

Partial Oxidation of Methane Over Silica Catalysts Promoted by 3d Transition Metal Ions

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Addition of a very small amount of 3d transition metal ions, particularly Fe³⁺, can appreciably enhance the catalytic activity of silica in the formation of formaldehyde in the partial oxidation of methane by oxygen.

The direct conversion of natural gas into chemical feedstocks or liquid fuels is currently attracting much interest. Partial oxidation of methane into formaldehyde or methanol is one of the most challenging subjects in catalysis research.^{1,2} Research efforts have focused on silica-based catalysts,³⁻⁸ because they can bring about selective formaldehyde formation in the oxidation of methane by oxygen, provided methane conversion is kept low.

It is becoming apparent that a high formaldehyde yield is obtained if the deposited quantity of MoO₃^{3,8} or V₂O₅⁶ is limited to less than monolayer coverage of the silica surface. In the case of silica activated by adding SnO₂ or ZrO₂,⁹ a small amount of deposition is also necessary for the selective oxidation of methane. One plausible explanation for this is that these promoters provide redox centres on the silica surface.^{3,6} Such a redox centre can enhance the catalytic activity of the bare silica through activation of oxygen from the gas phase.⁷

Even unloaded silica itself can catalyse the partial oxidation of methane to produce formaldehyde.^{3,9-14} Formation of C₂ compounds or methanol is observed if radical reactions in the gas phase are concomitant.^{9,11,13} The activity of silica catalysts for formaldehyde formation depends strongly on their origin and history, and the most active one has been reported to be superior even to the MoO₃-loaded silica.^{7,14} The reasons for the great differences in activity among silica catalysts are still not clear; however, it has been suggested that they may be due to differences in the surface area,¹¹ the amount of contaminating sodium¹² and the number of defect sites.^{12,13}

It is probable that some other minor contaminants bring about the observed differences in activity among silica catalysts. The role of various additives is also interesting for the study of new catalytic promoters. We report here how the addition of 3d transition metal ions can increase the catalytic activity of silica in the direct partial oxidation of methane by oxygen. As these metal ions are expected to be very active for redox reactions, they were added in much smaller quantities than are usually used for the promotion of silica catalysts.^{3,6,8}

A pure silica [Catalysis Society of Japan (JRC-SIO-4; specific surface area 347 m² g⁻¹; impurity Na < 1.5 ppm, Al₂O₃ < 6.6 ppm, CaO < 0.3 ppm)] was used in this study and impregnated with aqueous solutions of nitrates of Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, or NH₄VO₃. The quantity of the metal ions added in each case was 0.05 atom % (metal ion: Si = 5:10 000). The precursors of the catalysts were dried at 100 °C and calcined at 650 °C in air for 1 h. Prior to use, the catalysts in a reactor were heat-treated again at 650 °C in air for 20 min.

A 0.05 g sample of each catalyst was loaded into a quartz tube reactor (inner diameter 6 mm) and quartz wool was used to hold the catalyst in place. A mixture of methane and oxygen (CH₄:O₂ = 95:5) at ambient pressure was passed through the reactor at a flow rate of 100 cm³ min⁻¹. Effluent from the reactor was analysed by FTIR (Model 205, Nicolet) with a gas analytical cell (optical length 130 mm). A gas chromatograph with a thermal conductivity detector (Model G-2800, Yanaco) was also used for the analysis of the products which were separated by use of a Porapak T column and an activated carbon column. The oxygenates of methane, and carbon oxides at levels as low as 50 ppm can be detected by this analytical system. Neither homogeneous gas phase reactions¹⁵

nor the reaction catalysed by the quartz wool in the present reactor were detected up to 650 °C.

Fig. 1 shows the products of the methane oxidation over various promoted silica catalysts at 600 °C. Unpromoted silica itself shows a certain activity for formaldehyde formation.^{3,10-14} Addition of small amounts of metal ions can enhance the catalytic activity for the formaldehyde formation as well as the formation of carbon oxides. The effect is most pronounced for Fe-promoted silica, which shows a tenfold increase in yield of formaldehyde compared with that observed for the simple silica catalyst. The space-time yield (STY) of formaldehyde was calculated to be 292 g kg⁻¹ cat h⁻¹. This value is almost identical to that observed at 600 °C for the V₂O₅-promoted silica,^{14,16} which is one of the best catalysts for this reaction reported so far.

From Fig. 1, one can notice a trade-off relationship between formaldehyde selectivity and conversion of methane. Such a dependence is often observed for promoted silica catalysts.³⁻⁵ The relatively small effect of vanadium observed in this study is not surprising, but coincides well with the results reported previously^{6,7} in that less than 1% m/m loading of V₂O₅ on silica is not effective for enhancement of formaldehyde formation.

Simple oxides of 3d transition metals have been well known as active catalysts for complete methane oxidation.¹⁷ Indeed, under the present reaction conditions, a precipitated α-Fe₂O₃ catalyst produces CO₂ with 100% selectivity (CO₂ yield: 0.06% v/v at 400 °C, 0.21% v/v at 450 °C). When the amount of deposited Fe, Co or Cr on silica catalysts becomes as much as 2% m/m, the selectivity for carbon oxides reportedly exceeds 99% for methane oxidation by N₂O.^{6,18} These facts

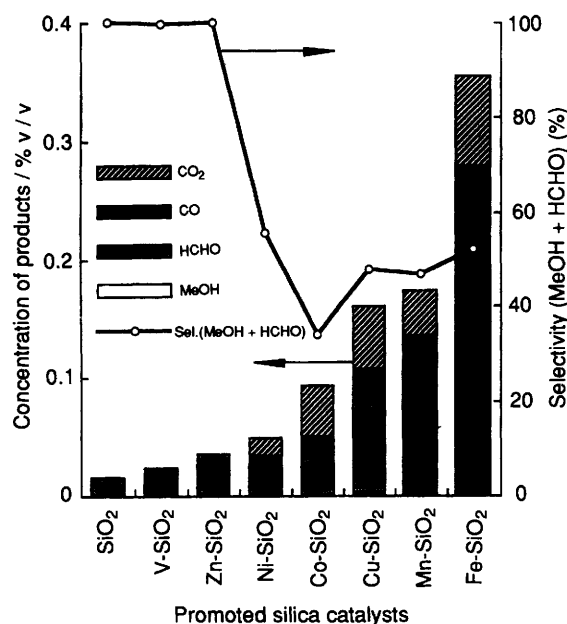


Fig. 1 Activity of silica catalysts loaded with a small amount of transition metal ions for the oxidation of methane. Metal ion loadings (Me/Si) = 0.05 atom %; reaction temp. = 600 °C; reaction gas, CH₄:O₂ = 95:5; space velocity = 120 000 cm³ cat⁻¹ h⁻¹.

indicate that the deposited Fe in the present catalyst may not exist as a simple oxide form but as atomically dispersed ions on silica. The number of deposited metal ions corresponds roughly to only 0.14% of the surface Si atoms (*ca.* 10^{15} cm⁻²) of the catalyst, if the number of surface atoms is estimated by use of the specific gravity of quartz.

For comparison, TiO₂, Al₂O₃ and ZrO₂ supporting 0.05 atom % of Fe were prepared. However, no enhancement of formaldehyde formation in methane oxidation was observed on these catalysts. This result strongly suggests that the observed high formaldehyde yield on the Fe-promoted silica is a consequence of a synergistic interaction between silica and the highly dispersed Fe ions on it. As Fe is believed to provide a very active redox centre, even a very small amount of Fe seems to be enough for the oxygen activation on silica.^{3,6,7}

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