Synthesis of Methyl Formate from Methanol over Metal Carbide Catalysts

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Catalytic decomposition of methanol has been studied on the transition metal carbides TiC, TaC, Mo_2C, W_2C, and WC; on WC methyl formate was produced with high selectivity (> 90%), whereas other catalysts produced mainly CO and H_2.

The dehydrogenation of methanol to produce methyl formate selectively is currently an important problem in heterogeneous catalysis in relation to C_1 chemistry and a great deal of research has been conducted into the catalysis of this reaction by metal and metal oxide surfaces. However, the catalysts for producing methyl formate with high selectivity (>~70%) always include copper in various forms: *e.g.* $CuO–ZnO–Cr_2O_3$, $CuO–MnO_2$, CuO–ZnO–Se, *etc.*[1]

It was found previously that when powdered metal carbides (300—350 mesh) such as TaC, TiC, W_2C, WC, HfC, ZrC, and Mo_2C were evacuated at high temperatures, they were catalytically activated and formed a group of new sinter-resist catalysts[2] for, *e.g.* the hydrogenation of benzene,[3] ethylene,[4] and carbon monoxide;[5] TiC, TaC, and Mo_2C produced hydrocarbons of higher molecular weight than methane in the hydrogenation of CO. In the present work, similar catalysts (TiC, TaC, Mo_2C, W_2C, and WC) have been used for studying methanol decomposition; WC is an excellent catalyst for producing methyl formate.

The metal carbide catalysts were activated as described previously[3] at 3×10^{-6} Torr (1 Torr = 133.3 Pa) at various high temperatures prior to the measurements. The reaction measurements were carried out in the temperature range 180—400 °C, with an initial pressure of methanol of up to 23 Torr using a conventional closed circulation system. The products were analysed by mass spectrometry and g.l.c.; *X*-ray photoelectron spectroscopy (X.P.S.) was used for studying the characteristics of the surfaces.

The kinetic results and product distributions for 20% conversion of methanol are summarized in Table 1. The activity of TiC was negligible below 300 °C whereas above 400 °C small amounts of CH_4 and H_2O were produced. TaC produced mainly CO and H_2 with a small amount of CO_2 and the product distribution did not depend on the temperature for activation of the catalyst. The activity gradually decreased with repeated use; as previously observed, this is due to the accumulation of graphite-like carbon which acts as a strong poison. The products on Mo_2C, however, varied with evacuation temperature; following evacuation at 800 °C the main products were CO, H_2, and methyl formate, but at 1000 °C they were CO and H_2. X.P.S. studies showed that on evacuation at 800 °C the peaks due to Mo 3d states are asymmetrical and appeared at E_b (binding energy) = 228.1 and 231.5 eV assigned to metallic Mo, along with shoulders at a higher E_b which can be assigned to the oxidized species. However, after evacuation at 1000 °C, the peaks due to the oxidized state were absent. The molar ratio Mo/C, calculated from the peak intensity, was found to be 4.8 and 5.5 for evacuation at 800 and 1000 °C, respectively suggesting that metallic Mo formed on the surface is more effective for the decomposition of methanol into CO and H_2. The main products on W_2C were CO, H_2, and methyl formate, but the selectivity for methyl formate was <30%. On the other hand, the selectivity for methyl formate formation on the WC catalyst was very high and comparable with that on the Cu ion exchanged catalyst recently found by Morikawa *et. al.*[6] The dependence of selectivity on conversion of methanol is shown in Figure 1; the selectivity is >90% for <10% conversions and extrapolation to zero conversions gives a value of nearly 100%, indicating that the initial products are solely methyl formate and hydrogen.

In order to investigate the mechanism for methyl formate formation on the WC catalysts, the kinetics of dehydrogenation of CH_3OH and CH_3OD were studied, with the following results. (i) The initial rate of the reaction (r_0) followed the

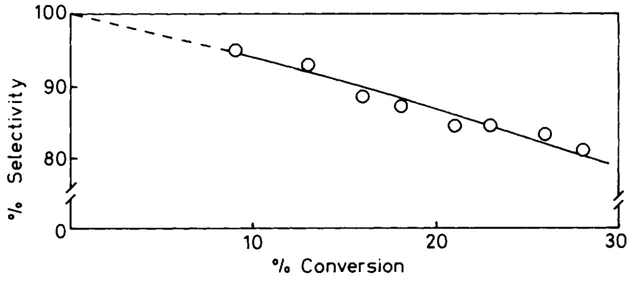

Figure 1. Selectivity for methyl formate production as a function of conversion of methanol.

Table 1. Kinetic results and product distributions for 20% conversion of methanol.

Catalysts	Evacuation temperature /°C	Reaction temperature /°C	Initial rate[a] of CH_3OH consumption /(molecule s^{-1} g^{-1})	% Distribution of carbon-containing products
TiC	1000	300	~0	—
TaC	1100	190	3.1×10^{17}	CO(91), CO_2(9)
Mo_2C	800	200	2.5×10^{17}	CO(59), HCO_2CH_3(41)
Mo_2C	1000	200	5.0×10^{17}	CO(100)
W_2C	1200	220	3.5×10^{17}	CO(83), HCO_2CH_3(17)
WC	900	200	1.5×10^{17}	HCO_2CH_3(81), CO(19)

[a] Methanol pressure 23 Torr.

relationship $r_0 = aP/(1 + bP)$, where a and b are constants and P is the pressure of methanol. (ii) When CH_3OD was used under the same conditions as for CH_3OH, non-deuteriated methyl formate (HCO_2CH_3) was predominantly produced at the initial stages of the reaction. These kinetic results are similar to those previously obtained for copper catalysts.[7] Thus, a similar mechanism *via* formaldehyde as an intermediate is strongly suggested, *i.e.* steps (I)—(III), with step (II), the dehydrogenation of adsorbed methanol to form formaldehyde, as the rate-determining step.

$$CH_3OH\ (g) \rightarrow CH_3OH\ (ads) \qquad (I)$$

$$CH_3OH\ (ads) \rightarrow H_2CO\ (ads) + H_2 \qquad (II)$$

$$2H_2CO\ (ads) \rightarrow HCOOCH_3 \qquad (III)$$

Thus, in their catalytic behaviour for methanol reactions, TaC resembles group 8 transition metals such as Ni,[8] whereas WC resembles metals such as Cu,[7] for reasons which are not clear at present.

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