Journal of Catalysis **198,** 116–121 (2001)
doi:10.1006/jcat.2000.3117, available online at http://www.idealibrary.com on

Low-Temperature Selective Oxidation of Methane into Formic Acid with H_2–O_2 Gas Mixture Catalyzed by Bifunctional Catalyst of Palladium–Heteropoly Compound

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Received August 17, 2000; revised November 6, 2000; accepted November 8, 2000; published online January 24, 2001

The selective oxidation of methane catalyzed by heteropoly compounds having the formulas $M_xCs_{2.5}H_{0.5-2x+y}PV_yMo_{12-y}O_{40}$ (M = Pd^{2+}, Rh^{2+}, Ru^{2+}, Pt^{2+}, Mn^{2+}, Hg^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}; $x = 0$–3, $y = 0$–3) was investigated. It was demonstrated that addition of Pd and incorporation of V had a strong influence on oxidation with a H_2-O_2 gas mixture and that $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ showed the highest yield of formic acid. The reaction proceeded at temperatures as low as 423–593 K. Moreover, the reaction rate reached 1.2×10^{-4} mol h^{-1} g^{-1} at 573 K; this value is about 300 times higher than that with $FePO_4$ catalyst. Addition of steam promoted the production of formic acid, and the yield reached a maximum at a partial pressure of steam of 9.1 kPa. The coexistence of H_2 and O_2 was indispensable for the selective oxidation of methane. It is suggested that an active oxygen species is formed by the reaction of H_2 with O_2 catalyzed by Pd and acidic sites of supports. Pressure dependencies were expressed by $-dP_{CH_4}/dt = kP_{H_2}^{1.0}P_{O_2}^{1.0}P_{CH_4}^{1.0}$, and is consistent with the idea that the reaction of an active species formed from H_2 and O_2 with CH_4 is rate determining. © 2001 Academic Press

Key Words: **selective oxidation; methane; formic acid; hydrogen–oxygen gas mixture; palladium; vanadium substitution; heteropoly compound.**

INTRODUCTION

The activation and functionalization of methane have attracted much attention because of the abundance in natural gas and low reactivity (1–18). Various catalysts have been tested with a variety of oxidants in heterogeneous (10–18) and homogeneous systems (19–22).

The utilization of molecular oxygen for the oxidation of methane is a rewarding goal since it has the highest content of active oxygen and forms no by-products. However, direct oxidation with molecular oxygen cannot be achieved using heterogeneous catalysts under atmospheric pressure because high temperatures and high pressures, which induce the radical formation, are required for the activation of methane and/or oxygen, and high-temperature oxidation induces the overoxidation of oxygenated products. Therefore, a lowering of the reaction temperature is a key requirement for the selective oxidation. We have reported the direct oxidation of lower alkanes with molecular oxygen alone catalyzed by heteropoly compounds, but the oxidation of methane was unsuccessful (23).

On the other hand, reductants such as carbon monoxide (24), aldehyde (25), hydrogen (26, 27), and zinc (28) promoted the oxidation of alkanes and alkenes with molecular oxygen and significantly lowered the reaction temperature in homogeneous systems. However, with respect to the catalytic oxygenation of methane with molecular oxygen in the presence of reductants in heterogeneous systems, only the $FePO_4$–O_2–H_2 system has been studied (26). Even in this system, temperatures as high as 623 K were required, much higher than those in homogeneous systems. We preliminarily reported that $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ is an active catalyst for the low-temperature oxidation of methane into formic acid in a H_2–O_2 gas mixture (29). However, little is known of the roles of the catalyst components for the reaction including the reaction mechanism.

In this study, we report how catalytic performance is changed by reaction conditions, kinds of metal additives, supports, and addenda atoms, and attempt to investigate the reaction mechanism.

EXPERIMENTAL

Heteropoly acids were commercially obtained from Nippon Inorganic Colour and Chemical Company, Ltd., and used after purification with ether extraction. The other reagents were analytical grade and used without further purification. Catalysts were prepared as follows: Aqueous solution of metal nitrates (0.08 mol dm^{-3}) was added dropwise to an aqueous solution of $H_{3+x}PV_xMO_{12-x}O_{40}$ ($x = 0-4$; 0.06 mol dm^{-3}) followed by addition of aqueous solution of cesium carbonate (0.08 mol dm^{-3}) at 323 K. The resulting suspension or solution was evaporated to dryness at 323 K.

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0021-9517/01 $35.00

TABLE 1

Surface Areas and Acidity of Supports

Support	BET surface area ($m^2\ g^{-1}$)	Acid amount ($\mu mol\ g^{-1}$)	Temperature range of NH_3 desorption (K)
SO_4^{2-}/ZrO_2	110	148	383–823
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	14	102	393–773
γ-Al_2O_3	170	420	383–773
SiO_2	250	0	—
MgO	110	0	—

The actual composition may be $Cs_qM_{0.08}H_yPV_xMo_{12-x}O_z$, but in this paper it is designated as $Cs_qM_{0.08}H_{2.84+x-q}PV_xMo_{12-x}O_{40}$ according to the stoichiometry of the starting materials. Al_2O_3 (JRC-ALO4), MgO, SiO_2, and Pd/C were obtained from the Catalysis Society of Japan, Ube Industries, Ltd., Fuji Sylisia Chem., Ltd., and N.E. Chemcat Company, respectively. Surface areas and acid amounts of the supports are summarized in Table 1. Pd/SO_4^{2-}/ZrO_2 was prepared as follows: $Zr(OH)_4$, which was obtained by the hydrolysis of $ZrOCl_2$ solution by NH_3, was impregnated by aqueous solution of $PdCl_2$ followed by drying at 383 K. The resulting solid was treated with aqueous solution of H_2SO_4 (1 N) with stirring at 323 K for 1 h followed by drying at 383 K and calcination at 833 K for 2 h in air. Al_2O_3, SiO_2, and MgO were impregnated with aqueous solution of $Pd(NO_3)_2$ by the incipient wetness method. The amounts of Pd loaded were 0.33 wt% in agreement with that of $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$.

The reaction was performed in a flow reactor at applied temperatures of 423–593 K under atmospheric pressure. The feed gas consisted of 28 vol% methane, 33 vol% H_2, 14 vol% O_2, and N_2 balance, unless otherwise stated. The total flow rate was 22 $cm^3\ min^{-1}$. Prior to each reaction, 120 mg of as-prepared catalyst was treated in O_2 (60 $cm^3\ min^{-1}$) for 1 h at 573 K. Pd/C was pretreated in H_2 (50 $cm^3\ min^{-1}$) for 1 h at 573 K. The gases at the outlet of the reactor were taken out intermittently with the aid of a sampler directly connected to the system and analyzed by a gas chromatograph equipped with a methanizer. Product gases of formic acid, methanol, CO, and CO_2 were separated with a Porapak QS column, converted to methane with the methanizer, and analyzed with a flame ionization detector (FID) kept at 473 K. Selectivity was calculated on C1 (methane) basis.

Acidic properties of catalysts were measured by temperature-programmed desorption (TPD) of NH_3. Catalysts (80 mg) were treated in He for 2 h at 573 K, and NH_3 was adsorbed at a partial pressure of 1.33 kPa and 373 K. After excess ammonia was flushed in He for 1 h at 373 K, the sample was heated to 1073 K at the rate of 10 K min^{-1}. The gases desorbed were analyzed with a quadrupole mass spectrometer. The TPD spectra for NH_3 were obtained from mass numbers (m/z) of 16 and 17. Amounts of acid sites were estimated with those of NH_3 desorbed.

Brunauer–Emmett–Teller (BET) surface areas were measured by means of N_2 adsorption using Coulter Omnisorp 100MP. After use for the oxidation reaction, the catalyst was evacuated at room temperature, and then the surface area was measured again. Just before and after the catalytic reaction, the change in surface area was within ±10%. The infrared spectra of KBr pellets were recorded on a Perkin–Elmer Paragon 1000PC spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a powder X-ray diffractometer (MAC Science Co., MXP^3) using Cu$K\alpha$ radiation.

RESULTS

Oxidation of Methane

Figure 1 shows the time course of the oxidation of methane catalyzed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst at 573 K. Conversion and selectivity reached almost constant values after 2 h. Similarly, the conversion and selectivity for the other catalysts reached constant values after 2–5 h. Therefore, the conversion and selectivity data were collected after 2–5 h of reaction, when nearly steady-state conversion and selectivities were obtained for each catalyst. The products were formic acid (HCOOH), methanol (CH_3OH), CO, and CO_2, and the same products were observed for each catalyst.

Dependencies of partial pressures of O_2 and H_2 on rates of CH_4 conversion were investigated in the ranges 0–28 and 0–48 kPa, respectively. The results are shown in Figs. 2a and 2b, respectively. The rates of CH_4 conversion increased linearly with increases in the partial pressure of O_2 or H_2, showing approximately first-order dependency on the partial pressures of O_2 and H_2. As shown in Fig. 2c, conversions

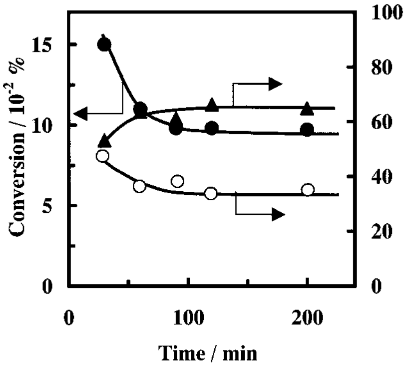

FIG. 1. Time course of the oxidation of methane catalyzed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst at 573 K. ●, ▲, ○ represent conversion of methane and selectivities to formic acid and CO_x, respectively.

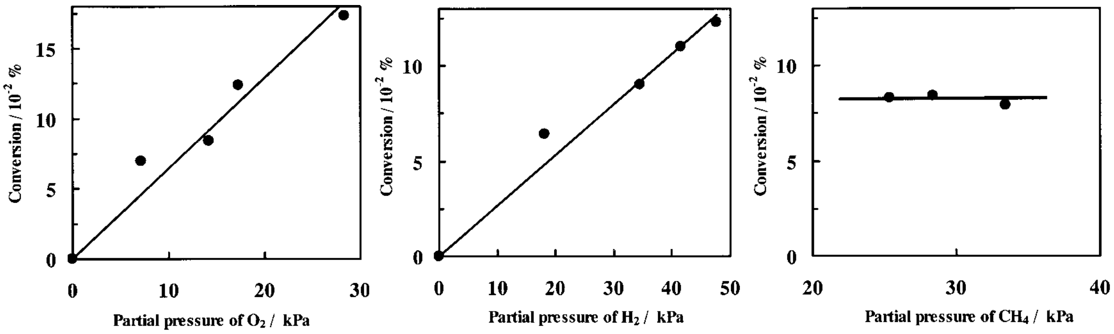

FIG. 2. Dependencies of rates on partial pressures of oxygen, hydrogen, and methane. Catalyst, $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$; reaction temperature, 573 K. (a) Dependency on partial pressure of oxygen. Partial pressures of H_2 and CH_4 were maintained at 33 and 28 kPa, respectively. (b) Dependency on partial pressure of hydrogen. Partial pressures of O_2 and CH_4 were maintained at 14 and 28 kPa, respectively. (c) Dependency on partial pressure of methane. Partial pressures of O_2 and H_2 were maintained at 14 and 33 kPa, respectively.

of methane at 573 K were 0.083, 0.084, and 0.079% at partial pressures of 25, 28, and 33 kPa, respectively, showing first-order dependency of rates on partial pressure of methane. With an increase in catalyst amounts up to 0.12 g, the conversion almost linearly increased, while the selectivity to HCOOH did not change much. Then, the conversion was decreased at a catalyst weight of 1.2 g.

Figure 3 shows the temperature dependency of the conversion and selectivity for $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst. Noted that the reaction proceeded even at 423 K. Conversion of methane monotonously increased with increase in the reaction temperature and reached a maximum at 573 K. The rate for methane conversion at 573 K was 1.2×10^{-4} mol h^{-1} g^{-1}, ca. 300 times greater than that of $FePO_4$ reported to be active for this reaction (25). The highest yield of HCOOH was also obtained at 573 K. $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ also catalyzed the oxidation of ethane into acetic acid under the same conditions: The conversion was 1.2% and the selectivities to acetic acid, ethene, and CO_2 were 25, 14, and 61%, respectively. No selective oxidation proceeded with a gas mixture of CO–O_2.

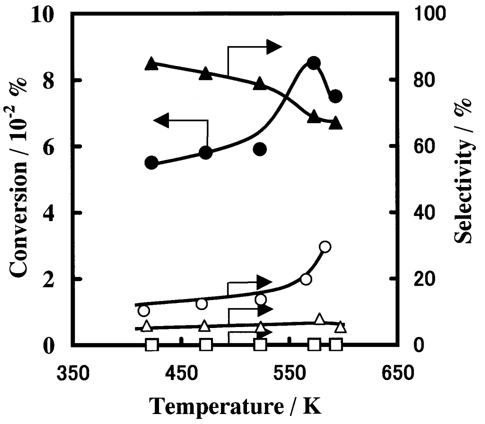

FIG. 3. Temperature dependency of conversion and selectivity for $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst. ●, ▲, □, △, and ○ represent conversion of methane and selectivities to formic acid, methanol, CO, and CO_2, respectively.

Effects of Steam

Effects of steam on the oxidation of methane catalyzed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst were investigated. The results are summarized in Table 2. With an increase in the partial pressure of steam (P_{H_2O}), the conversion of methane decreased, while the selectivity to HCOOH showed a maximum of 85% at 9 kPa. The highest yield of HCOOH was obtained at a P_{H_2O} of 9 kPa. Thus, it was revealed that the presence of a small amount of steam promoted the formation of HCOOH.

Effects of V Substitution

HCOOH yield was increased by V^{5+} substitution. The results are shown in Fig. 4. The conversions for $Pd_{0.08}Cs_{2.5}H_{0.34+x}PV_xMo_{12-x}O_{40}$ ($x = 0$, 1, 2 and 3) catalysts were 0.08, 0.08, 0.10, and 0.14%, respectively, and increased with V^{5+} substitution. The selectivities to HCOOH were 46, 70, 76, and 60% for $x = 0$, 1, 2, and 3, respectively, and the highest selectivity to HCOOH was observed at $x =$ ca. 2. It follows that the substitution of V^{5+} for Mo^{6+} in $Pd_{0.08}Cs_{2.5}H_{0.34}PMo_{12}O_{40}$ resulted in the enhancement of HCOOH production and the yield reached a maximum at $x = 2$–3.

TABLE 2

Effect of Steam on Oxidation of Methane at 573 K Catalyzed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ Catalyst

Partial pressure of H_2O (kPa)	Conversion (10^{-2}%)	Selectivity (%)		Yield of HCOOH (10^{-2}%)
		HCOOH	CO_x	
0.0	8.4	69	31	5.8
9.1	7.7	85	15	6.5
18.2	5.3	68	32	3.6

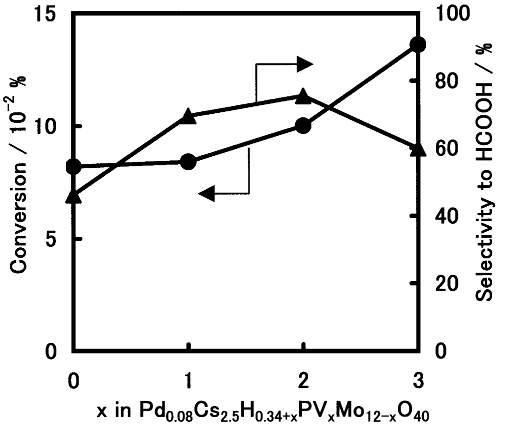

FIG. 4. Effect of V^{5+} substitution for Mo^{6+} in $Pd_{0.08}Cs_{2.5}H_{0.34}PMo_{12}O_{40}$ catalyst on the oxidation of methane at 573 K.

Effects of Addition of Metal Ions

Effects of the addition of various transition metal ions were studied for $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$-based catalysts at 473–573 K, keeping the amounts of transition metals constant ($x = 0.08$). The results at 473 K are listed in Table 3. Without transition metal additives, no reaction proceeded. Among transition metal ions tested, Pd^{2+}-, Pt^{2+}-, and Rh^{2+}-added catalysts exhibited high selectivity to HCOOH and the Pd^{2+}-added catalyst showed the highest yield to HCOOH, while selective oxidation products were hardly observed for the other transition metal ion-added catalysts. Similar results were obtained at 573 K: Yields of HCOOH for Pd^{2+}- and Pt^{2+}-added catalysts were 0.038 and 0.054%, respectively, and higher than those (trace and 0.020%) for Fe^{3+}- and Mn^{2+}-added catalysts.

Effects of Supports

Effects of supports such as SO_4^{2-}/ZrO_2, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, Al_2O_3, C, SiO_2, and MgO on the selective oxidation of methane were studied. The results at 473 K are summarized in Table 4. The catalytic activity depended on the kinds of supports and decreased in the order $SO_4^{2-}/ZrO_2 > Cs_{2.5}H_{0.5}PMo_{12}O_{40} > Al_2O_3 \geq C \approx SiO_2 \geq MgO$. A similar order was observed for the catalytic activity at 573 K.

TABLE 3

Effects of Addition of Transition Metal Ions (M^{n+}) to $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ on Oxidation of Methane at 473 K

M	Conversion (10^{-2}%)	Selectivity (%) HCOOH	CH_3OH	CO	CO_2	Yield of HCOOH (10^{-2}%)
H^+	0.0	0	0	0	0	0.0
Pd^{2+}	8.7	75	0	5	20	6.5
Rh^{2+}	4.1	66	0	17	17	2.7
Ru^{2+}	15.6	2	0	95	3	0.3
Pt^{2+}	6.7	83	2	0	15	5.6
Mn^{2+}	6.0	3	0	89	8	0.2
Hg^{2+}	4.4	0	0	90	10	0.0
Fe^{3+}	6.3	1	0	90	8	0.1
Co^{2+}	6.2	3	0	88	9	0.2
Cu^{2+}	4.9	3	0	84	13	0.1

TABLE 4

Effects of Supports on Oxidation of Methane at 473 K

Catalyst	BET surface area ($m^2\ g^{-1}$)	Conversion (10^{-2}%)	Yield (10^{-2}%) HCOOH	CO	CO_2
$Pd^{2+}/SO_4^{2-}/ZrO_2$	120	11	4.3	1.4	5.0
$Pd^{2+}/Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	15	9	6.5	0.4	1.8
Pd^{2+}/γ-Al_2O_3	180	6	5.5	0.0	0.8
Pd^{2+}/C	1100	6	4.6	0.0	1.0
Pd^{2+}/SiO_2	330	6	4.9	0.0	0.7
Pd^{2+}/MgO	110	5	4.6	0.0	0.0

Oxidation of Methane with Hydrogen Peroxide

The oxidation of CH_4 with H_2O_2 was carried out using the flow system. H_2O_2 (30 wt% aqueous solution) was fed with a mixture of CH_4 and N_2 to $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ catalyst by a microfeeder. The results are shown in Table 5. No products were observed for a gas mixture of CH_4 and O_2 or H_2 (runs 1 and 2), while the addition of H_2O_2 produced HCOOH and CH_3OH (run 3), and this was also the case when a H_2–O_2 gas mixture was used as oxidant (run 4). When H_2O_2 was cofed with H_2 (run 5), the conversion of CH_4 increased compared with that in run 3, and this was also the case when H_2O_2 was cofed with a H_2–O_2 gas mixture (run 7) compared with that in run 6. The increase in the presence of H_2 may be caused by the reduction of catalyst surface as has been suggested (26). The color of the H_2-cofed catalyst was more greenish than the color of the catalyst without H_2, showing deeper reduction, supporting the idea.

TABLE 5

Effects of Oxidants on Oxidation of Methane at 573 K Catalyzed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ Catalyst

Run	Oxidant[a]	Conversion (10^{-2}%)	Selectivity (%) HCOOH	CH_3OH	CO_x
1	$O_2 + H_2O$	0.0	—	—	—
2	$H_2 + H_2O$	0.0	—	—	—
3	$H_2O_2 + H_2O$	7.5	49	13	38
4	$H_2 + O_2 + H_2O$	7.7	85	0	15
5	$H_2 + H_2O_2 + H_2O$	11.4	62	11	27
6	$O_2 + H_2O_2 + H_2O$	7.1	35	11	55
7	$H_2 + O_2 + H_2O_2 + H_2O$	10.9	43	12	45

[a] H_2O, 9 kPa; H_2O_2, 1.5 kPa; H_2, 33 kPa; O_2, 14 kPa.

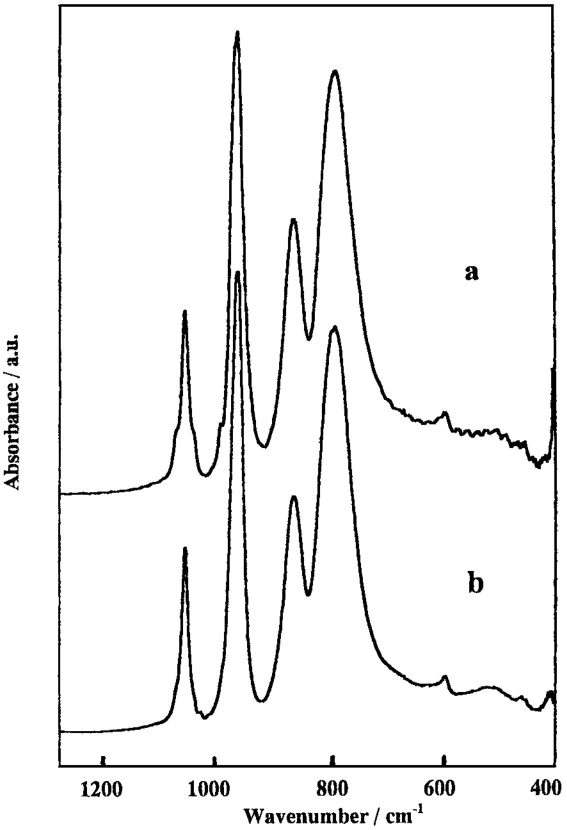

FIG. 5. Infrared spectra of $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ catalyst before (a) and after (b) the oxidation of methane at 573 K.

Stability of $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ Catalyst

To confirm the structure change of $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ catalyst during the reaction, IR spectra and XRD patterns were measured before and after the reaction. The IR results are shown in Figs. 5a and 5b. The IR spectrum before the reaction showed intense bands at 1060 cm^{-1} (with a shoulder at 1075 cm^{-1}), 964 cm^{-1}, 864 cm^{-1}, and 800 cm^{-1}, characteristic of Keggin structure. The bands are assigned to ν(P–O), ν(Mo=O), ν(Mo–O–Mo) (corner-sharing), ν(Mo–O–Mo) (edge-sharing), by analogy with assignments for $PMo_{12}O_{40}^{3-}$ Keggin anion (30). The IR spectrum did not change after the reaction except for a slight decrease in the intensities of the 864- and 800-cm^{-1} bands. The decrease is probably due to the reduction of Mo^{6+} to Mo^{5+}, as described in the previous section. The presence of V in the structure leads to a decrease in the symmetry of the PO_4 tetrahedron and then to a splitting of the ν(P–O). A shoulder at 1075 cm^{-1} observed for the fresh catalyst (Fig. 5a) disappeared after the catalytic reaction (Fig. 5b), showing that vanadium ion is eliminated from the polyanion structure according to Refs. (31–33).

The XRD pattern for $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ catalyst before the reaction showed a cubic structure, and no changes were observed after the oxidation of methane. No signals due to PdO ($2\theta = 33.8°$), Pd^0 ($2\theta = 39.9°$), and V_2O_5 ($2\theta = 20.3°$) were observed before and after the reaction. This suggests high dispersion of Pd and V.

DISCUSSION

As shown in runs 1, 2, and 4 in Table 5, feed of a H_2–O_2 gas mixture produced oxygenated products, while selective oxidation products were not obtained with O_2 or H_2 alone. This indicates that the coexistence of O_2 or H_2 is indispensable to the progress of selective oxidation of methane. The selective oxidation products were also observed when H_2O_2 was used as oxidant as shown in run 3 in Table 5, suggesting that an active oxygen species is H_2O_2 or H_2O_2-derived species. It has been reported that precious metal ions such as Pd^{2+} and Pt^{2+} were active for reaction of H_2 and O_2 to form H_2O_2 (24, 34–37). As shown in Table 2, these metal ions, Pd^{2+}, Pt^{2+}, and Rh^{2+}, were also effective additives for production of HCOOH and CH_3OH. The agreement of active catalysts for the production of H_2O_2 with those for the production of HCOOH and CH_3OH with H_2 and O_2 supports the idea that an active oxygen species is formed from H_2O_2. It has also been reported that the presence of strong protonic acids enhances H_2O_2 production by Pd. As shown in Table 1, the acid strength the supports decreased in the order $SO_4^{2-}/ZrO_2 > Cs_{2.5}H_{0.5}PMo_{12}O_{40} \approx Al_2O_3 \gg C, SiO_2, MgO$. The order is in fair agreement with that of catalytic activity in Table 4, also supporting the idea. The acid amounts of SO_4^{2-}/ZrO_2, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, and Al_2O_3 were 148, 102, and 420 μmol/g, respectively, and were not related to catalytic activity. The aforementioned results show that an active oxygen species with a H_2–O_2 gas mixture is H_2O_2 or H_2O_2-derived species, as has been reported for Fe–Al–P–O catalyst (26). The decrease in the conversion above 573 K in Fig. 3 may be due to decomposition of H_2O_2 or H_2O_2-derived species.

It has been reported that monoperoxovanadate is formed by reaction of VO_2^+ with H_2O_2 in acidic solution and active for selective oxidation of methane (38). The enhancement with V^{5+} substitution in Fig. 4 may be due to the formation of monoperoxovanadate. A decrease in rate with an increase in catalyst weight is probably due to some contribution of a radical path. It has been reported that a peroxovanadium radical is active for selective oxidation of methane (38).

On the basis of the above results, we tentatively propose a reaction scheme:

$$H_2 + O_2 \underset{\text{heteropoly compound}}{\underset{\text{Pd+acidic sites of}}{\rightleftarrows}} \underset{(H_2O_2 \text{ or } H_2O_2\text{-derived species})}{\text{active oxygen species}}$$

$$\xrightarrow{CH_4} HCOOH,\ CH_3OH$$

The first step is the reaction of H_2 with O_2 to form an active oxygen species catalyzed by Pd with acidic sites on the heteropoly compound. The second step is probably catalyzed mainly by the heteropoly compound. The activity of $Cs_{2.5}H_{1.5}PVMo_{11}O_{40}$ for oxidation of methane with H_2O_2 was almost the same as that of Pd^{2+}-added catalyst ($Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$), supporting the idea. The rate-determining step may be the reaction of an active oxygen species with methane. Dependencies of rates of methane conversion are expressed by $-P_{\mathrm{CH}_4}/dt = kP_{\mathrm{H}_2}^{1.0}P_{\mathrm{O}_2}^{1.0}P_{\mathrm{CH}_4}^{1.0}$ under reaction conditions generally used and the rate equation is consistent with the idea.

ACKNOWLEDGMENTS

We acknowledge Professor T. Kudo (University of Tokyo) for his encouragement of this work. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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