Low-temperature oxygenation of methane into formic acid with molecular oxygen in the presence of hydrogen catalysed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$

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The title reaction is catalysed by $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ at temperatures as low as 423–593 K, and the catalytic rate, which reached a maximum at 573 K, is 1.2×10^{-4} mol h^{-1} g^{-1}, *ca.* 3×10^2 times higher than $FePO_4$, the most active catalyst previously reported.

The activation and functionalization of methane has attracted much attention owing to its abundance in natural gas and low reactivity.[1–8] Recently, there has been a renewed interest in the direct conversion of methane into oxygenates.[6–19] Various catalysts have been tested with a variety of oxidants in heterogeneous[9–17] and homogeneous systems.[18–20]

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 the high temperatures and pressures required, which induce radical formation, needed for the activation of methane and/or oxygen leads to overoxidation of the oxygenated products. Therefore, a lowering of the reaction temperature is a key requirement for selective oxidation. We have reported the direct oxidation of lower alkanes with molecular oxygen catalysed by heteropoly compounds, but oxidation of methane was unsuccessful.[21]

On the other hand, reductants such as aldehyde,[22] hydrogen[23] and zinc[24] promoted the oxidation of alkanes and alkenes with molecular oxygen and significantly lowered the reaction temperature in homogeneous systems. However, concerning catalytic oxygenation of methane with dioxygen in the presence of reductants in heterogeneous systems, only the $FePO_4$–O_2–H_2 system has been studied;[15] Even in this system, a temperature as high as 623 K was required which is much higher than for homogeneous systems. Here we report the selective oxygenation of methane into formic acid with a O_2–H_2 mixture at temperatures as low as 423–593 K.

$H_{3+x}PV_xMo_{12-x}O_{40}$ heteropolyacids were obtained commercially from Nippon Inorganic Colour and Chemical Co., Ltd. The other reagents used were of analytical grade and used without further purification.

The catalysts were prepared as follows: 3.6 cm^3 of an aqueous solution of palladium nitrate (0.08 mol dm^{-3}) was added dropwise to 60.0 cm^3 of an aqueous solution of $H_4PVMo_{11}O_{40}$ (0.06 mol dm^{-3}), followed by the addition of 56.3 cm^3 of an aqueous solution of caesium carbonate (0.08 mol dm^{-3}) at 323 K and the powder samples were carefully collected and the resulting suspension evaporated to dryness at 323 K. The actual composition of the powder is $Pd_{0.08}Cs_{2.5}H_yPVMo_{11}O_z$, but are designated $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ according to the stoichiometry of the starting materials.

Catalytic reactions were performed in a flow reactor. Prior to the reaction, 120 mg of catalyst was treated in an O2 stream (60 cm^3 min^{-1}) for 1 h at 573 K. The reactions were performed at atmospheric pressure and the feed gas typically consisted of 28 vol% methane, 14 vol% O_2 with the balance N_2, and the total flow rate was 22 cm^3 min^{-1}. The gases at the outlet of the reactor were analysed by FID (equipped with methanizer) and a TCD gas chromatograph. Selectivity was calculated on the C_1 (methane)-basis. The products were formic acid, methanol and CO_x. Similar products were observed for the other heteropoly catalysts used. The conversion and the selectivity data were collected after 2–5 h of reaction, when nearly steady-state conversion and selectivity were obtained for each catalyst.

Fig. 1 shows the temperature dependency of the conversion and selectivity for $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$. It is noted that the reaction proceeded even at 423 K. The conversion of methane monotonously increased with increase in the reaction temperature and reached a maximum at 573 K. The rate for the methane conversion at 573 K was 1.2×10^{-4}, *ca.* 3×10^2 greater than that of the most active heterogeneous catalyst ($FePO_4$) reported previously.[15] The selectivity to formic acid was $> 67\%$. Such high selectivity towards formic acid has not been reported previously in heterogeneous oxidation of methane.[1–8] The highest yield of formic acid was obtained at 573 K. $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$ also catalysed the oxidation of ethane into acetic acid under similar conditions. Similar conversion and selectivity with reaction temperature were observed for $Pd_{0.08}Cs_{2.5}H_{3.34}PV_3Mo_9O_{40}$.

An increase in the yield of formic acid was achieved by further V^{5+}-substitution. 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) were 0.08, 0.08, 0.10 and 0.14%, respectively and increased with V^{5+} substitution. The selectivities to formic acid were 46, 70, 76 and 60% for $x = 0$, 1, 2 and 3, respectively, and the highest selectivity to formic acid 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 formic acid production and the yield reached a maximum at $x = 2$–3.

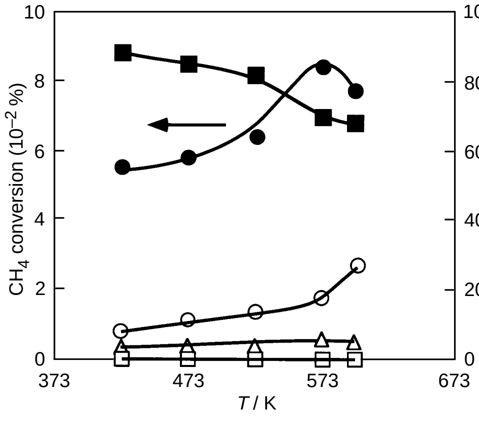

Fig. 1 Temperature dependence of conversion and selectivity; catalyst, $Pd_{0.08}Cs_{2.5}H_{1.34}PVMo_{11}O_{40}$. Conversion of methane (●) and selectivities towards formic acid (■), methanol (□), CO (△) and CO_2 (○).

No selective oxidation proceeded in the absence of Pd or when carbon monoxide was used instead of hydrogen. The addition of 1.9 vol% hydrogen peroxide instead of a gaseous mixture of H_2 and O_2 led to similar conversion and selectivity to oxygenates. This suggests that the active oxygen species arises from hydrogen peroxide formed by an H_2–O_2 reaction catalysed by Pd. Reports that Pd in acidic medium catalyses the reaction of dioxygen with dihydrogen to form hydrogen peroxide,[25] and the fact that heterpolyacids and their caesium salts are strongly acidic[26] supports this hypothesis. Formic acid is formed by the liquid-phase oxidation of methane with hydrogen peroxide catalysed by $H_4PVMo_{11}O_{40}$;[27] this suggests that successive oxidation of methane *via* hydrogen peroxide can be catalysed by heteropolyacids.

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Footnote

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