Photoinduced Partial Oxidation of Methane into Formaldehyde on Silica-supported Molybdena

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Photoinduced partial oxidation of methane over silica-supported molybdena selectively gave formaldehyde at 463—493 K by using a fluidized bed reaction system under UV irradiation.

Although the photoinduced oxidation of various alkanes over a solid oxide surface has been well investigated,[1] surprisingly few attempts at the selective photo-oxidation of methane into valuable compounds have been successful.[2—4] Kaliaguine *et al.*[2] reported that hole centres O^- generated by γ-ray excitation abstract hydrogen from methane to form ethane and formaldehyde along with CO, but amounts of these products were extremely small.

In this communication, we report the selective formation of formaldehyde from methane by photo-oxidation under UV irradiation at an elevated temperature.

The supported molybdenum oxide catalyst (5 wt%) was prepared by impregnating finely powdered silica gel (Alpha, surface area 300 m^2/g) with an aqueous solution of ammonium heptamolybdate. The dried catalyst was calcined in a stream of air at 823 K for 2 h just before the reaction. The reaction was carried out for 2 h using an upstream flow type quartz reactor (Figure 1), which has a window for UV irradiation (11 × 20 mm; inner thickness 1 mm) covered with a quartz glass tube. A high-pressure mercury vapour lamp (200 W) was used for UV irradiation. The reactant gas mixture was passed through a preheater (623—823 K) in order to maintain the temperature of the fluidized catalyst bed. Formaldehyde and methanol were collected in a H_2O trap cooled by an ice bath. Products were analysed by gas chromatography (detection limit: carbon oxides ~0.002 vol%; HCHO and MeOH ~10 ppm).

Table 1 shows the results. We did not observe any traces of CO and CO_2 in the effluent gases. The reaction in the absence of a catalyst at a preheater temperature of 823 K did not afford any products (run 1).

While a silica support gave only a trace amount of HCHO,

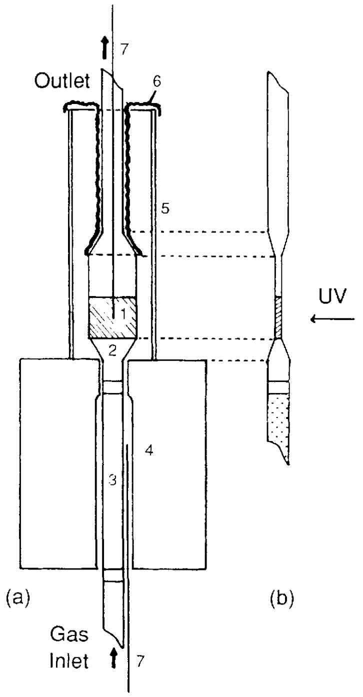

Figure 1. (a) Part of experimental apparatus for the photo-oxidation of methane; (b) side view of the quartz glass reactor: 1, fluidized catalyst bed; 2, silica sand (22—60 mesh); 3, silica sand (>22 mesh); 4, furnace; 5, quartz glass tube cover; 6, aluminium foil cover; 7, thermocouples.

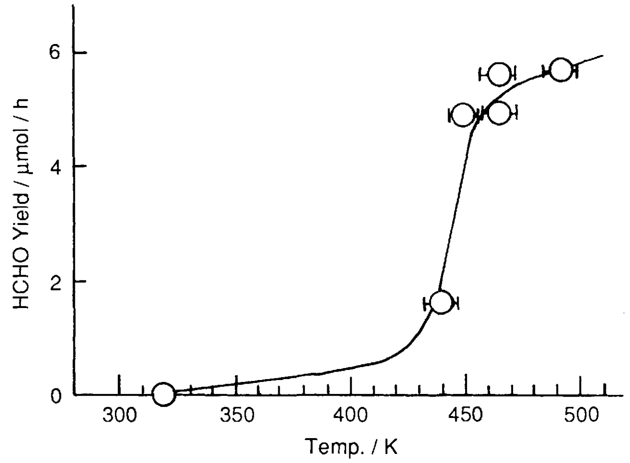

Figure 2. The formaldehyde yield over MoO_3 (5 wt%)/SiO_2 catalyst at various catalyst bed temperatures.

Table 1. Photo-oxidation of methane into formaldehyde.[a]

Run	Catalyst	Temp.[b] /K	Yield/μmol h^{-1} HCHO	Yield/μmol h^{-1} MeOH
1[c]	None	—	n.d.	n.d.
2	SiO_2[d]	463	trace	n.d.
3	MoO_3 (5 wt%)/SiO_2	463	4.9	0.2
4	MoO_3 (5 wt%)/SiO_2	493	5.8	0.2
5	MoO_3 (10 wt%)/SiO_2[d]	463	2.8	0.1
6[e]	MoO_3 (5 wt%)/SiO_2	523	n.d.	n.d.
7[f]	MoO_3 (10 wt%)/SiO_2[d]	463	trace	n.d.
8[g]	MoO_3 (5 wt%)/SiO_2	318	trace	n.d.

[a] Amount of catalyst = 25 mg, W/F = 0.62 g h mol^{-1}, space velocity = 10 000 h^{-1}, CH_4 feed rate = 7.4 mmol h^{-1}, $CH_4:O_2:He$ = 6:2:25, n.d. = not detected. [b] Temperature at the centre of the fluidized bed. [c] Preheater temp. 823 K. [d] Amount of catalyst = 50 mg, $CH_4:O_2:He$ = 2:3:17. [e] Without UV irradiation. [f] With Pyrex filter. [g] Without preheating.

the silica-supported molybdenum oxide catalyst afforded the highest yield of formaldehyde [5.8 μmol h^{-1}, 0.69 mol (mol Mo)$^{-1}$ h^{-1}] along with 0.2 μmol h^{-1} of methanol (run 4). The yields of HCHO and MeOH did not change during a prolonged run for 9 h at 463 K. Without UV irradiation the reaction did not take place even at 523 K (run 6). The reaction with UV irradiation through a Pyrex filter (run 7) suggests that a wavelength shorter than 300 nm is required to activate the MoO_3/SiO_2 catalyst.

Figure 2 shows the changes in the HCHO yield over the MoO_3/SiO_2 catalyst with variation in the catalyst bed temperature. A sharp increase in the HCHO yield was observed above 440 K, suggesting that HCHO formation requires a reaction temperature higher than 440 K. The colour of the catalyst, which was white before the reactant gas was introduced, became blue after reactions at temperatures below 440 K, whereas it remained white after reactions at higher temperatures.[2—4]

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