

## Partial Oxidation of Methane by Nitrous Oxide over Molybdenum Oxide supported on Silica

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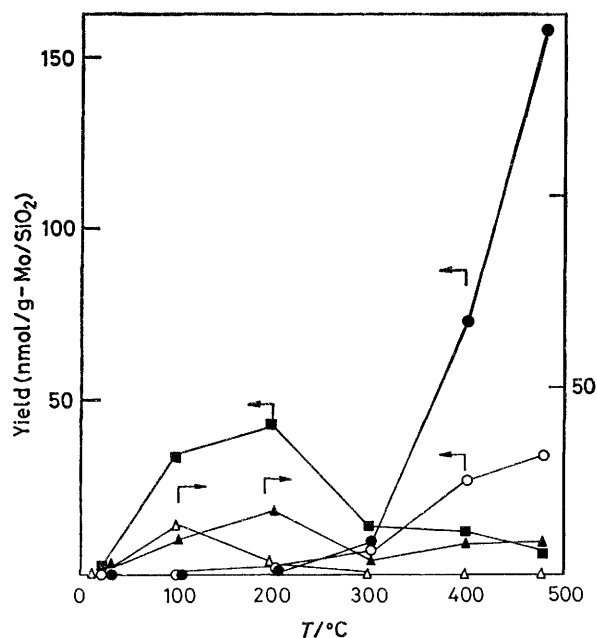
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Methanol and formaldehyde were formed as major products at a moderate conversion level (16%) in the partial oxidation of methane by nitrous oxide in the presence of water over molybdenum oxide supported on silica.

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The partial oxidation of methane by  $N_2O$  has been studied extensively,<sup>1</sup> principally in the gas phase. Little success has been achieved in obtaining methanol or formaldehyde in substantial amounts and the main products are  $CO$  and  $CO_2$

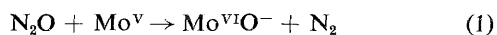
even at very low conversion levels. Recent reports<sup>2</sup> have demonstrated that  $N_2O$  is a very effective oxidant in the oxidative dehydrogenation of ethane over supported molybdenum oxides. The  $O^-$  ions, formed by surface decomposition



**Figure 1.** Yield of products as a function of the thermal desorption program following the reaction of  $\text{CH}_4$  with  $\text{O}^-$  at  $25^\circ\text{C}$ :  $\bullet$ ,  $\text{CH}_3\text{OH}$ ;  $\circ$ ,  $\text{CO}_2$ ;  $\blacksquare$ ,  $\text{CH}_4$ ;  $\blacktriangle$ ,  $\text{C}_2\text{H}_6$ ;  $\triangle$ ,  $\text{C}_2\text{H}_4$ .

of  $\text{N}_2\text{O}$ , have been postulated as active species in initiating the catalytic process *via* a hydrogen abstraction reaction. Recently e.s.r. studies by Kazanskii and coworkers<sup>3</sup> have shown that  $\text{O}^-$  reacts with methane over various supported metal oxides. In an attempt to understand the role of  $\text{O}^-$  in the partial oxidation of methane, we investigated both the stoichiometric reaction of  $\text{CH}_4$  with  $\text{O}^-$  and the catalytic oxidation of  $\text{CH}_4$  with  $\text{N}_2\text{O}$  over molybdenum oxide supported on silica.

The stoichiometric reaction of  $\text{CH}_4$  with  $\text{O}^-$  was studied in a conventional gas-circulating system with a catalyst prepared by impregnating silica gel with ammonium heptamolybdate at  $\text{pH} = 2$ . The catalyst which contained 6.6 wt. % Mo was calcined in air for 16 h at  $500^\circ\text{C}$ , heated in 100 Torr of  $\text{O}_2$  for 30 min at  $500^\circ\text{C}$ , heated *in vacuo* at  $500^\circ\text{C}$  and reduced in 100 Torr of  $\text{CO}$  at  $500^\circ\text{C}$  for 30 min. The partially reduced catalyst contained  $\text{Mo}^{\text{V}}$  on the surface, which upon exposure to  $\text{N}_2\text{O}$  gave  $\text{O}^-$  ions according to reaction (1).



The  $\text{O}^-$  ions, characterized by an e.s.r. spectrum having  $g_{\parallel} = 2.002$  and  $g_{\perp} = 2.019$ , reacted rapidly with  $\text{CH}_4$  at  $25^\circ\text{C}$  and more slowly at  $-196^\circ\text{C}$ . No new radicals were detected; however, the reaction products were followed by analysing the gas phase after desorption or decomposition of the surface species. These gas phase products were collected in a cold trap after heating the catalyst for 1 h increments at progressively higher temperatures. The amount of each product, as determined by gas chromatography, is shown in Figure 1. Methanol was observed as the main product at desorption temperatures exceeding  $300^\circ\text{C}$ .

The catalytic oxidation was followed in a continuous-flow reactor which was operated at 1 atm. The reactor contained 3 g of 1.7%  $\text{Mo}/\text{SiO}_2$  in a 23 mm i.d. Vycor tube, which was connected to a 2 mm i.d. tube so that the products  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$  could be quenched, thus reducing subsequent gas phase reactions. In the experiment, helium gas was used as a diluent and the flow rate was controlled at 1.33 ml/s.

**Table 1.** Conversion and selectivity during methane oxidation.

Mo/SiO <sub>2</sub> wt %	P/Torr			T /°C	Conv. /% <sup>a</sup>	Selectivity/% <sup>b</sup>			
	CH <sub>4</sub>	N <sub>2</sub> O	H <sub>2</sub> O			CH <sub>3</sub> OH	H <sub>2</sub> CO	CO	CO <sub>2</sub>
1.7	72	277	0	600	14.8	0.9	14.1	59.7	25.3
	72	277	93	600	16.5	13.7	18.1	51.6	16.6
	72	277	145	600	15.7	19.3	20.4	45.6	14.7
	72	277	195	600	15.6	28.0	20.1	40.2	11.7
	72	277	266	600	16.4	46.8	19.0	26.0	8.2
	72	277	266	580	12.5	55.1	23.9	15.6	5.4
	72	277	266	560	8.1	60.5	24.1	12.6	2.8
	6.6	72	277	266	560	12.7	34.2	20.4	39.6

<sup>a</sup> Conversions were calculated at steady state. <sup>b</sup> Trace amounts of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  were observed in all cases.

Water was introduced from a syringe pump and evaporated in a preheater oven. Results are summarized in Table 1. Under the experimental conditions, silica gel was an order of magnitude less active. The combined 60% selectivity to  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$  at 16% conversion is considerably better than results reported in the literature.<sup>4</sup> The 6.6 wt. %  $\text{Mo}/\text{SiO}_2$  catalyst gave qualitatively similar results, although selectivities for  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$  were less.

As shown in Table 1, water is required to maintain the selectivities for  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$ . The amounts of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$  increased with increasing amounts of water, and no decrease in activity has been observed in the presence of water. The role of water may be twofold. Pernicone *et al.*<sup>5</sup> reported that water retards the oxidation of  $\text{CH}_3\text{OH}$  to  $\text{H}_2\text{CO}$  by  $\text{O}_2$  over iron molybdate catalysts. The retardation effect by the water in the partial oxidation of  $\text{CH}_3\text{OH}$  by  $\text{N}_2\text{O}$  over  $\text{Mo}/\text{SiO}_2$  has also been observed in our laboratory;<sup>6</sup> thus, water may inhibit secondary reactions of both  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{CO}$ .

In addition, the stoichiometric results demonstrate that the reaction between  $\text{O}^-$  and  $\text{CH}_4$  on  $\text{Mo}/\text{SiO}_2$  catalysts leads to the formation of  $\text{CH}_3\text{O}^-$ . This may involve  $\text{CH}_3\text{O}^-$  ions, and indeed alkoxide ions are formed when  $\text{C}_2\text{—C}_4$  alkanes react with  $\text{O}^-$  ions on  $\text{MgO}$ .<sup>7</sup> The formation of methanol may result from the reaction of these  $\text{CH}_3\text{O}^-$  ions with water or surface protons. One cannot, however, exclude the possibility that at elevated temperatures hydroxyl radicals derived from water or Si-OH groups react with  $\text{CH}_3\cdot$  radicals to form  $\text{CH}_3\text{OH}$ .

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