Chemical Species Active for Selective Oxygenation of Methane with Hydrogen Peroxide Catalyzed by Vanadium-containing Compounds

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UV-vis data revealed that monoperoxomonovanadate is an active species for liquid-phase oxygenation of methane with hydrogen peroxide catalyzed vanadium-containing catalysts in trifluoroacetic anhydride.

Methane is the most abundant compound in natural gas and its utilization is of great practical interest.[1,2] Recently, vanadium-containing catalysts have been reported to be active for the selective liquid-phase oxygenation of methane with hydrogen peroxide.[3-5] We have also reported that Keggin-type vanadium-containing $H_4PVMo_{11}O_{40}$ is an active catalyst precursor for the selective oxygenation.[6] However, little is known of the chemical species active for the reaction catalyzed by vanadium-containing catalysts.

In this letter, we attempted to elucidate species active for the selective oxygenation by UV-vis spectroscopy.

The $H_4PVMo_{11}O_{40}$ heteropolyacid (Nippon Inorganic Colour and Chemical Co., Ltd.), $VO(acac)_2$ (Kanto Chemical Co., Inc.), $VOSO_4 \cdot 5H_2O$ (Nacalai Tesque., Inc.), V_2O_5 (Wako Pure Chemical Industries., Ltd.), CF_3COOH (Tokyo Chemical Co., Ltd.), and $(CF_3CO)_2O$ (Tokyo Chemical Co., Ltd.) were commercially obtained and used as received. Aqueous solutions of $VO(O_2)^+$ and $VO(O_2)_2^-$ were prepared according to Refs. (8)-(10): Sodium vanadate (2.5×10^{-3} M) was used as a vanadium(V) source and perchloric acid (0.5 M) and sodium perchlorate (0.3 M) were used to control the acidity and ionic strength. The ionic strength was kept constant (0.3 M) at 25 ℃. The conditions of aqueous solutions containing $VO(O_2)_2^-$ and $VO(O_2)^+$ were as follows; $VO(O_2)_2^-$, $[V(V)] = 1.0 \times 10^{-3}$ M, $[H_2O_2] = 2.0 \times 10^{-3}$ M, pH = 5.4; $VO(O_2)^+$, $[V(V)] = 1.0 \times 10^{-3}$ M, $[H_2O_2] = 2.0 \times 10^{-3}$ M, pH = 0.3.

The reaction was carried out with an autoclave having a Teflon vessel as described previously.[6] The standard procedure was as follows. Specified amounts of heteropoly compounds (5 mmol) and 35.5% hydrogen peroxide (2.4 mmol) were dissolved in 1.8 mL of trifluoroacetic anhydride in the Teflon vessel. Next, this Teflon vessel was quickly attached inside an autoclave. The gas phase above the liquid was removed by evacuation and then the autoclave was pressurized with methane to 50 atm. The autoclave was heated up to 80 ℃ in an oil bath for 24 h. After the reaction, the autoclave was cooled to room temperature. Then the gas phase was sampled with the aid of a sampler directly connected to a gas chromatograph. The liquid was sampled with the aid of a gas-tight microsyringe and analyzed on a gas chromatography. Methylformate, methyltrifluoroacetate, formic acid, methanol, and carbon dioxide were produced and the first three compounds were the main oxygenates for each reaction.

Amounts of unreacted hydrogen peroxide were determined by cerium (IV) titration according to Ref. (7). 1 - 2 g of solution was accurately weighed and quickly dissolved in 200 mL water. The solution was stirred with a magnetic stir bar at 23 ℃. The potential was monitored as a solution of $Ce(NH_4)(SO_4)_4 \cdot 2H_2O$ in water (0.1 M) was added with a buret in 0.1 mL intervals.

UV-vis spectra were recorded on a UV-vis scanning spectrophotometer (SHIMADZU UV-2100PC). A 2.5 mM reaction solution of catalyst was sampled and the solution was diluted with 400 mL acetonitrile (0.5 mM). Then the UV-vis spectrum of the solution was measured.

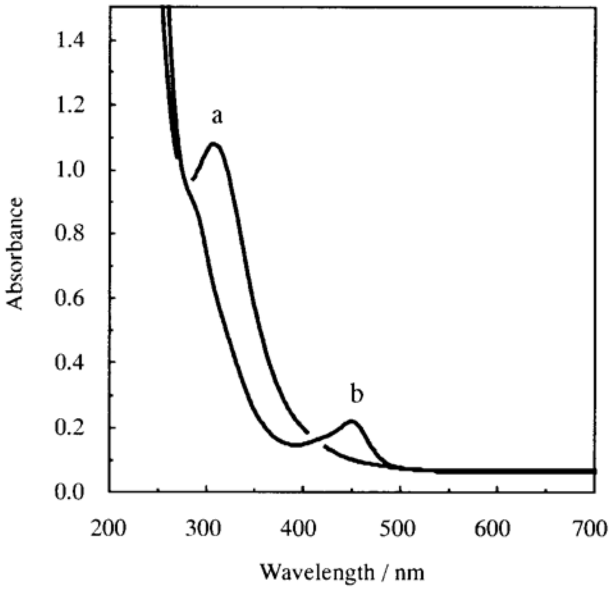

Figure 1. UV-vis spectra of solutions of $H_4PV_1Mo_{11}O_{40}$. (a), before reaction; (b), after reaction. Reaction conditions; 80 °C, 24 h. The reaction solution was diluted with CH_3CN (reaction solution/CH_3CN = 4/1).

Figures 1a and 1b show UV-vis spectra of solutions of $H_4PVMo_{11}O_{40}$ before and after reactions, respectively. In Figure 1a a band was observed at 308 nm characteristic of $PVMo_{11}O_{40}^{4-}$ (ε_{max} = 21620 $M^{-1}cm^{-1}$). The band intensity much decreased and a new band appeared at 447 nm with a shoulder at ca. 290 nm. The band at 447 nm was also observed for the other V-containing catalysts active for the selective oxygenation of methane. The most intense band was observed for $H_4PVMo_{11}O_{40}$. The band disappeared when H_2O_2 was completely consumed as shown in Figure 2, suggesting the idea that the band is assigned to a peroxo species. No mono-, di-, and tri-peroxomonomolybdates showed bands in the region 400 - 500 nm.[10-12] Tetraperoxomonomolybdate shows the UV-vis band at 450 nm.[11] However, this compound is stable only at pH 5 - 12, much higher than that in the present system and considered to be unstable in the present case. Therefore, the band at 447 nm is most probably assigned to species containing vanadium atom. It follows that the band is assigned to a peroxovanadate species.

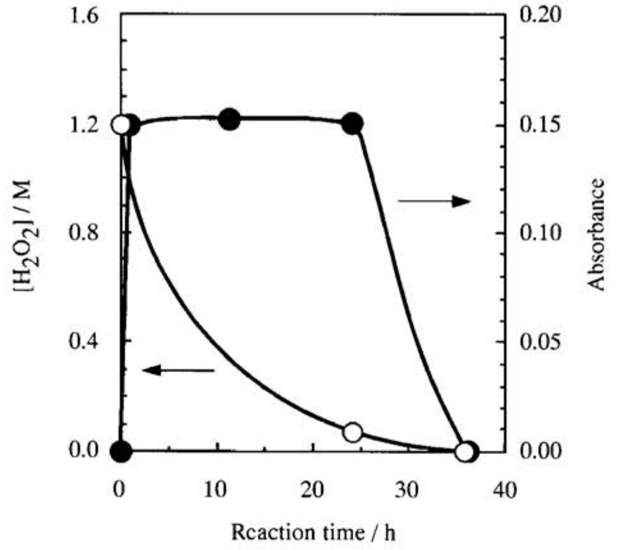

Figure 2. Changes in band intensity at 447 nm and concentration of hydrogen peroxide ($[H_2O_2]$) with reaction time. Reaction conditions; 80 °C. ●, band intensity at 447 nm; ○, $[H_2O_2]$.

Vanadium (V) exists as VO_2^+ in an acidic solution (pH ≤ 2).[10-16] It has also been reported that peroxovanadates of $VO(O_2)^+$ and $VO(O_2)_2^-$ are formed by the addition of H_2O_2 to VO_2^+ and these compounds show absorption bands at 455 and 330 nm, respectively.[10-16] In addition, a pH value of our reaction solution was 1 - 2, where $VO(O_2)^+$ is stable,[10-16] and the band position of $VO(O_2)^+$ is very close to 447 nm shown in Figure 1. The slight change of the band position is probably caused by the coordination of trifluoroacetate or water. In fact, the band position of $VO(O_2)^+$ at 453 nm was shifted to 446 nm by the addition of trifluoroacetic acid. Therefore, these facts show that the band at 447 nm in Figure 1 is assigned to $VO(O_2)^+$ formed according to the equation, $PVMo_{11}O_{40}^{4-} + H_2O_2 \rightarrow PMo_{11}O_{39}^{7-} + VO(O_2)^+ + 2H^+$.

The $PMo_{11}O_{39}^{7-}$ polyoxometalate shows the characteristic band at 290 (ε_{max} = 17400 $M^{-1}cm^{-1}$) nm.[17] The band position is in agreement with that of a shoulder band in Figure 1b. Therefore, the shoulder in Figure 1 is likely assigned to $PMo_{11}O_{39}^{7-}$ and the concentration calculated was 0.41 M. The value was in approximate agreement with the initial concentration of $H_4PVMo_{11}O_{40}$, 0.5 M. Therefore, most of $PVMo_{11}O_{40}^{4-}$ polyoxometalates decomposed to form $PMo_{11}O_{39}^{7-}$ and $VO(O_2)^+$. The band at 447nm steeply increased and then reached the constant value in Figure 2. These facts suggest that the reaction of $H_4PVMo_{11}O_{40}$ with H_2O_2 to form $PMo_{11}O_{39}^{7-}$ and $VO(O_2)^+$ is fast and that $VO(O_2)^+$ with methane is slow.

Figure 3 shows correlation between yields of the selective oxygenates and the band intensities at 447 nm for vanadium-containing catalysts. The band intensities increased with an increase in the yields, supporting that chemical species giving the band at 447 nm corresponds to an active species for the selective oxygenation of methane. The lower solubilities of V_2O_5, $VOSO_4 \cdot 5H_2O$, and $VO(acac)_2$ than $H_4PV_1Mo_{11}O_{40}$ into the reaction solution are probably related to the weaker band intensities.

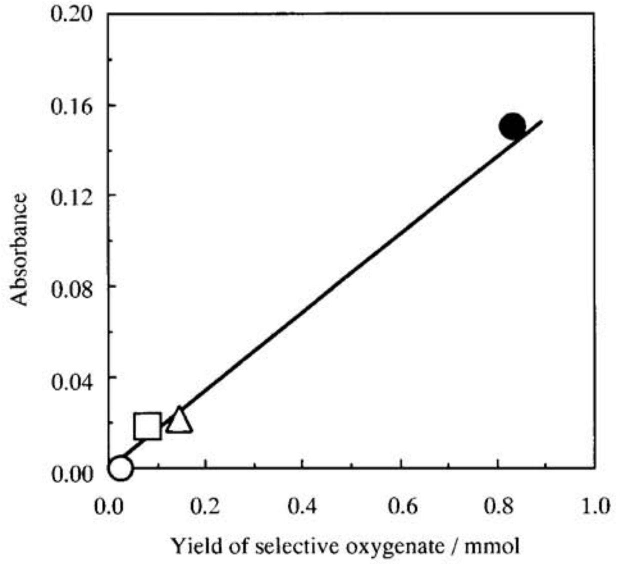

Figure 3. Correlation between yields of selective oxygenates and UV-vis band intensities at 447 nm. Reaction condition; 80 °C, 24 h. ●, $H_4PV_1Mo_{11}O_{40}$; ○, $VOSO_4 \cdot 5H_2O$; □, $VO(acac)_2$; △ , V_2O_5. The conversions for $H_4PV_1Mo_{11}O_{40}$, $VOSO_4 \cdot 5H_2O$, $VO(acac)_2$, and V_2O_5 were 4.7, 0.1, 0.3, and 1.0 %, respectively.

In conclusion, the present results indicate that monoperoxomonovanadate, $VO(O_2)^+$, is an active species for the selective oxygenation of methane in trifluoroacetic anhydride catalyzed by V-containing catalysts.

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