Oxidative carbonylation of methane to methyl acetate on a rhodium-doped iron phosphate catalyst

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The carbonylation of methane with carbon monoxide in the presence of nitrous oxide produces methyl acetate on a rhodium-doped iron phosphate catalyst under atmospheric pressure and at 573–673 K.

Methane is the main constituent of the abundant natural gas resources. The direct transformation of methane to more useful chemicals or liquid fuels has long been a desirable goal for chemists. However, because methane is a very unreactive molecule, the conversion of methane to useful chemicals has proven to be a great challenge. Although there are many reports of the functionalisation of methane, the most viable process and effective catalyst are still unsettled.[1–5] Recently, we have reported that the conversion of methane is enhanced and methanol is selectively produced by co-feeding a reductant such as hydrogen over an iron phosphate ($FePO_4$) catalyst.[6–8] When nitrous oxide is used as an oxidant in the presence of hydrogen, methane can be selectively converted into methanol with high selectivity at moderate temperatures (*ca.* 620 K).[8] If carbon monoxide is used as the reductant instead of hydrogen, we can expect that the activated carbon monoxide may react with the methanol produced or with reaction intermediates such as methyl species to form acetic acid or methyl acetate. The wasteful consumption of the co-feeding reductant, which is a common problem for many biomimetic monooxygenase catalytic systems, may thus be overcome. Acetic acid is a very important chemical and is produced mainly by the carbonylation of methanol as typically demonstrated in the Monsanto process. If acetic acid or its derivatives such as methyl acetate can be produced directly from methane, the impact on the chemical industry would be significant because the production cost of many chemical products based on acetic acid will become remarkably cheaper. Reports concerning the direct carbonylation of methane to acetic acid are very scarce[9–11] and all these studies have been performed using a high pressure ($>$ 20 bar) liquid-phase reaction system. The use of expensive reagents such as $FHSO_3$–SbF_5,[9] $K_2S_2O_8$[10] and I^- or perfluorobutyric acid[11] is required in these complicated systems. Furthermore, the separation of these expensive reagents or catalysts such as $RhCl_3$ from the solvents is another drawback for these homogeneous reaction systems. Therefore, a simple heterogeneous catalytic system would be more desirable and promising. This communication is the first contribution to attempt direct carbonylation of methane using a simple heterogeneous catalytic system.

The experiments were carried out using a conventional fixed-bed flow reactor (quartz tube) operated at atmospheric pressure. The Rh-doped iron phosphate catalysts with various Rh content were prepared by mixing aqueous solutions of $RhCl_3$ or $Rh(NO_3)_3$, $Fe(NO_3)_3$ and $NH_4H_2PO_4$ and evaporating water from the resultant solution to obtain the catalyst precursors. The precursors were finally calcined at 823 K for 5 h in air. The catalysts were pretreated in an oxygen flow at 723 K in the reactor and the reaction was started by introducing the reactants CH_4, N_2O and CO. The outlet gases were bubbled into a water trap cooled with water/ice bath to collect the products, MeOH, $MeCO_2H$ and $MeCO_2Me$. These collected products were analysed by a FID-equipped gas chromatograph with acetonitrile as internal standard. Other components which could not be dissolved in the water trap were analysed by an on-line TCD-equipped gas chromatograph.

Fig. 1 compares the reaction results over $FePO_4$ and various metal-ion-doped $FePO_4$ catalysts at 648 K. Using pure $FePO_4$, a considerable amount of MeOH was formed. We have reported that oxygen species generated from the reductive activation of N_2O on iron sites are responsible for the activation of CH_4 at such a moderate temperature.[8] However, the carbonylation products, $MeCO_2H$ and $MeCO_2Me$ were not observed at all on $FePO_4$. This result indicates that another site for the effective activation of CO for the carbonylation is required on the catalyst surface. Thus, many additives have been incorporated into $FePO_4$ to enhance the ability for the activation of CO for the carbonylation. The results in Fig. 1 suggest that rhodium is very specific for the formation of $MeCO_2Me$. Instead of $FePO_4$, a large variety of materials including SiO_2, Al_2O_3, H-ZSM-5, Ga-H-ZSM-5, H-mordenite, active carbon, SO_4^{2-}/ZrO_2, MoO_3 and V_2O_5 were also used as bases for rhodium. However, none of

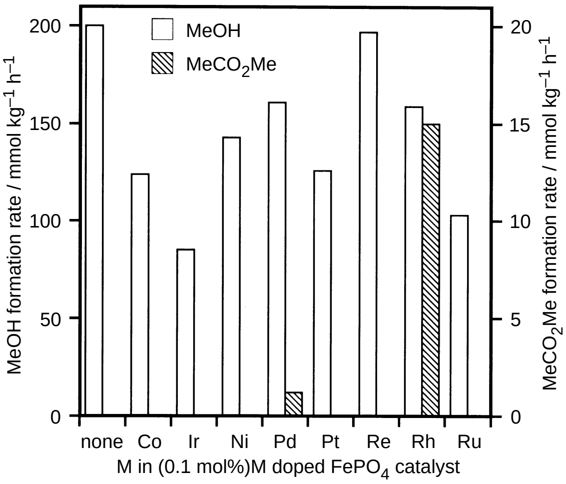

Fig. 1 Oxidative carbonylation of methane over various metal-ion-doped $FePO_4$ catalysts. *Reaction conditions*: T = 648 K, $P(CH_4)$ = P(CO) = 25.3 kPa, $P(N_2O)$ = 12.7 kPa, W = 0.2 g, F = 80 ml min^{-1}.

Table 1 Effect of rhodium content on the formation of methyl acetate from methane[a]

Rh content (%)	Formation rate/ mmol g^{-1} h^{-1} MeOH	Formation rate/ mmol g^{-1} h^{-1} $MeCO_2Me$	CO conv. (%)
0	200.5	0	2.5
0.1	125.5	16.0	2.2
0.3	113.0	26.5	4.3
0.5	92.0	28.5	2.5
1.0	90.0	21.2	2.5
2.0	126.7	18.3	2.8

[a] *Reaction conditions*: T = 648 °C, $P(CH_4)$ = P(CO) = 25.3 kPa, $P(N_2O)$ = 12.7 kPa, total flow rate = 80 ml min^{-1}.

them showed activity for the carbonylation of CH_4. Therefore, $Rh/FePO_4$ is a unique catalyst. Further detailed studies were thus carried out using the $Rh/FePO_4$ catalyst.

In order to increase the rate of the carbonylation reaction, catalysts with various mol% Rh were investigated. As shown in Table 1, an increase in Rh content up to 0.5% increased the formation rate of $MeCO_2Me$ at the expense of MeOH. For the Rh (0.5%)/$FePO_4$ catalyst, the formation rate of $MeCO_2Me$ reached *ca*. one third of that of MeOH. Further increase of Rh content decreased the formation rate of $MeCO_2Me$ as well as the ratio of $MeCO_2Me$ to MeOH. This fact probably indicates that highly dispersed Rh^{3+} on the surface of $FePO_4$ is responsible for the carbonylation reaction.

Naturally, the conversion of CO shown in Table 1 was mainly ascribed to the formation of CO_2. Only 1–5% of CO converted took part in the carbonylation reaction. Table 1 shows that the conversion of CO is not changed appreciably by the addition of Rh to $FePO_4$. This result suggests that the direct oxidation of CO into CO_2 occurs mainly on the host $FePO_4$.

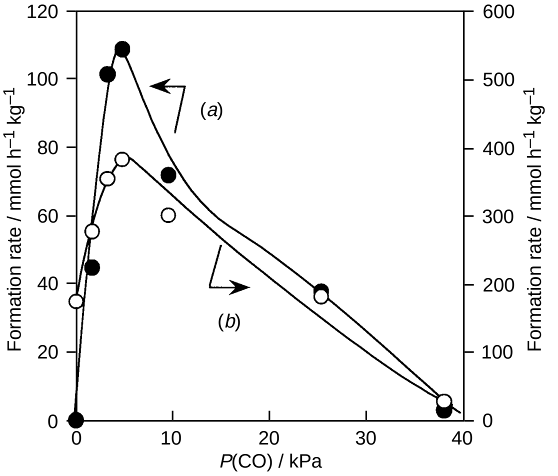

Fig. 2 Effect of CO pressure on the formation of MeOH and $MeCO_2Me$ on Rh (0.5%)/$FePO_4$ catalyst. (*a*) $MeCO_2Me$, (*b*) MeOH. *Reaction conditions*: T = 648 K, $P(CH_4)$ = $P(N_2O)$ = 25.3 kPa, W = 0.2 g, F = 160 ml min^{-1}.

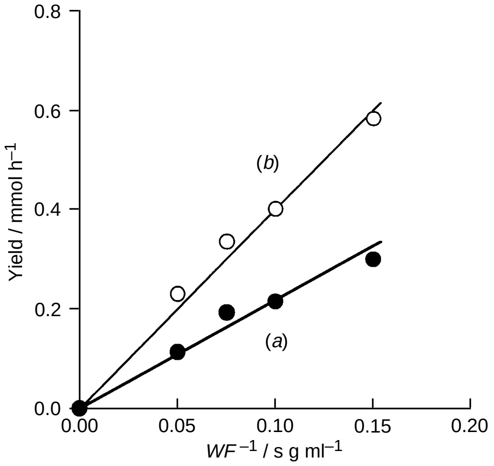

Fig. 3 Effect of WF^{-1} on the formation of MeOH and $MeCO_2Me$ on Rh (0.5%)/$FePO_4$ catalyst. (*a*) $MeCO_2Me$, (*b*) MeOH. *Reaction conditions*: T = 648 K, $P(CH_4)$ = $P(N_2O)$ = 25.3 kPa, F = 300 ml min^{-1}.

Fig. 2 shows the effect of CO pressure on the carbonylation reaction over the Rh (0.5%)/$FePO_4$ catalyst. No $MeCO_2Me$ was produced in the absence of CO. The introduction of CO caused the formation of $MeCO_2Me$. It should be noted that MeOH was also remarkably increased at low partial pressures of CO [P(CO) < 5 kPa]. This result suggests that CO functions not only as a reactant in the carbonylation reaction but also as an activator for the conversion of CH_4. Probably, CO reduces Fe^{III} to Fe^{II} on the $FePO_4$ surface and the produced Fe^{II} site acts as the active site for the generation of the active oxygen species from N_2O.[6–8] On the other hand, higher pressures of CO are not favourable for the formation of both MeOH and $MeCO_2Me$. Competitive oxidation between CO and CH_4 with the active oxygen species must be the main reason.

Whether $MeCO_2Me$ is formed from the direct carbonylation of CH_4 or from the carbonylation of the produced MeOH is a key point in the reaction mechanism. Thus, the influence of WF^{-1} (weight of catalyst/flow rate) on the yields of MeOH and $MeCO_2Me$ has been investigated. As shown in Fig. 3, the yields of both MeOH and $MeCO_2Me$ increased almost linearly with increase in WF^{-1}. This result indicates that MeOH and $MeCO_2Me$ are formed in parallel from CH_4.

The results described above allow us to speculate on a reaction mechanism as follows. CH_4 must be activated by the active oxygen species generated on the iron site, producing an Me species as a transient intermediate. This Me species may easily be oxidized to an MeO species on the surface of $FePO_4$. It must also migrate and adsorb on a Rh site where CO is activated. The insertion of CO into Rh–Me may occur on this Rh site, producing Rh–COMe. $MeCO_2Me$ is then formed by the reaction of Rh–COMe with the MeO species produced on $FePO_4$ near this Rh site, while the addition of a proton (probably from OH groups) to the adsorbed MeO produces MeOH. According to this mechanism, the high dispersion of Rh at sites surrounded by iron sties is a key factor for the carbonylation reaction. Further confirmation of this mechanism and the design of catalysts with high concentration of Rh sites with surrounding iron sites are underway.

Footnote

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