

## Partial Oxidation of Methane by Nitrous Oxide over $\text{Bi}_2\text{O}_3\text{-SnO}_2$

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On a  $\text{Bi}_2\text{O}_3\text{-SnO}_2$  catalyst,  $\text{N}_2\text{O}$  partially oxidizes methane to formaldehyde with a selectivity of 95–84% at 1.7–2.7% conversion at 550 °C.

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In spite of the potential technological importance of the partial oxidation of methane, very little fundamental work has been reported on this reaction. Liu *et al.*<sup>1,2</sup> observed that  $\text{N}_2\text{O}$  is a suitable oxidant by yielding  $\text{O}^-$  ions and molybdenum supported on silica is an effective catalyst for the production of methanol and formaldehyde in the presence of water. Khan

and Somorjai<sup>3</sup> confirmed this observation, and performed a detailed kinetic analysis of the reaction. In the present work we report the partial oxidation of  $\text{CH}_4$  by  $\text{N}_2\text{O}$  over a  $\text{SnO}_2\text{-Bi}_2\text{O}_3$  catalyst, which was earlier found to be particularly effective in the oxidative dehydrodimerization and aromatization of propylene.<sup>4</sup>

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

Catalyst	Surface area/ m <sup>2</sup> g <sup>-1</sup>	Pressure/Torr			T/°C	Conversion/%	Selectivity/%			
		CH <sub>4</sub>	N <sub>2</sub> O				H <sub>2</sub> CO	MeOH	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>
Bi <sub>2</sub> O <sub>3</sub>	0.85	76	304		550	0.3	45.0	—	8.0	47.0
94% Bi <sub>2</sub> O <sub>3</sub> +6% SnO <sub>2</sub>	7.3	76	304		550	1.7	92.5	—	1.6	5.9
		76	304		528	0.8	89.6	—	1.3	9.2
		76	76		550	0.7	87.2	—	—	12.8
		76	608		550	2.6	92.2	—	1.2	6.6
60% Bi <sub>2</sub> O <sub>3</sub> +40% SnO <sub>2</sub>	21.4	76	304		550	2.8	83.0	—	0.5	16.5
		76	304		530	1.5	83.7	—	—	16.3
		76	304		510	0.8	83.6	—	—	16.4
		76	76		550	1.3	73.4	—	—	26.6

The Bi<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> catalysts were prepared in the following way: appropriate amounts of Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O and SnCl<sub>4</sub> were dissolved in dilute nitric acid, and the calculated amount of 10 M ammonium hydroxide was added to the solution to obtain pH 6. The precipitate was washed, dried for 12 h at 120 °C, and calcined for 6 h at 600 °C. The final product was pressed into pellets and broken into small fragments. The catalytic experiments were carried out in a fixed-bed flow reactor operating at a total pressure of 1 atm. The reactor contained 0.5 g catalyst fragments; the catalyst bed was usually 5 mm thick. Helium or nitrogen was used as a diluent to achieve a total pressure of 760 Torr. The space velocity of the reactants was 6000 h<sup>-1</sup>. A Hewlett-Packard Model 5750 dual-column g.c., equipped with a thermal conductivity and a flame ionization detector was used for analysis. For the quantitative analysis of CH<sub>2</sub>O a previously described method was used.<sup>3</sup>

Oxidation of CH<sub>4</sub> with N<sub>2</sub>O on pure Bi<sub>2</sub>O<sub>3</sub> was detected only at and above 550 °C. The conversion at 550 °C was 0.3%. Formation of ethane (selectivity, S, = 8%), formaldehyde (S = 45%), and CO<sub>2</sub> (S = 47%) was also observed.

However, a much better catalytic performance was obtained when the Bi<sub>2</sub>O<sub>3</sub> contained SnO<sub>2</sub> (6 wt%). Oxidation of CH<sub>4</sub> on this catalyst was observed at temperatures as low as 500 °C. The CH<sub>4</sub> conversion varied from 0.13% at 500 °C to as much as 8% at 600 °C. The main product of oxidation was formaldehyde; ethane and CO<sub>2</sub> were produced only in traces. No methanol was detected. The conversion of CH<sub>4</sub> and the product distribution were practically constant while the measurements were carried out over a period of *ca.* 180 min. The effects of temperature and gas composition on the CH<sub>4</sub> conversion and the selectivities for the various products are shown in Table 1. On this catalyst, H<sub>2</sub>CO is produced with a very high selectivity, 90–94%, which is constant in the temperature range 520–550 °C and the conversion range 0.6–1.7%.

Kinetic orders with respect to CH<sub>4</sub> and N<sub>2</sub>O for H<sub>2</sub>CO production were *ca.* 0.4 and *ca.* 0.5 respectively, as determined at 550 °C. The activation energy for the reaction was calculated as 60 ± 2 kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ).

An increase of the SnO<sub>2</sub> content to 40% slightly increased the conversion of CH<sub>4</sub> at 550 °C, from 1.7% to 2.8%. The selectivity of H<sub>2</sub>CO production was still very high, *ca.* 85%.

When water was injected into the reactant mixture, MeOH formation (3–8%) was observed. The amount increased with the rise in the partial pressure of H<sub>2</sub>O, and at the same time the production of formaldehyde decreased.

One possible mechanism for the partial oxidation of methane is that oxygen ions on the surface abstract hydrogen from the methane to yield methyl radicals, which react further with surface oxygen ions to form a methoxide complex. Under dry conditions this methoxide species may decompose to formaldehyde, with coupling to form ethane also occurring, but to a lesser extent. When water is present, the species reacts to produce methanol. It should be noted that methane is oxidized to formaldehyde by the oxygen ions of mixed oxides and N<sub>2</sub>O is not required. However, the initial conversion of methane (after 2 min reaction time) is 0.6–0.8%, and the selectivity to formaldehyde is *ca.* 80%. When the surface oxygen has been depleted, the reaction drops to a low level (*ca.* 0.2% conversion), in 10–15 min.

The favourable effect of SnO<sub>2</sub> addition to Bi<sub>2</sub>O<sub>3</sub> is due to several factors: (i) it promotes the dispersion of the Bi<sub>2</sub>O<sub>3</sub>, (ii) it may decrease the strength of the Bi–O bond (addition of a small amount of SnO<sub>2</sub> to Bi<sub>2</sub>O<sub>3</sub> markedly increases the reducibility of Bi<sub>2</sub>O<sub>3</sub>),<sup>4</sup> and (iii) it accelerates the decomposition of N<sub>2</sub>O, enabling it to participate directly in the oxidation processes.

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