Direct conversion of methane to methanol and formaldehyde over a double-layered catalyst bed in the presence of steam

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Using a double-bed reactor configuration with an up-stream 1 mass% SO_4^{2-}/1 mass% SrO/La_2O_3 catalyst to generate methyl radicals and a down-stream 1 mass% V_2O_5/SiO_2 catalyst to stabilize the methyl radicals for reaction to form hydrolysable methoxide species, the methanol and formaldehyde space–time yields are increased up to five-fold for partial oxidation of methane in the presence of air and steam at moderate temperatures of 550–600 °C as compared with the single-bed 1 mass% V_2O_5/SiO_2 catalyst, while little of these oxygenates are formed over a mechanically mixed catalyst bed.

The direct conversion of natural gas[1,2] to easily transportable chemicals and fuels has attracted the attention of the scientific and engineering communities for more than a decade. Recently, there has been a renewed interest in the direct conversion of methane to oxygenates. Various oxide catalysts have been studied for the partial oxidation of methane to oxygenates,[1,3–6] among which silica-supported MoO_3 and V_2O_5 catalysts have been reported to be the most active and selective for oxygenate production, with V_2O_5 outperforming MoO_3 according to most reports.[5,6]

Dowden *et al.*[7] proposed that MoO_3 was capable of an oxygen insertion into a C–H bond of CH_4, while V_2O_5 was capable of both hydrogen abstraction from and oxygen insertion into the CH_4 molecule, which explains the better performance of the latter. Recent research[4,8,9] also suggested that higher yields of oxygenates could be obtained when the silica surface was partially covered by surface molybdenum oxide and vanadium oxide species.[10,11]

To date, most efforts on direct conversion of methane to methanol and formaldehyde have focused on developing a single catalyst that is capable of both activating methane and producing oxygenates. A different approach has been adopted in the present research by using a double-layered catalyst bed in an attempt to circumvent the difficulty of abstracting a hydrogen atom from CH_4 and reacting the methyl radical with activated O by using the same catalyst.

Pitchai and Klier[1] proposed that the role of steam in partial oxidation of methane to oxygenates was to hydrolyse the surface methoxide species formed during the reaction. Using IR spectroscopy, Lunsford and coworkers[12] reported evidence for the formation of methoxide ions during partial oxidation of methane with N_2O as the oxidant over an MoO_3/SiO_2 catalyst. The present paper demonstrates that the abstraction of hydrogen from methane and the subsequent formation and hydrolysis of methoxide species could be accomplished more efficiently by utilizing two separate catalysts closely packed one after the other.

The first presently used catalyst bed, the function of which is that of a methane C–H bond activating catalyst, is a 1 mass% SO_4^{2-}/1 mass% SrO/La_2O_3 catalyst which is a very good methyl radical generating catalyst at relatively low temperatures.[13] The second catalyst bed, on which methoxide species are proposed to form and subsequently hydrolyse, is a 1 mass% V_2O_5/SiO_2 catalyst.

The 1 mass% SrO/La_2O_3 catalyst was obtained from AMOCO Corporation after being prepared as described elsewhere.[14,15] The catalyst was impregnated with aqueous $(NH_4)_2SO_4$, stirred until dry, and then dried at 120 °C overnight. The resulting catalyst was calcined in air at 600 °C for 6 h. The silica-supported V_2O_5 catalyst was prepared by using $VO(OPr^i)_3$ and amorphous silica. The amorphous silica (Cabosil EH-5, surface area = 380 $m^2\ g^{-1}$) was first mixed with deionized water and then the mixture was stirred and dried at 140 °C to increase the density of the silica.[16] A methanol solution of $VO(OPr^i)_3$ was prepared and mixed with the dried silica in a glove box under N_2 in order to avoid reaction with atmospheric moisture. The resulting mixture was thoroughly mixed by vigorous stirring on a magnetic hot plate until a thick paste was formed, which was dried overnight under N_2 and then calcined in air at 600 °C for 6 h. Raman spectroscopy and solid-state ^{51}V NMR characterization demonstrated that only surface vanadium species were present and that crystalline V_2O_5 particles were absent.[16]

The initial catalytic experiments were carried out over both the single-layered catalyst bed (100 mg of 1 mass% V_2O_5/SiO_2 catalyst) and the double-layered catalyst bed (consisting of 100 mg of 1 mass% SO_4^{2-}/1 mass% SrO/La_2O_3 followed by 100 mg of 1 mass% V_2O_5/SiO_2) at 525–600 °C. The space–time yields were calculated based on the total mass of the catalyst bed consisting of both catalyst layers. Addition of water vapour to the reactant mixture was achieved by injecting distilled water into the heated volume preceding the catalyst bed with an ISCO liquid metering pump (Model 314). The water was vapourized and the resulting steam was then mixed with CH_4–air (1.5 : 1). The analyses of the reactant and product gases were carried out using a Hewlett–Packard 5890 gas chromatograph with a molecular sieve 13X column and a Chrompack Model 7550 PoraPLOT Q fused silica capillary column in parallel and TCD detectors. Condensable products, methanol and formaldehyde, were trapped by using an ice bath at 0 °C and were separately analysed by a Hewlett–Packard 5970 GC MS instrument. The GC MS formaldehyde analysis was calibrated by a series of standard solutions that were quantified by iodiometric titration.

Comparison of the direct conversion of methane from CH_4–air–steam (1.5 : 1.0 : 0.2) at ambient pressure to methanol and formaldehyde over the single and double-layered catalyst beds is shown in Fig. 1. It is evident from Fig. 1 that at temperatures below 600 °C, the amount of methanol and formaldehyde produced by the single-bed 1% V_2O_5/SiO_2 catalyst is relatively low. However, when the double-bed configuration was used, a significant enhancement of the oxygenate space–time yields was observed. At 575 and 600 °C, the increase in oxygenate space–time yield was nearly five-fold. Over the single V_2O_5/SiO_2 catalyst, the C atom selectivities toward oxygenates at 525, 550, 575 and 600 °C were 93.5, 87.3, 41.8 and 33.4%, respectively, but the CH_4 conversion levels were low. The remaining products over this catalyst were carbon oxides. Over the double-layered $SO_4^{2-}/SrO/La_2O_3\|V_2O_5/SiO_2$ catalyst bed, the selectivities of the oxygenates over this temperature range

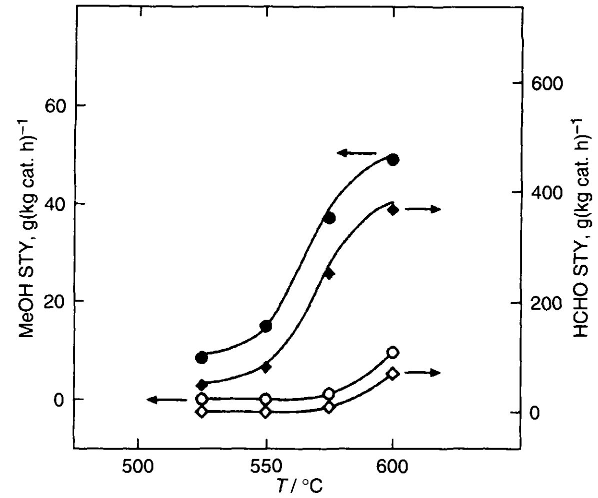

Fig. 1 Comparisons of the productivities of methanol (○,●) and formaldehyde (◇,◆) observed over the single V_2O_5/SiO_2 catalyst and the double-layered $SO_4{}^{2-}/SrO/La_2O_3 \| V_2O_5/SiO_2$ catalyst bed configuration (0.100 g catalyst in each layer) from a reactant mixture consisting of CH_4–air–steam = 140–95–20 ml min^{-1} [GHSV = 153 000 l (kg cat. h)$^{-1}$ for each single catalyst bed and 76 500 l (kg cat. h)$^{-1}$ for the combined double bed] at atmospheric pressure

Table 1 The conversions of methane and the space–time yields of products formed over double bed[a] and mixed bed[b] 1 mass% $SO_4{}^{2-}/SrO/La_2O_3$ and 1 mass% V_2O_5/siO_2 catalysts (0.1 g of each of the two components). The reactant stream consisted of CH_4–air–steam (1.4 : 0.95 : 0.40 molar ratio) with total GHSV = 82 500 l (kg cat. h)$^{-1}$ [or 165 000 l (kg cat. h)$^{-1}$ relative to each of the two bed components]

T/°C	CH_4 conv. (mol%)	Space–time yields/g (kg cat. h)$^{-1}$				
		C_2 HC	HCHO	MeOH	CO	CO_2
575[a]	10.6	1782	524	78	3195	4729
600[a]	11.4	2497	635	96	3214	3552
625[a]	13.1	2988	844	105	3325	4140
575[b]	10.3	1812	7	23.5	3354	4770
600[b]	10.7	2568	5	38.4	3012	3598
625[b]	12.4	3074	11	48.5	3120	4442

[a] Double-bed experiments in which 1 mass% $SO_4{}^{2-}/SrO/La_2O_3$ was placed on top of 1 mass% V_2O_5/SiO_2. [b] Mixed-bed experiments in which well mixed 1 mass% $SO_4{}^{2-}/SrO/La_2O_3$ and 1 mass% V_2O_5/SiO_2 were uniformly loaded as one bed in the reactor.

were all < 5% with the rest of the products being carbon oxides and C_2 hydrocarbon (C_2 HC). A single-bed 1 mass% $SO_4{}^{2-}$/1 mass% SrO/La_2O_3 catalyst at 600 °C produced only 14.0 and 2.8 g (kg cat. h)$^{-1}$ of formaldehyde and methanol, respectively, under the same reaction conditions.

As a direction for optimizing this catalyst system, the effect of increasing the water vapour content in the reactant mixture on the synthesis of the oxygenates was probed. The quantity of steam was doubled compared with the experiment described in Fig. 1, and the results shown in Table 1 indicate that the productivity of formaldehyde and methanol was further significantly increased. To demonstrate the effectiveness of the double catalyst bed configuration, a well mixed physical mixture of the 1 mass% $SO_4{}^{2-}/SrO/La_2O_3$ and V_2O_5/SiO_2 catalysts (1 : 1 mass ratio) was tested under the same reaction conditions. Table 1 shows that the physically mixed catalysts produced nearly no formaldehyde and a greatly diminished amount of methanol, while producing slightly more C_2 hydrocarbons and CO_2, indicating that the methyl radicals generated over the very active $SO_4{}^{2-}/SrO/La_2O_3$ catalyst tended to undergo gas-phase coupling or oxidation before being stabilized on the effectively diluted V_2O_5/SiO_2 catalyst. In addition, formaldehyde formed in the presence of abundant methyl radicals will react with them,[17,18] with an activation energy appreciably lower than for the reaction of methanol with methyl radicals,[17] to form CH_4 + CHO, where the formyl radical is readily oxidized to CO_2.

$$2\,CH_4 + 0.5\,O_2 \rightarrow 2\,{}^{\bullet}CH_3 + H_2O \qquad \text{First catalyst layer} \quad (1)$$

$$\left.\begin{array}{l} 2\,{}^{\bullet}CH_3 + 2\,M^{(n+1)+}O^{2-} \rightarrow 2\,M^{n+}(OCH_3)^- \\ 2M^{n+}(OCH_3)^- + 2H_2O \rightarrow 2M^{n+}(OH)^- + 2CH_3OH \\ 2\,M^{n+}(OH)^- \rightarrow M^{n+}O^{2-} + M^{n+}\square_O + H_2O \\ M^{n+}O^{2-} + M^{n+}\square_O + 0.5\,O_2 \rightarrow 2\,M^{(n+1)+}O^{2-} \\ 2M^{n+}(OCH_3)^- + 1.5\,O_2 \rightarrow 2M^{(n+1)+}O^{2-} + 2HCHO + H_2O \end{array}\right] \begin{array}{c}\text{Second}\\ \text{catalyst}\\ \text{layer}\end{array} \quad \begin{array}{r}(2)\\(3)\\(4)\\(5)\\(6)\end{array}$$

Scheme 1

The data presented in Fig. 1 and Table 1 demonstrate the significant contributions of the first bed catalyst and the presence of steam to oxygenate production. The results strongly corroborate the role of the first catalyst layer as a methyl radical generating catalyst and that of the second layer as the methyl radical trapping and oxygenate-forming catalyst. The principal reactions are schematically illustrated in Scheme 1, where $\square_O$ represents an oxygen vacancy and reactions (3) and (6) occur in parallel.

A further direction for improving the oxygenate synthesis is to balance the number of methyl radicals leaving the first bed to the rate of hydrolysis of the methoxide species by adjusting the mass ratio of the two catalyst beds.

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References

1 R. Pitchai and K. Klier, *Catal. Rev.-Sci. Eng.*, 1986, **28**, 13.
2 H. D. Gesser, N. R. Hunter and C. B. Prakash, *Chem. Rev.*, 1985, **85**, 235.
3 M. Kennedy, A. Sexton, B. Kartheuser, E. Mac Giolla Coda and J. B. McMonagle, *Catal. Today*, 1992, **13**, 447.
4 M. A. Banares, J. L. G. Fierro and J. B. Moffat, *J. Catal.*, 1993, **142**, 406.
5 N. D. Spencer and C. Pereira, *J. Catal.*, 1989, **116**, 399.
6 A. Parmaliana, F. Frusteri, A. Mezzapica, D. Miceli, M. S. Scurrell and N. Giordano, *J. Catal.*, 1993, **143**, 262.
7 D. A. Dowden, C. R. Schell and G. T. Walker, The Design of Complex Catalysts, *Proc. 4th Intern. Congr. Catal.*, Moscow, 1968, p. 201.
8 N. D. Spencer, *J. Catal.*, 1988, **109**, 187.
9 M. Kennedey, A. Sexton, B. Kartheuser and B. K. Hodett, *Catal. Today*, 1992, **13**, 447.
10 Q. Sun, R. G. Herman and K. Klier, *Catal. Lett.*, 1992, **16**, 251.
11 Q. Sun, J. I. Di Cosimo, R. G. Herman, K. Klier and M. M. Bhasin, *Catal. Lett.*, 1992, **15**, 371.
12 H.-F. Liu, R.-S. Liu, K. Y. Liew, R. E. Johnson and J. H. Lunsford, *J. Am. Chem. Soc.*, 1984, **106**, 4117.
13 J. Sarkany, Q. Sun, R. G. Herman and K. Klier, *Preprints, Div. Pet. Chem., ACS*, 1994, **39**, 226.
14 J. M. DeBoy and R. F. Hicks, *Ind. Eng. Chem. Res.*, 1988, **27**, 1577.
15 J. M. DeBoy and R. F. Hicks, *J. Catal.*, 1988, **113**, 517.
16 N. Das, H. Eckert, H. Hu, I. E. Wachs, J. Walzer and F. Feher, *J. Phys. Chem.*, 1993, **97**, 8240.
17 J. C. Mackie, *Catal. Rev. Sci. Eng.*, 1991, **33**, 169.
18 C. Shi, M. Hatano and J. H. Lunsford, *Catal. Today*, 1992, **13**, 191.

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