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Breakthrough in the direct conversion of methane into C_1-oxygenates

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The partial oxidation of methane to CH_3OH and HCHO (C_1-oxygenates) was evaluated over a low surface area V_2O_5/SiO_2 catalyst. The introduction of low amounts of NO (0–2.92 %vol) to the reaction feed strongly enhanced both the conversion of methane and selectivity to C_1-oxygenates. In the presence of NO, both the reaction temperature and the CH_4/O_2 ratio affected selectivity to CH_3OH and HCHO. Selectivity values of C_1-oxygenates as high as 40% at a methane conversion close to 40% were obtained.

The partial oxidation of methane into C_1-oxygenates through a single catalytic step is of tremendous chemical and technological importance because it overcomes the energy-intensive methane steam reforming process ($CH_4 + H_2O \rightarrow 3H_2 + CO$).[1]

Most efforts to obtain C_1-oxygenates have been unable to achieve yields beyond 4%.[2] Currently, no C_1-oxygenates have been reported at methane conversion values higher than 20% with any catalyst working under atmospheric pressure. The reaction is affected by many parameters, including the CH4/O2 ratio, the void volume upstream and downstream from the catalyst bed, total pressure, and radical initiators. Among the latter, nitrogen oxides (NOx) have recently been used to promote gas-phase reactions of methane and oxygen.[2–9] Bromly *et al.*[4] developed a kinetic model for the $CH_4 + O_2 + NO$ reaction and found CO to be the sole oxidation product, but in no case were HCHO and CH_3OH detected. Otsuka *et al.*[6] used NOx to promote the oxidation of light alkanes to oxygenates; the addition of NO to the feed of the alkane and oxygen enhanced the selectivity and yield towards oxygenates. However, these oxygenated intermediates tend to be oxidized to COx in the presence of a catalyst .[10] Conversely, a high yield of CH_3OH and HCHO—up to 7.2% at atmospheric pressure—was reported when a low specific area V_2O_5/SiO_2 catalyst was used in the partial oxidation of methane in the presence of NO.[5] In a series of recent papers, Tabata *et al.*[7,8] have proposed a reaction model for the conversion of CH_4 to HCHO and CH_3OH, using either NO_x (x = 1,2)[7] or $NO_2 + O_2$[8] as oxidant agents, which satisfactorily describes the experimental results of selectivity to C_1-oxygenates. In this work, careful analysis of the influence of the CH_4/O_2 ratio and amounts of NO in the feed stream is made with a view to optimising the yield of HCHO and CH_3OH.

A SiO_2 support (specific area *ca.* 1 $m^2 g^{-1}$) was impregnated with an aqueous solution of NH_4VO_3 (Aldrich) in the presence of hydrogen peroxide ($NH_4VO_3M : H_2O_2$ = 1 : 2 molar) at 343 K. The vanadium oxide loading, as determined by ICP–AES, was 0.03%. This loading corresponds to a surface coverage below the monolayer of vanadia. The impregnate was dried at 383 K, calcined at 923 K for 5 h and sieved to a particle size range of 0.125–0.250 mm. For activity measurements, catalyst samples of 0.20 g were placed in a quartz reactor of 10 mm ID with no dead volume, GHSV of 6.6×10^4 h^{-1}, a $N_2 : CH_4 : O_2$ = 4 : 2 : 1 mixture (molar) at a methane flow rate of 100 ml min^{-1}, atmospheric pressure and temperature from 803 to 1023 K were used. NO concentrations (0, 200, 534, 4000, 6000, 10000, 14000 and 29200 ppm) were used, maintaining the CH_4 and O_2 concentrations constant. The effluents from the reactor were analyzed by on-line GC. On average, the estimated error in replica experiments with fresh catalyst samples and a clean quartz reactor was within ±5%.

The homogeneous $CH_4 + O_2$ reaction to methanol and formaldehyde is negligible at atmospheric pressure but is important in the presence of NO. The presence of catalyst further improves the performance. The homogeneous reaction between CH_4 and O_2 was studied using a 10 mm ID reactor with 6 ml void volume, and feeding simultaneously in the 0–29200 ppm NO concentration range. HCHO, CH_3OH and small amounts of dimerization (C_{2+}) products were observed. The maximum HCHO and CH_3OH yields were 0.8 and 0.3%, respectively, at the lowest temperature (823 K), these remaining almost constant over the whole NO concentration range used. The yield of HCHO and CH_3OH decreased with increasing temperature, whereas the C_{2+} hydrocarbon yield followed the opposite trend. The increase in C_{2+} hydrocarbon yield with the reaction temperature was sharper in the low NO concentration region.

The effect of NO concentration on the conversion values and on the yield of C_1-oxygenates in the presence of catalyst is shown in Fig. 1. The presence of NO in the feed stream significantly increased the conversion of methane and oxygen, leading to a C_1-oxygenate yield higher than 8%, However, as the NO concentration increased, the conversion of oxygen approached 100%, which would limit the reaction. If the CH_4/O_2 ratio increases, the production of HCHO and CH_3OH decreases. Thus, a NO concentration of 1% appears appropriate to evaluate the performance of the low-specific area V_2O_5/SiO_2 catalyst.

The effects of both CH_4/O_2 ratio and temperature on the conversion of methane and on the yield values of C_1-oxygenates are shown in Fig. 2. The conversion of methane increased with temperature (isothermal bed conditions) at any partial pressure of oxygen (Fig. 2A). CO_2 accounts for most of the increase in the methane conversion values, which also increased with the partial pressure of oxygen. The production of CO revealed a different dependence on the oxygen partial pressure, since it increased CO production at lower temperatures and decreased it at higher temperatures. The yield values of C_1-oxygenates

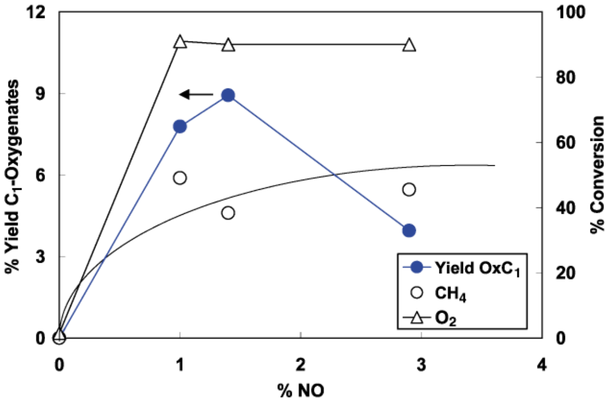

Fig. 1 Effect of NO concentration on the conversion of CH_4 and O_2 and on the yield of C_1-oxygenates (catalyst weight 0.22 g, total flow 89.8 ml min^{-1}, 29.0% O_2, 41.5% CH_4 and 0.0–2.92% NO in N_2.

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follow a behaviour similar to that of CO; that is, the yield of C_1-oxygenates increases with the oxygen partial pressure at the lower temperatures and this trend is reversed at the higher temperatures (Figure 2B). The combined effect of both temperature and oxygen partial pressure afforded a yield which reached a maximum value at high temperatures (923 K and a low partial pressure of oxygen; $CH_4/O_2 = 1.8$ molar). The yield of C_1-oxygenates reached 16% at atmospheric pressure, which to our knowledge is the highest value reported.

The generation of radicals triggers the activity and different radical initiators afford different performances. Klier *et al.*[11] used a double-bed catalyst: the upstream 1% Sr/La_2O_3 catalyst generated methyl radicals, and the downstream MoO_3/SiO_2 catalyst enhanced conversion. Another approach consists in dosing azomethane to generate methyl radicals in the gas-phase, which then favour the activation of methane, yielding methanol and formaldehyde.[12] NO incorporation to the feed stream behaves similarly since it increases conversion and shifts selectivity to O-containing products.[5] The generation of radicals is one role of the catalyst for methane conversion, and is related to its high specific area but it is detrimental for its selectivity for the formation of HCHO, CH_3OH and C_{2+} hydrocarbons. To circumvent these two antagonistic effects, the approach followed here was to use a very low-specific area V_2O_5/SiO_2 catalyst combined with the addition of the NO radical initiator to the feed stream as a means to promote the conversion of methane but not the degradation of the selective oxidation products. Since the generation of radicals is one of the roles of the catalysts for methane conversion,[13] the very low activity observed in the absence of NO is due to poor ability of the low-specific area V_2O_5/SiO_2 catalyst to generate radicals. The sharp effect of NO appears to be due to the chain propagation of radical reactions in the close vicinity of the catalyst bed. These trends are predicted by the reaction models developed by Tabata *et al.*[8] The profiles in Fig. 2B clearly underline the relevance of both the oxygen partial pressure and the reaction temperature for a given NO concentration in the feed stream. The radical-due reactions are strongly affected by the reaction conditions. In particular, the methyl–methylperoxo ($CH_3^\cdot$–$CH_3O_2^\cdot$) radical equilibrium depends on the concentration of oxygen and on temperature, and is shifted to O-containing radicals as temperature decreases.[14] The results shown in Fig. 2 show how important these two parameters are in the reaction conditions used for the present work. An appropriate combination of both temperature and oxygen partial pressure affords very high yields to C_1-oxygenates. In addition, under the conditions necessary to reach a 16% yield to C_1-oxygenates, the production of CO_2 is minimized.

It can thus be concluded that the partial oxidation of methane by oxygen takes place at moderate temperatures if NO is added to the reaction mixture. NO gas alters the $CH_3^\cdot$–$CH_3O_2^\cdot$ radical ratio and promotes the activation of methane. This activation procedure affords conversions comparable to those obtained on high-specific area catalysts, with significantly better selectivity of HCHO and CH_3OH. Accordingly, C_1-oxygenates reach yields as high as 16% in the presence of 1% NO in the feed stream.

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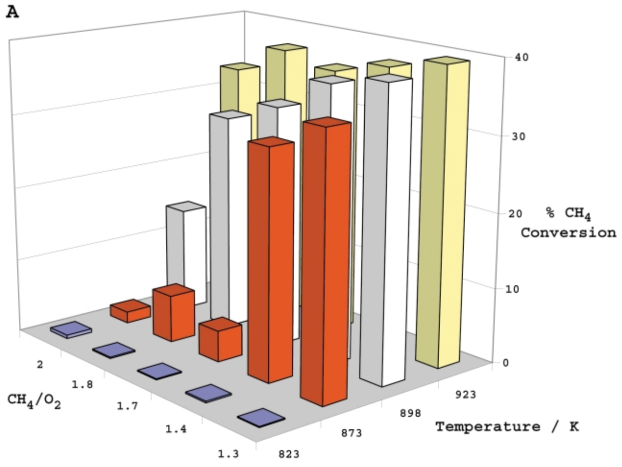

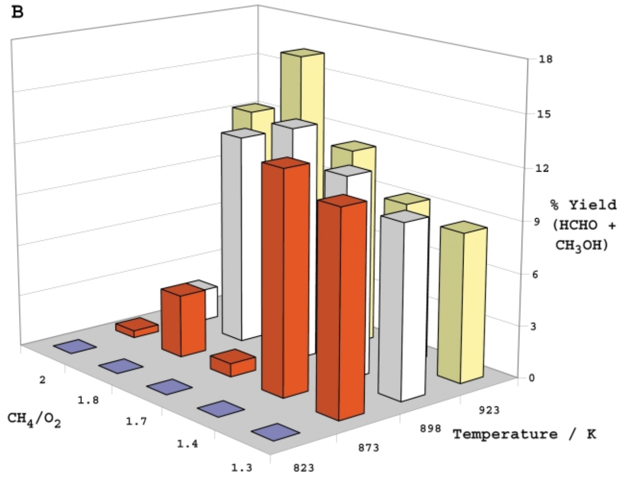

Fig. 2 Effect of temperature and of CH_4/O_2 ratio on the CH_4 conversion (A), and on the yield of C_1-oxygenates (B). (Reaction conditions: catalyst weight 0.30 g, total flow 122 ml min^{-1}, 22.9–34.4% CH_4, 1.0% NO in N_2.

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