. The V_2O_5 + C system gave 60% yield of adipic acid (at 96% conversion) and the V_2O_5 + C + CsPMo system gave 73% yield (at 97% conversion). On the other hand, V_2O_5 catalyst without any additive decreased its selectivity at higher conversion level (80% → <60%), and the adipic acid yield was lower than those of V_2O_5 + C and V_2O_5 + C + CsPMo systems.

2.4. Application to other substrates

We applied the V_2O_5 + C and V_2O_5 + C + CsPMo systems to carbohydrate substrates. The main products of carbohydrate oxidation by vanadium species are formic acid and CO_2. Table 5 shows the results of dihydroxyacetone oxidation. Main products of dihydroxyacetone are glycolic acid, formic acid and CO_2. Small amount of acetic acid was also detected. At short reaction time the products are mainly glycolic acid and formic acid. At longer reaction time the yield of glycolic acid decreased and those of formic acid and CO_2 increased. As an ideal case one dihydroxyacetone molecule is converted to two formic acid molecules and one CO_2 (Scheme 3) although the oxidation of glycolic acid was slow. The slow oxidation of glycolic acid was verified by the reaction tests with glycolic acid as the substrate (Table S1, Supporting Information): the reaction rate of glycolic acid was about 1 order slower than that of dihydroxyacetone, and about 1:1 formation of formic acid and CO_2 from glycolic acid was confirmed. The order of conversion rate of dihydroxyacetone with different catalyst systems was as follows: V_2O_5 + C + CsPMo > V_2O_5 + C > V_2O_5 + CsPMo > V_2O_5, which was similar to the case of 2-hydroxycyclohexanone substrate. However, at longer reaction time the yields were similar between V_2O_5 + C + CsPMo and V_2O_5 + C.

Table 6 shows the results of oxidation of fructose and glucose. Fructose oxidation was much faster than glucose oxidation (entries 1-8). The identified products of fructose oxidation were formic acid, CO_2 and glycolic acid, while glycolic acid can be the intermediate of formic acid and CO_2 as described above. The order of conversion rate of fructose with different catalyst systems was also almost the same as that for 2-hydroxycyclohexanone and dihydroxyacetone (V_2O_5 + C + CsPMo ≥ V_2O_5 + C > V_2O_5 + CsPMo > V_2O_5) (entries 1-4). However, the oxidation of glucose showed a different trend. The order of conversion rate was much higher when CsPMo was present in the system (entries 5-8). An important point is that significant amount of fructose was formed in V_2O_5 + CsPMo and V_2O_5 + C + CsPMo systems (entries 7 and 8). With only CsPMo, fructose as the sole product was formed (entry 9). Considering the higher reactivity of fructose, fructose works as an intermediate of glucose oxidation to formic acid, and CsPMo promote the isomerization of glucose to fructose. Ye Wang et al. proposed that the main route of glucose oxidation with vanadium (IV)/(V) catalyst is isomerization of glucose to fructose, retro-aldol reaction to two C3 units (glyceraldehyde and dihydroxyacetone), and oxidation of the C3 units to formic acid and CO_2.[19] Our results agree with this reaction route. Although the involvement of retro-aldol reaction was not confirmed in our system, the formation of glycolic acid in both dihydroxyacetone and fructose oxidations (Tables 5 and 6) supports that dihydroxyacetone works as an intermediate of fructose oxidation. On the other hand, under severer conditions to complete the reaction, the final yield of formic acid from glucose was similar (~45%) among V_2O_5 + C, V_2O_5 + CsPMo, and V_2O_5 + C + CsPMo catalyst systems (entries 12-14). The yield values were comparable to those reported for glucose oxidation with PVMo catalysts (~50%).[17a,18,20] Nevertheless, the reaction rate of V_2O_5 + C system was much higher than that of $H_5PV_2Mo_{10}O_{40}$, a typical PVMo catalyst (entry 15) in our reaction conditions. The lower activity of PVMo than V_2O_5 + C was in contrast to the comparable activity for 2-hydroxycyclohexanone oxidation between these catalysts (Table 2). The PVMo catalyst may have low activity in glucose isomerization.

Therefore, for both dihydroxyacetone and glucose, the final yields are similar between V_2O_5 + C and V_2O_5 + C + CsPMo systems, although CsPMo has some positive effect in substrate conversion. V_2O_5 + C system is attractive in view of catalyst cost.

2.5. Reaction mechanism

Reaction of molecular oxygen is always a key step of oxidation with molecular oxygen under mild conditions because of the biradical nature of molecular oxygen. We conducted the reaction under different oxygen pressures to investigate the effect of oxygen pressure in the kinetics. The results are shown in Table 7. Here, we added small amount of polyoxometalate to the system to oxidize vanadium(IV) and then to exclude the effect of the formation amount of inactive vanadium(IV) species under different oxygen pressure. Although the exact reaction order could not be calculated because of the high conversion level even at short reaction time (0.5 h), the reaction rate was clearly increased by increasing the oxygen pressure, and the effect can be regarded as first order. These results indicate that the rate-determining step involves free or catalyst-bound molecular oxygen.

There is no widely-accepted mechanism of ketol oxidation with vanadium catalyst. Vennat et al. proposed the mechanism that starts with abstraction of alpha-hydrogen of coordinated alcohol group (C<u>H</u>-OV) by vanadium(V) center.[16] The formed “biradical” consisting of vanadium(IV) and

$\mathrm{R\text{-}\dot{C}(\text{-}OV)\text{-}R'}$ quickly reacts with $\dot{\mathrm{O}}{=}\dot{\mathrm{O}}$ to give alkylperoxovanadium(V) species without unpaired electron. However, this mechanism does not agree with our data that oxygen pressure has clear positive effect while hydrogen abstraction is a slow reaction (rate-determining step). There are other proposed mechanisms for vanadium-catalyzed ketol oxidation which involve free vanadium(IV) species in the redox cycle.[19,21,22] This type of mechanisms also do not agree with our data that free vanadium(IV) has much lower activity. On the other hand, Finke et al. proposed a mechanism for 3,5-di-*tert*-butylcatechol oxidation to dicarboxylic acids with homogeneous vanadium catalyst where one electron in the aromatic ring of coordinated substrate is transferred to vanadium(V) to give semiquinone and vanadium(IV), and then molecular oxygen reacts with the semiquinone and vanadium(IV) to give peroxo-bridged quinone-vanadium(V) species.[24] The kinetics of the 3,5-di-*tert*-butylcatechol oxidation follows first order for oxygen pressure. Inspired by the 3,5-di-*tert*-butylcatechol oxidation mechanism, we propose a mechanism as shown in Scheme 4. First, ketol is coordinated to vanadium(V) center with the -OH group as alkoxide (step (i)). Biradical species is reversibly formed by transfer of one π electron in C=O to vanadium(V) (step (ii)). Molecular oxygen reacts with the biradical state of vanadium-substrate complex (step (iii)), and the rearrangement cleaves the C-C bond (step (iv)) to give vanadium-bound percarboxylate and aldehyde. The steps (iii) and (iv) may proceed simultaneously, because the intermediate between steps (iii) and (iv) has unstable positively-charged oxygen. The rate-determining step will be step (iii) (assumed that this step (iii) is irreversible) or step (iv) (assumed that the step (iii) is reversible). The vanadium-bound percarboxylate and aldehyde are converted to two carboxylic acids by vanadium-catalyzed Baeyer-Villiger-like reaction (step (v)).[38] As a side reaction, homolytic O-O dissociation of V(V)-O-O moiety[39] produces free inactive vanadium(IV) species and free radicals, which leads to various kinds of by-products by radical-chain autoxidation. The role of carbon support may include a reservoir of electrons and it may stabilize the “biradical” state of vanadium-substrate complex.

We also carried out DFT (density functional theory) calculation for the proposed scheme. The activated carbon ligand was simulated by 1,8-naphthalenediolate. The transition states were not calculated because the steps (i) and (v) involve solvent molecules and the step (iii) clearly has multi-configurational nature that should not be treated by single-determinant theory. Nevertheless, the geometry optimization for the step (iii) product leads to C-C dissociation and finally the step (iv) product was obtained. The energy level of the step (iv) product is significantly lower (92 kJ/mol) than the step (i) product. These calculations support that the steps (iii) and (iv) proceed simultaneously. The detailed results of these calculations are described in Figure S3, Supporting Information.

3. Conclusions

Catalytic activity of aqueous V_2O_5 for ketol oxidation with molecular oxygen is promoted by addition of activated carbon. Addition of carbon materials with smaller amount of functional groups such as carbon black and carbon nanotube is not effective on the catalytic activity of vanadium. Although much amount of vanadium is present in homogenous phase during the reaction, vanadium(V) species adsorbed on activated carbon has high activity. Vanadium(IV) species are much less active. This point also suggests that the main reaction path of ketol oxidation does not include free vanadium(IV) species. The vanadium(V) + carbon system can be applied to carbohydrate oxidation to formic acid. The activity of vanadium(V) + carbon in glucose oxidation is much higher than that of V_2O_5 alone or acid-type P-V-Mo polyoxometalate ($H_5PV_2Mo_{10}O_{40}$), while the activity of vanadium(V) + carbon and $H_5PV_2Mo_{10}O_{40}$ is similar in 2-hydroxycyclohexanone oxidation. The

10.1002/cctc.201700566

final yield of formic acid (42%) from glucose is comparable to those reported for acid-type P-V-Mo polyoxometalates. The addition of cesium phosphomolybdate ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) to vanadium(V) + carbon system further increases the activity. The activity increase may be due to the oxidation of vanadium(IV) species assisted by polyoxometalate, although the chemistry of polyoxometalate addition is very complex because of the reactivity, acidity and redox ability of polyoxometalate. While the final yield of formic acid from glucose is almost unchanged by addition of cesium phosphomolybdate, the yield of adipic acid from 2-hydroxycyclohexanone is slightly increased. Based on the data that free vanadium(IV) is not involved in the main reaction cycle and high oxygen pressure increases the activity, a reaction mechanism is proposed where reversibly formed “biradical” state of vanadium-ketol complex reacts with molecular oxygen, and accompanying rearrangement dissociates the C-C bond. The effective functional groups of carbon support have not been determined, and the determination is one of the targets of future study such as by using model ligands.

4. Experimental section

Materials

Organic reagents and catalysts used in this study were commercially available and used as received. The used carbon materials were: Osaka Gas Chemicals Shirasagi FAC-10 activated carbon (lignocellulosic, activated by steam, BET surface area 851 m^2/g), Osaka Gas Chemicals Carboraffin activated carbon (lignocellulosic, activated by zinc chloride, 1215 m^2/g), Vulcan XC-72 carbon black (224 m^2/g), graphene oxide purchased from Aldrich, and carbon nanotube (multi-walled, 10-30 nm) purchased from Wako. V_2O_5 and $H_3PMo_{12}O_{40}$•$23H_2O$ were purchased from Wako. $VOSO_4$•$6H_2O$ was purchased from Kanto Chemicals. $H_5PV_2Mo_{10}O_{40}$•$25H_2O$ was kindly given by Nippon Inorganic

Colour & Chemical Co., Ltd. $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ (CsPMo) was prepared by slow addition of 0.08 M aqueous cesium carbonate to 0.06 M aqueous $H_3PMo_{12}O_{40}$ in stoichiometric amount (molar ratio Cs : P = 2.5 : 1) at 323 K and subsequent evaporation and calcination at 573 K.[40] The BET surface area of prepared CsPMo was 15.7 m^2/g. XRD pattern of CsPMo confirmed the cubic structure of cesium phosphomolybdate.[40] These measurements were conducted with Shimadzu Gemini 2360 (BET) and Rigaku MiniFlex 600 (XRD) instruments. Dihydroxyacetone (Wako) and 2-hydroxycyclohexanone (Aldrich) was received as the dimer solid. The molar amount of dihydroxyacetone and 2-hydroxycyclohexanone was shown as that of the monomer unit.

Activity tests

The oxidation reaction was performed in a 190 mL stainless-steel autoclave with an inserted glass vessel. The catalysts, substrate and water (10 mL) were put into the autoclave together with a spinner. The amount of V_2O_5 was below the solubility limit (0.8 g / 100 mL at 293 K) in all cases. The pH was measured with a pH meter when necessary. After sealing, the reactor was filled with 0.3 MPa oxygen. The autoclave was heated to 353 K (~20 min to reach, as monitored by thermocouple inserted in the autoclave). The stirring rate was fixed at 500 rpm (magnetic stirring). After an appropriate reaction time the reactor was cooled down by cold water bath, 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 with membrane filter. Analysis of liquid phase was conducted with HPLC (Shimadzu Prominence; Aminex HPX-87 H column (Bio-rad), 0.01 M sulfuric acid as eluent, UV detector (210 nm) and RID). The gas phase was analyzed with FID-GC (Shimadzu GC-2014, Porapak N packed column, FID combined with methanator). Conversion, selectivity and yield were calculated as the following formula: Conversion (%) = {mol of consumed substrate}/{mol of charged substrate} × 100; Selectivity (%) = {(mol of product)(number of carbon atoms in the product)}/{(mol of consumed substrate)(number of carbon atoms in the substrate)} × 100; Yield (%) = {(mol of product)(number of carbon atoms in the product)}/{(mol of charged substrate)(number of carbon atoms in the substrate)} × 100. When the conversion level was very low (<10%), the conversion was calculated by the sum of product yields. The carbon balance was 100±10%.

In the case of oxidation under atmospheric pressure, a 15 mL test tube was used instead of an autoclave. The removal of catalyst after the reaction was conducted without cooling (hot filtration).

Metal amount in the solution was analyzed by ICP-OES (Thermo Fisher Scientific Inc., iCAP6500). UV-Vis measurements were conducted with the Shimadzu 2450 UV-visible spectrometer, using silica quartz square cell. Methanol (1 mL) and phthalate pH standard solution (pH 4.01; 1 mL) was added to the sample (2 mL) in order to make the coordination mode of vanadium species the same in different samples. The amount of dissolved vanadium(V) and (IV) species was determined by the absorbance in 450-500 nm and 700-800 nm regions, respectively. V_2O_5 and $VOSO_4$ solutions were used as standards. Solutions of V_2O_5 and NH_4VO_3 showed the same spectrum pattern in this protocol. It was confirmed that mixed solution of NH_4VO_3 and $VOSO_4$ (33% and 67% of the original concentration, respectively; similar concentrations observed in Table 3) gives the correct concentration of each species. The raw spectra are shown in Figure S1 (Supporting Information). It was confirmed that dissolved $VOSO_4$ was not oxidized during the measurement processes.

DFT calculations were conducted with Materials Studio DMol^3 software.[41,42] The used functional was PW91 (default setting for GGA-level DFT in this program), and the basis sets were built-in double numerical functions plus d-functions for non-hydrogen atoms (DND3.5; comparable to 6-31G(d)). Core electrons were represented by DSPP (DFT semi-core pseudopotentials)[43] built in the software. Orbitals for compounds with unpaired electrons (O_2) were unrestricted. The initial state was set as $VO(OH)(C_{10}H_6O_2)$ ($C_{10}H_6O_2$ = 1,8-naphthalenediolato), and all the calculations were carried out for gas-phase states.

Acknowledgments

Part of this work is supported by JSPS KAKENHI “Grant-in-Aid for Scientific Research (C)” K15K065640.

References

[1] T. K. M. Shing in *Comprehensive Organic Synthesis* Vol. 7 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, 1994, pp. 703.

[2] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411-2502.

[3] C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, *Chem. Rev.* **2015**, *115*, 11559-11624.

[4] R. Floresca, M. Kurihara, D. S. Watt, A. Femir, *J. Org. Chem.* **1993**, *58*, 2196-2200.

[5] I. Carrera, M. C. Brovetto, J. C. Ramos, G. A. Seoane, *Tetrahedron Lett.* **2009**, *50*, 5399-5402.

[6] 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.

[7] S. J. H. F. Arts, F. van Rantwijk, R. A. Sheldon, *J. Carbohydr. Chem.* **1996**, *15*, 317-329.

[8] E. Takezawa, S. Sakuguchi, Y. Ishii, *Org. Lett.* **1999**, *1*, 713-715.

[9] K. Yamaguchi, N. Mizuno, *Chem. Eur. J.* **2003**, *9*, 4353-4361.

[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] V. Escande, C. H. Lam, C. Grison, P. T. Anastas, *ACS Sustainable Chem. Eng.* **2017**, *5*,

3214-3222.

[12] a) M. Wang, J. Lu, J. Ma, Z. Zhang, F. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14061-14065; *Angew. Chem.* **2015**, *127*, 14267-14271; b) M. Wang, X.-K. Gu, H.-Y. Su, J.-M. Lu, J.-P. Ma, M. Yu, Z. Zhang, F. Wang, *J. Catal.* **2015**, *330*, 458-464; c) M. Wang, J. Lu, X. Zhang, L. Li, H. Li, N. Luo, F. Wang, *ACS Catal.* **2016**, *6*, 6086-6090; d) H. Lu, M. Wang, H. Li, N. Luo, S. Xu, F. Wang, *J. Catal.* **2017**, *346*, 170-179; e) H. Liu, M. Wang, H. Li, N. Luo, S. Xu, F. Wang, *J. Catal.* **2017**, *346*, 170-179; f) M. Wang, L. H. Li, J. M. Lu, H. J. Li, X. C. Zhang, H. F. Liu, N. C. Luo, F. Wang, *Green Chem.* **2017**, *19*, 702.

[13] C. Díaz-Urrutia, B. Sedai, K. C. Leckett, R. T. Baker, S. K. Hanson, *ACS Sustainable Chem. Eng.* **2016**, *4*, 6244-6251.

[14] Z. Zhou, M. Liu, C. Li, *ACS Catal.* **2017**, *7*, 3344-3348.

[15] a) L. E. Aakel, F. Launay, A. Atlamsani, J.-M. Brégeault, *Chem. Commun.* **2001**, 2218-2219; b) L. E. Aakel, F. Launay, J.-M. Brégeault, A. Atlamsani, *J. Mol. Catal. A* **2004**, *212*, 171-182.

[16] M. Vennat, P. Herson, J.-M. Brégeault, G. B. Shul'pin, *Eur. J. Inorg. Chem.* **2003**, 908-917.

[17] a) R. Wölfel, N. Taccardi, A. Bösmann, P. Wasserscheid, *Green Chem.* **2011**, *13*, 2759-2763; b) J. Albert, R. Wölfel, A. Bösmann, P. Wasserscheid, *Energy Environ. Sci.* **2012**, *5*, 7956-7962.

[18] J. Li, D.-J. Ding, L. Deng, Q.-X. Guo, Y. Fu, *ChemSusChem* **2012**, *5*, 1313-1318.

[19] Z. Tang, W. Deng, Y. Wang, E. Zhu, X. Wan, Q. Zhang, Y. Wang, *ChemSusChem* **2014**, *7*, 1557-1567.

[20] J. Zhang, M. Sun, X. Liu, Y. Han, *Catal. Today* **2014**, *233*, 77-82.

[21] a) W. Wang, M. Niu, Y. Hou, W. Wu, Z. Liu, Q. Liu, S. Ren, K. N. Marsh, *Green Chem.* **2014**, *16*, 2614-2618; b) M. Niu, Y. Hou, S. Ren, W. Wang, Q. Zheng, W. Wu, *Green Chem.* **2015**, *17*, 335-342; c) M. Niu, Y. Hou, S. Ren, W. Wu, K. N. Marsh, *Green Chem.* **2015**, *17*, 453-459.

[22] T. Lu, M. Niu, Y. Hou, W. Wu, S. Ren, F. Yang, *Green Chem.* **2016**, *18*, 4725-4732.

[23] H. Weiner, R. G. Finke, *J. Am. Chem. Soc.* **1999**, *121*, 9831-9842.

[24] a) C.-X. Yin, R. G. Finke, *J. Am. Chem. Soc.* **2005**, *127*, 13988-13996; b) A. M. Morris, C. G. Pierpont, R. G. Finke, *J. Mol. Catal. A* **2009**, *309*, 137-145.

[25] a) S. K. Hanson, R. T. Baker, J. C. Gordon, B. L. Scott, D. L. Thorn, *Inorg. Chem.* **2010**, *49*, 5611-5618; b) S. K. Hanson, R. Wu, L. A. Silks, *Angew. Chem. Int. Ed.* **2012**, *51*, 3410-3413; *Angew. Chem.* **2012**, *124*, 3466-3469; c) B. Sedai, C. Díaz-Urrutia, R. T. Baker, R. Wu, L. A. Silks, S. K. Hanson, *ACS Catal.* **2011**, *1*, 794-804.

[26] Y. Ma, Z. Du, J. Liu, F. Xia, J. Xu, *Green Chem.* **2015**, *17*, 4968-4973.

[27] J. Mottweiler, M. Puche, C. Räuber, T. Schmidt, P. Concepción, A. Corma, C. Bolm, *ChemSusChem* **2015**, *8*, 2106-2113.

[28] Y.-Y. Jiang, L. Yan, H.-Z. Yu, Q. Zhang, Y. Fu, *ACS Catal.* **2016**, *6*, 4399-4410.

[29] J. Liu, Z. Du, Y. Yang, T. Lu, F. Lu, J. Xu, *ChemSusChem* **2012**, *5*, 2151-2154.

[30] J. Lan, J. Lin, Z. Chen, G. Yin, *ACS Catal.* **2015**, *5*, 2035-2041.

[31] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171-198.

[32] N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199-218.

[33] N. Obara, S. Hirasawa, M. Tamura, Y. Nakagawa, K. Tomishige, *ChemCatChem* **2016**, *8*, 1732-1738.

[34] S. Van de Vyver, Y. Román-Leshkov, *Catal. Sci. Technol.* **2013**, *3*, 1465-1479.

[35] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228-240.

[36] a) D. C. Crans, A. S. Tracy, in *ACS Symposium Series*, Vol. 711, American Chemical Society, 1998, pp. 2; D.C. Crans, J. J. Smee, E. Gaidamauskas, L. Yang, *Chem. Rev.* **2004**, *104*, 849-902.

[37] N. Mizuno, M. Tateishi, M. Iwamoto, *J. Catal.* **1996**, *163*, 87-94.

[38] a) R. Gopinath, B. K. Patel, *Org. Lett.* **2000**, *2*, 577-579; b) R. Gopinath, B. Barkakaty, B. Talukdar, B. K. Patel, *J. Org. Chem.* **2003**, *68*, 2944-2947.

[39] a) G. B. Shul'pin, M. C. Guerreiro, U. Schuchardt, *Tetrahedron* **1996**, *52*, 13051-13062; b) G. Süss-Fink, L. Gonzalez, G. B. Shul'pin, *Appl. Catal. A* **2001**, *217*, 111-117.

[40] M. Langpape, J. M. M. Millet, U. S. Ozkan, M. Boudeulle, *J. Catal.* **1999**, *181*, 80-90.

[41] B. Delley, *J. Chem. Phys.* **1990**, *92*, 508-517.

[42] B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756-7764.

[43] B. Delley, *Phys. Rev. B* **2002**, *66*, 155125.

Table 1. Oxidation of 2-hydroxycyclohexanone with V_2O_5 + carbon catalysts

Entry	Catalysts	Conv. [%]	Selectivity [%]					
			AA	GA	SA	CDO	CO_x	Others
1	None	1.9	69	1	<1	5	6	19
2	V_2O_5	28	80	5	2	<1	2	11
3	V_2O_5 + FAC-10	61	63	4	<1	<1	2	31
4	V_2O_5 + Carboraffin	46	72	4	6	7	<1	11
5	V_2O_5 + XC-72	33	74	4	2	<1	6	14
6	V_2O_5 + graphene oxide	33	59	5	5	9	2	21
7	V_2O_5 + carbon nanotube	32	77	4	1	<1	8	10
8	FAC-10	5.1	76	2	1	9	<1	12
9	XC-72	2.5	35	<1	<1	8	<1	57
10	Carboraffin	6.8	63	2	1	12	<1	22
11	Graphene oxide	11	48	2	<1	37	<1	13
12	Carbon nanotube	6.4	66	2	<1	21	<1	11

Reaction conditions: 2-Hydroxycyclohexanone 5 mmol, V_2O_5 0 or 9.1 mg (0.1 mmol-V), carbon 0 or 0.1 g, water 10 g, O_2 0.3 MPa, 353 K, 1 h. AA = adipic acid, GA = glutaric acid, SA = succinic acid, CDO = 1,2-cyclohexanedione. "Others" include both identified products and unidentified RID peaks.

10.1002/cctc.201700566

Table 2. Oxidation of 2-hydroxycyclohexanone with V_2O_5 under different pH values

Entry	Catalysts	Initial pH	Conv. [%]	Selectivity [%]					
				AA	GA	SA	CDO	CO_x	Others
1	V_2O_5	3.7	7	71	5	<1	<1	5	19
2	V_2O_5 + C	5.0	27	71	4	<1	2	3	20
3	V_2O_5 + NaOH	5.8	11	59	1	<1	<1	5	35
4	V_2O_5 + C + H_2SO_4	3.0	27	61	<1	<1	2	3	33
5	V_2O_5 + C + H_2SO_4	1.8	25	58	2	<1	<1	4	37
6	$H_5PV_2Mo_{10}O_{40}$[a]	1.7	30	34	3	<1	6	1	55

Reaction conditions: 2-Hydroxycyclohexanone 4.3 mmol, V_2O_5 0 or 2 mg (22 μmol-V), carbon (C; FAC-10) 0 or 0.1 g, water 10 g, O_2 0.3 MPa, 353 K, 1 h. AA = adipic acid, GA = glutaric acid, SA = succinic acid, CDO = 1,2-cyclohexanedione. “Others” include both identified products and unidentified RID peaks. [a] $H_5PV_2Mo_{10}O_{40}$ 11 μmol.

Table 3. Oxidation of 2-hydroxycyclohexanone with V_2O_5 under different pH values

Entry	Catalyst	Time [min]	Dissolved V(V) [%]	Dissolved V(IV) [%]	Conv. [%]	Selectivity / % AA	CDO	Others
1	V_2O_5	10[a]	34	12	4	56	<1	44
2	V_2O_5	60[a]	<5	36	17	72	<1	28
3	$VOSO_4$	10	<5	99	2	57	<1	43
4	$VOSO_4$	60	<5	97	7	76	<1	24
5	V_2O_5 + C	0	<5	<3	-	-	-	-
6	V_2O_5 + C	10	<5	60	18	49	7	44
7	V_2O_5 + C	60	<5	56	46	59	5	36
8	$VOSO_4$ + C	0	<5	94	-	-	-	-
9	$VOSO_4$ + C	60	6	82	27	64	1	35

Reaction conditions: 2-Hydroxycyclohexanone 0.86 mmol, catalyst 22 μmol-V, carbon (C; FAC-10) 0 or 0.02 g, water 2 g, O_2 0.1 MPa, 353 K. Oxygen refilling was performed every 10 minutes. AA = adipic acid, CDO = 1,2-cyclohexanedione. “Others” include both identified products and unidentified RID peaks. Dissolved vanadium species were determined by UV-Vis spectra. The raw UV-Vis data are shown in Figure S1. [a] Black solid was also formed.

Table 4. Oxidation of 2-hydroxycyclohexanone with V_2O_5 and various additives

Entry	Catalysts	Conv. [%]	Selectivity [%] AA	GA	SA	CDO	CO_x	Others	Dissolved V [%][a]	Dissolved Mo [%][a]
1	None	1.9	69	1	<1	5	6	19	-	-
2	V_2O_5	28	80	5	2	<1	2	11	48	-
3	V_2O_5 + C	61	63	4	<1	<1	2	31	54	-
4	C	5.1	76	2	<1	9	<1	13	-	-
5	V_2O_5 + C + CsPMo	72	77	3	<1	<1	2	17	48	3
6	V_2O_5 + C + HPMo	68	67	4	<1	1	2	26	37	32
7	V_2O_5 + CsPMo	37	74	3	1	2	1	18	45	3
8	V_2O_5 + HPMo	42	68	4	<1	3	1	25	42	43
9	C + CsPMo	9.6	53	12	<1	15	<1	20	-	n.d.
10	CsPMo	8.2	65	6	<1	12	<1	17	-	n.d.

Reaction conditions: 2-Hydroxycyclohexanone 5 mmol, V_2O_5 0 or 9.1 mg (0.1 mmol-V), carbon (C; FAC-10) 0 or 0.1 g, polyoxometalate 0 or 0.01 mmol, water 10 g, O_2 0.3 MPa, 353 K, 1 h. CsPMo = $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$. HPMo = $H_3PMo_{12}O_{40}$, AA = adipic acid, GA = glutaric acid, SA = succinic acid, CDO = 1,2-cyclohexanedione. "Others" include identified products and unidentified RID peaks. n.d. = not determined.

[a] Determined by ICP-OES; after reaction.

10.1002/cctc.201700566

Table 5. Oxidation of dihydroxyacetone with V_2O_5-carbon-polyoxometalate catalysts

Entry	Catalysts	Time [h]	Conv. [%]	C-based yield [%]		
				Glycolic acid	Formic acid	CO_2
1	V_2O_5	1	46	13	14	1
2	V_2O_5 + C	1	81	45	26	4
3	V_2O_5 + CsPMo	1	55	24	19	6
4	V_2O_5 + C + CsPMo	1	>99	53	35	6
5	V_2O_5	4	88	32	38	8
6	V_2O_5 + C	4	>99	43	40	13
7	V_2O_5 + CsPMo	4	91	33	36	9
8	V_2O_5 + C + CsPMo	4	>99	43	41	13

Reaction conditions: Dihydroxyacetone 5 mmol, V_2O_5 9.1 mg (0.1 mmol-V), carbon (C; FAC-10) 0 or 0.1 g, CsPMo ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) 0 or 0.01 mmol, water 10 g, O_2 0.3 MPa, 353 K.

Table 6. Oxidation of sugars with V_2O_5-carbon-polyoxometalate catalysts

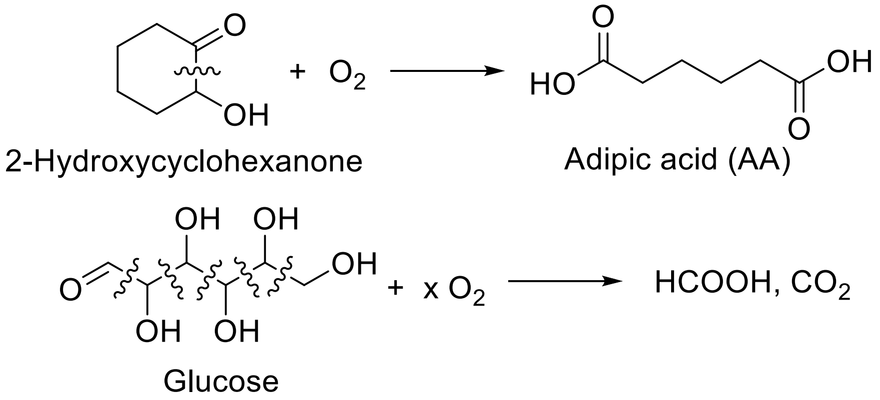
Entry	Substrate	Catalysts	Conditions	Conv. [%]	C-based yield [%]			
					Fructose	Glycolic acid	Formic acid	CO_2
1	Fructose	V_2O_5	A	50	-	8	11	3
2		V_2O_5 + C	A	79	-	10	20	9
3		V_2O_5 + CsPMo	A	62	-	9	18	5
4		V_2O_5 + C + CsPMo	A	81	-	9	21	10
5	Glucose	V_2O_5	A	2	<1	<1	<1	<1
6		V_2O_5 + C	A	8	<1	<1	2	<1
7		V_2O_5 + CsPMo	A	39	9	<1	6	<1
8		V_2O_5 + C + CsPMo	A	13	3	<1	3	<1
9		CsPMo	A	25	25	<1	<1	<1
10		C	A	<1	<1	<1	<1	<1
11	Glucose	V_2O_5	B	49	<1	1	13	1
12		V_2O_5 + C	B	98	2	2	43	26
13		V_2O_5 + CsPMo	B	>99	<1	<1	46	48
14		V_2O_5 + C + CsPMo	B	>99	<1	<1	42	57
15		$H_5PV_2Mo_{10}O_{40}$[a]	B	82	8	4	18	2

Reaction conditions: (A) substrate 5 mmol, V_2O_5 0 or 9.1 mg (0.1 mmol-V), carbon (C; FAC-10) 0 or 0.1 g, CsPMo ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) 0 or 0.01 mmol, water 10 g, O_2 0.3 MPa, 353 K, 4 h. (B) O_2 0.6 MPa, 24 h; other conditions were the same as (A). [a] $H_5PV_2Mo_{10}O_{40}$, 0.1 mmol-V.

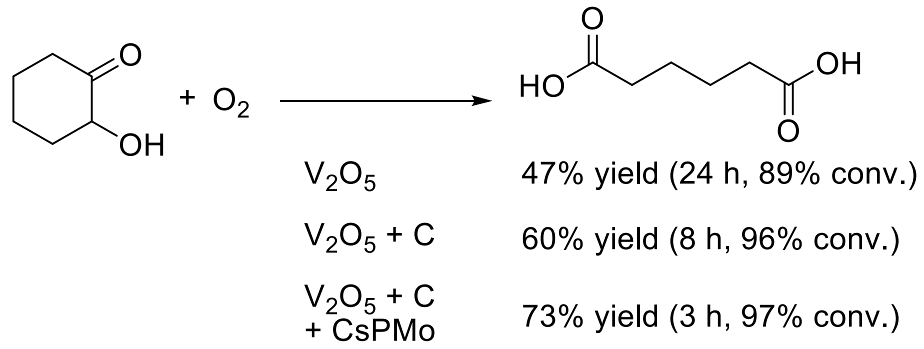
Table 7. Oxygen pressure dependence of 2-hydroxycyclohexanone oxidation with V_2O_5-carbon-polyoxometalate catalysts

Entry	O_2 [MPa]	Conv. [%)]	Selectivity [%]					
			AA	GA	SA	CDO	CO_x	Others
1	0.1	20	59	1	<1	11	<1	29
2	0.3	52	84	<1	<1	<1	<1	14
3	0.7	67	88	1	<1	<1	<1	9
4	1.2	74	85	1	<1	<1	<1	13

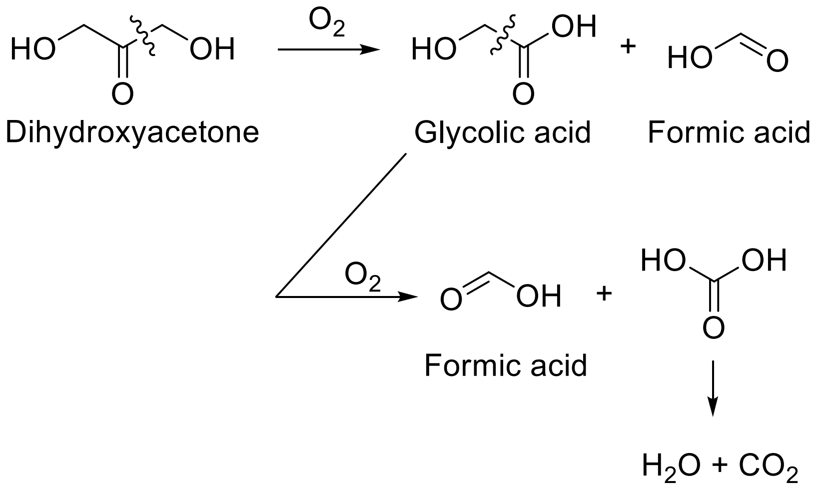
Reaction conditions: 2-Hydroxycyclohexanone 4.3 mmol, V_2O_5 1.8 mg (0.02 mmol-V), carbon (FAC-10) 0.1 g, $H_5PV_2Mo_{10}O_{40}$ 1 μmol, water 10 g, O_2 0.3 MPa, 353 K, 0.5 h. AA = adipic acid, GA = glutaric acid, SA = succinic acid, CDO = 1,2-cyclohexanedione. “Others” include identified products and unidentified RID peaks.



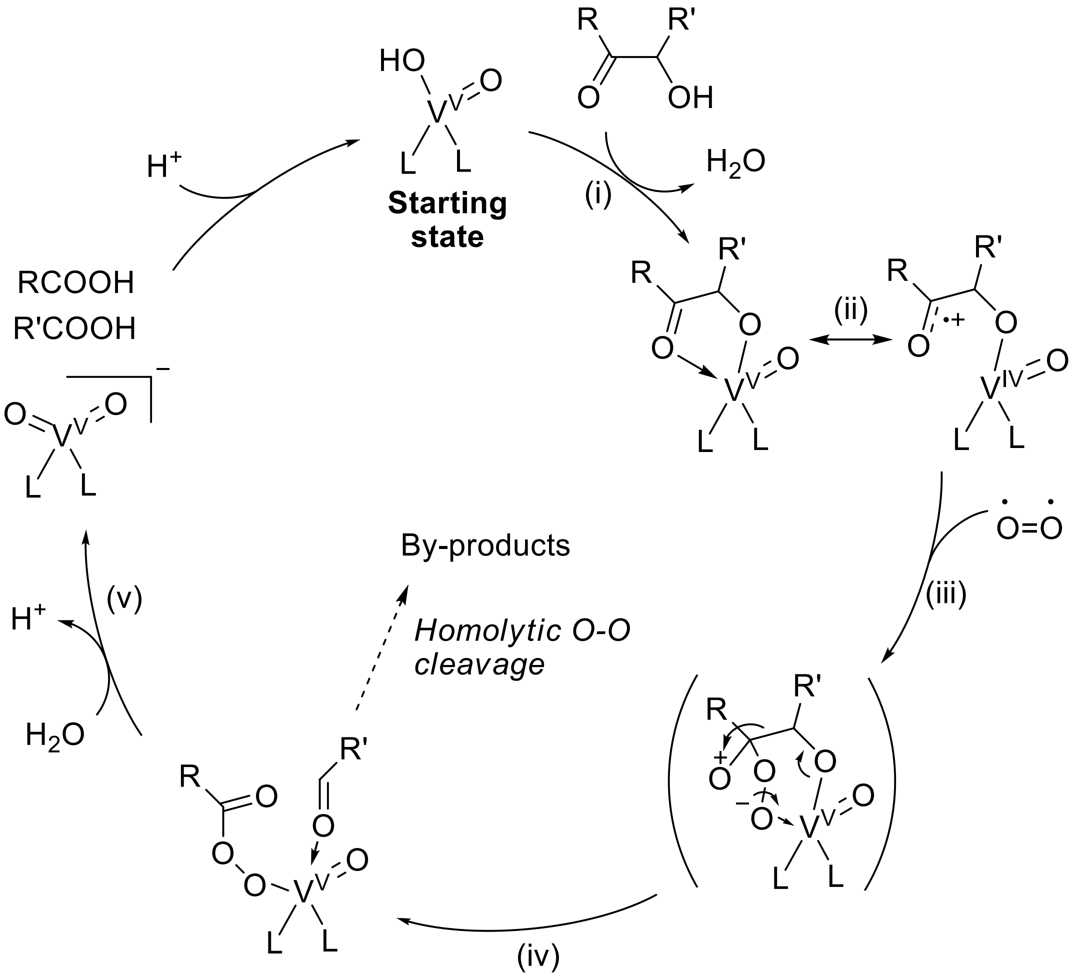
Scheme 1. Vanadium-catalyzed oxidation of ketol and carbohydrate.



Scheme 2. Adipic acid yield of different systems. Conditions: 2-hydroxycyclohexanone 4.3 mmol, V_2O_5 0.1 mmol-V, carbon (FAC-10) 0 or 0.1 g, CsPMo ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) 0 or 0.01 mmol, water 10 g, O_2 0.3 MPa, 353 K.

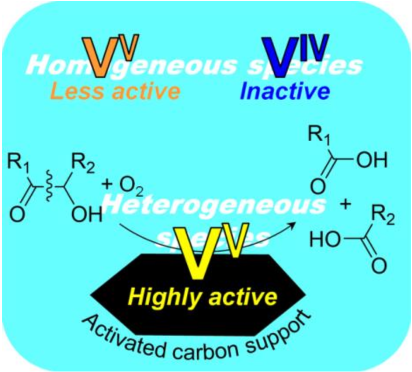


Scheme 3. Oxidation of dihydroxyacetone



Scheme 4. Proposed reaction mechanism of vanadium-catalyzed ketol oxidation with molecular oxygen. L = ligand with one negative charge. The negative charges of oxo (2-), alkoxo (1-) and percarboxylate (1-) ligands are omitted for clarity.

Graphical abstract



Bound catalyst: Vanadium(V) species adsorbed on activated carbon have higher activity for ketol oxidation to carboxylic acids than homogeneous vanadium species.