# Oxidative C-C cleavage over vanadium-carbon catalysts

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**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. Further addition of phosphomolybdate ($PMo_{12}O_{40}^{3-}$; PMo) was tested, and the activity was actually improved. The selectivity and yield of adipic acid from 2-hydroxycyclohexanone was slightly improved by addition of PMo. However, in the oxidation of glucose, the addition of PMo did not improve the final formic acid yield.

**Keywords:** Vanadium, Oxidation, Carboxylic acid.

## 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. Oxidative C-C cleavage of vicinal diols or ketols (hydroxyketones) is typically performed with stoichiometric oxidants such as lead tetraacetate and periodates.[1] Because of the non-green nature of such oxidants, catalytic systems using molecular oxygen as an oxidant have been searched. One of the typical catalysts for oxidative C-C cleavage with molecular oxygen is vanadium-based one. Homogeneous vanadium catalysts are active in oxidative C-C cleavage of aliphatic ketols such as 2-hydroxycyclohexanone and sugars to adipic acid and formic acid, respectively. In this study, we investigated the effect of co-catalysts on the vanadium-catalyzed ketol oxidation.[2]

## 2. Experimental (or Theoretical)

$V_2O_5$ and $H_3PMo_{12}O_{40}\cdot 23H_2O$ (HPMo) were purchased from Wako. Used activated carbon was Osaka Gas Chemicals Shirasagi FAC-10 (lignocellulosic, activated by steam, BET surface area 851 $m^2/g$). $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ (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.[3] 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. 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). 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 (Shimazdu GC-2014, Porapak N packed column, FID combined with methanator). Selectivity was calculated based on carbon amount.

## 3. Results and discussion

The results of 2-hydroxycyclohexanone oxidation with $V_2O_5$ catalyst and various additives are shown in Table 1. The addition of activated carbon (C) increases the catalytic activity (entry 3). The addition of CsPMo or HPMo further increases the activity of $V_2O_5$ + C system (entry 5, 6), and the selectivity to adipic acid was also increased. The promotional effect of CsPMo was larger than that of HPMo.

**Table 1.** Oxidation of 2-hydroxycyclohexanone with $V_2O_5$ and various additives.

| Entry | Catalysts | Conv. [%] | Sel. [%] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 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 | $V_2O_5$ + C | 61 | 63 | 4 | <1 | <1 | 2 | 31 |
| 4 | C | 5.1 | 76 | 2 | <1 | 9 | <1 | 13 |
| 5 | $V_2O_5$ + C + CsPMo | 72 | 77 | 3 | <1 | <1 | 2 | 17 |
| 6 | $V_2O_5$ + C + HPMo | 68 | 67 | 4 | <1 | 1 | 2 | 26 |
| 7 | $V_2O_5$ + CsPMo | 37 | 74 | 3 | 1 | 2 | 1 | 18 |
| 8 | $V_2O_5$ + HPMo | 42 | 68 | 4 | <1 | 3 | 1 | 25 |
| 9 | C + CsPMo | 9.6 | 53 | 12 | <1 | 15 | <1 | 20 |
| 10 | CsPMo | 8.2 | 65 | 6 | <1 | 12 | <1 | 17 |

Reaction conditions: 2-hydroxycyclohexanone 5 mmol, $V_2O_5$ 0 or 9.1 mg (0.1 mmol-V), C 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.

According to Table 1, $V_2O_5$ + C system has good performance, and $V_2O_5$ + C + CsPMo system has slightly higher performance. We applied the $V_2O_5$ + C and $V_2O_5$ + C + CsPMo systems to glucose as a carbohydrate substrate. Table 2 shows the results of glucose oxidation. 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 (entry 2-4), although CsPMo has some positive effect in substrate conversion. The yield values were comparable to those reported for glucose oxidation with $H_{3+n}PV_nMo_{12-n}O_{40}$ catalysts (~50%). [4, 5, 6]

**Table 2.** Oxidation of glucose with $V_2O_5$-carbon-polyoxometalate catalysts

| Entry | Catalysts | Conv. [%] | C-based yield [%] | | | |
|---|---|---|---|---|---|---|
| | | | Fructose | Glycolic acid | Formic acid | $CO_2$ |
| 1 | $V_2O_5$ | 49 | <1 | 1 | 13 | 1 |
| 2 | $V_2O_5$ + FAC-10 | 98 | 2 | 2 | 43 | 26 |
| 3 | $V_2O_5$ + CsPMo | >99 | <1 | <1 | 46 | 48 |
| 4 | $V_2O_5$ + FAC-10 + CsPMo | >99 | <1 | <1 | 42 | 57 |

Reaction conditions: glucose 5 mmol, $V_2O_5$ 0 or 9.1 mg (0.1 mmol-V), 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, $O_2$ 0.6 MPa, 353 K, 24 h.

## 4. Conclusions

Catalytic activity of aqueous $V_2O_5$ for ketol oxidation with molecular oxygen is promoted by addition of activated carbon (C). The $V_2O_5$ + C system can be applied to carbohydrate oxidation to formic acid. The activity of $V_2O_5$ + C in glucose oxidation is much higher than that of $V_2O_5$ alone. The final yield of formic acid (42%) from glucose is comparable to those reported for $H_{3+n}PV_nMo_{12-n}O_{40}$. The addition of CsPMo to $V_2O_5$ + C system further increases the activity. While the final yield of formic acid from glucose is almost unchanged by addition of CsPMo, the yield of adipic acid from 2-hydroxycyclohexanone is slightly increased (71%).

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