

## Partial Oxidation of Methane by Oxygen Over Silica

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Formaldehyde has been produced from the oxidation of methane with oxygen on silica at atmospheric pressure and at reaction temperatures between 773 and 873 K, in contrast to the results with nitrous oxide where complete oxidation products are formed.

It is known that the partial oxidation of methane can take place at a lower temperature than dimerization.<sup>1</sup> Unfortunately, however, it is frequently necessary to use nitrous oxide as the oxidant in order to generate partial oxidation products, since oxygen usually leads to complete oxidation, as shown for example on MoO<sub>3</sub>/SiO<sub>2</sub> catalysts.<sup>1-3</sup> Furthermore, with oxygen, high pressure appears to be necessary to achieve partial oxidation.<sup>1</sup> Procedures through which oxygen could be substituted for nitrous oxide are therefore of paramount importance in the direct utilization of methane.

Reactions were performed in a conventional flow quartz reactor (8 mm o.d.) at temperatures between 773 and 873 K, a total flow rate of 15 ml min<sup>-1</sup>, and a feed composition of 67%

CH<sub>4</sub> and 33% N<sub>2</sub>O or O<sub>2</sub>. Commercial silica (Grace-Davison, grade 400, 740 m<sup>2</sup> g<sup>-1</sup>, 800 mesh) was used as received. The aliquots of silica (2 g) were heated in a helium flow in the reactor at the reaction temperature (*ca.* 1 h) immediately prior to use in the reaction. The conversion and product distribution for both the CH<sub>4</sub> + O<sub>2</sub> and CH<sub>4</sub> + N<sub>2</sub>O reactions as obtained in a random manner at various temperatures are reported in Table 1. These values are those found at steady state which was reached after 3 h. Carbon and oxygen balances were always better than 95% and repeated measurements showed a good reproducibility.

The results of Table 1 show that partial oxidation products can be obtained from the oxidation of methane by oxygen

**Table 1.** Activity and selectivity of silica for methane oxidation at different reaction temperatures.

T/K	CH <sub>4</sub> + O <sub>2</sub>			Selectivity <sup>a</sup>		T/K	CH <sub>4</sub> + N <sub>2</sub> O		Selectivity <sup>a</sup>	
	% Conversion CH <sub>4</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>2</sub> O		% Conversion CH <sub>4</sub>	N <sub>2</sub> O	CO	CO <sub>2</sub>
787	0.7	1.3	9	81	10	791	0.7	2.1	80	20
793	0.9	1.6	18	73	9	805	0.8	2.5	78	22
805	1.3	2.1	29	62	9	811	0.9	2.6	78	22
817	1.7	2.7	35	57	8	828	1.1	3.2	75	25
833	2.3	3.7	33	58	9	843	1.2	3.6	74	26
846	2.9	4.4	33	58	9	852	1.3	3.9	70	30
854	3.3	5.0	35	56	9	864	1.35	4.1	67	33
866	4.5	6.2	43	48	8					

<sup>a</sup> In mol % of C containing products of reaction.

although the conversion and selectivity remain small. No methanol was detected but this product may be converted into formaldehyde as silica is active for that reaction.<sup>4</sup> This latter process is probably favoured by the small contact time used and the high temperature of reaction.

Strikingly, no partial oxidation is obtained under the same conditions by using nitrous oxide, in contrast to results usually observed with molybdenum based catalysts.<sup>2,3</sup> Furthermore, increase in reaction temperature favours the production of CO with O<sub>2</sub> as oxidant, whereas the selectivity to CO<sub>2</sub> is increased when N<sub>2</sub>O is employed. In addition it may be noted that oxygen leads to a higher conversion than that found with nitrous oxide.

Apparent activation energies have been estimated from Arrhenius plots of the data in Table 1. Two domains of linearity were found with either oxidant. With N<sub>2</sub>O, apparent activation energies of 67 and 42 kJ mol<sup>-1</sup> were found for 790–810 and 820–870 K, respectively, while those for O<sub>2</sub> were 250 and 117 kJ mol<sup>-1</sup> for 780–800 and 800–870 K, respectively. These results illustrate a particular reactivity of

silica and suggest the existence of different and complex phenomena when substituting oxygen for nitrous oxide.

In summary it is shown that O<sub>2</sub> produces a partial oxidation product from methane in rather mild conditions over a silica usually employed as a support.

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