

## Novel High Activity Catalysts for Partial Oxidation of Methane to Formaldehyde

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Vanadium oxide–silica catalysts can effect the partial oxidation of methane to formaldehyde with extremely high activities and the space time yield (STY) can reach a value in excess of  $800 \text{ g kg}^{-1}_{\text{cat}} \text{ h}^{-1}$ ; bare silica also shows appreciable STY value up to *ca.*  $300 \text{ g kg}^{-1}_{\text{cat}} \text{ h}^{-1}$ .

Efforts to bring about the partial oxidation of methane to formaldehyde or methanol continue to attract considerable attention. Catalytic behaviour is usually described in terms of conversion per pass of methane and selectivity to formaldehyde. In many cases an inverse relationship between these parameters is observed.<sup>1</sup> Yields per pass calculated from the two parameters are not infrequently found to be less than

about 2–3%.<sup>2</sup> Less attention has been given to specific catalytic activity expressed in terms of observed rate of formation of (formaldehyde + methanol) per unit mass of catalyst per unit time. This activity—space time yield (STY)—and yield per pass have in fact led to some confusion.<sup>3</sup> Thus, catalysts appear to exert a beneficial effect on STY<sup>3</sup> but not necessarily on yield per pass. In this communication we report

**Table 1** Partial oxidation of methane on SiO<sub>2</sub> and 5% V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalysts

Catalyst mass/g	Reaction temperature/°C	CH <sub>4</sub> conv. /mol%	HCHO Yield per pass (%)	Selectivity (%)			HCHO space time yield/g kg <sup>-1</sup> <sub>cat</sub> h <sup>-1</sup>
				CO <sub>2</sub>	CO	HCHO	
SiO <sub>2</sub>							
0.05	550	0.01 <sup>a</sup>	0.0079	10	11	79	33.9
0.05	600	0.036 <sup>a</sup>	0.027	7	18	75	116
0.05	650	0.110 <sup>a</sup>	0.069	14	23	63	304
5% V <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub>							
0.05	520	0.015 <sup>a</sup>	0.010	31	1	68	45.9
0.05	550	0.038 <sup>a</sup>	0.023	37	2	61	100
0.05	600	0.151 <sup>a</sup>	0.072	38	14	48	318
0.05	650	0.521 <sup>a</sup>	0.182	14	51	35	793
0.01	650	0.078 <sup>a</sup>	0.037	15	37	48	819
0.50	650	13.5 <sup>b</sup>	4.73	14	51	35	760

<sup>a</sup> Batch reactor, differential reactor mode; recycle gas flow rate, 1000 NTP cm<sup>3</sup> min<sup>-1</sup>. <sup>b</sup> Conventional flow reactor, integral reactor mode, gas flow rate, 500 NTP cm<sup>3</sup> min<sup>-1</sup>

**Table 2** Comparison of STY values for different catalysts

Catalyst	Reaction temperature/°C	Oxidant	HCHO STY/g kg <sup>-1</sup> <sub>cat</sub> h <sup>-1</sup>	Ref.
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	600	N <sub>2</sub> O	5.4 <sup>a</sup>	5
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	600	N <sub>2</sub> O	22.8	6
MoO <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	600	N <sub>2</sub> O	20.9	6
HPMo/SiO <sub>2</sub>	570	N <sub>2</sub> O	27.5	7
no catalyst	625	O <sub>2</sub>	15 <sup>b</sup>	2
BeO/B <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	600	O <sub>2</sub>	24	8
Cu/Fe/ZnO	750	O <sub>2</sub>	75	9
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	600	O <sub>2</sub>	77 <sup>c</sup>	10
Mo-Sn/SiO <sub>2</sub>	700	O <sub>2</sub>	80	11
MoO <sub>3</sub> /SiO <sub>2</sub>	650	O <sub>2</sub>	102 <sup>d</sup>	12
MgO	750	O <sub>2</sub>	270	13
SiO <sub>2</sub>	680	O <sub>2</sub>	77.7	14
SiO <sub>2</sub>	600	O <sub>2</sub>	116 <sup>e</sup>	This work
SiO <sub>2</sub>	650	O <sub>2</sub>	304 <sup>e</sup>	This work
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	600	O <sub>2</sub>	318 <sup>e</sup>	This work
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	650	O <sub>2</sub>	793-819 <sup>e</sup>	This work
V <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	650	O <sub>2</sub>	760 <sup>f</sup>	This work

<sup>a</sup> HCHO + CH<sub>3</sub>OH. <sup>b</sup> Yield quoted is g<sub>HCHO</sub> l<sup>-1</sup><sub>T</sub> h<sup>-1</sup>. <sup>c</sup> Yield quoted is g<sub>HCHO</sub> l<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> calculated according to procedure outlined in ref. 1. <sup>d</sup> Yield quoted is g<sub>HCHO</sub> l<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>. <sup>e</sup> Differential reactor mode with external recycle and condensation of HCHO. <sup>f</sup> Integral reactor mode.

on the activities of certain vanadium-silica catalysts which, in terms of STY, appear to be the most active systems so far documented for the partial oxidation of methane. Even the bare silica shows appreciable activity expressed in terms of STY.

Vanadia-silica catalysts have been prepared using silica type Si4-5P (Akzo product). Vanadium is introduced by incipient wetness impregnation with a basic (pH 11) solution of ammonium metavanadate. The impregnated samples were dried at 90 °C for 24 h and then calcined at 650 °C for 16 h. The final catalyst contained 5% V<sub>2</sub>O<sub>5</sub>.

Catalytic experiments have been performed using a specifically designed batch reactor, described elsewhere,<sup>4</sup> provided with an external recycle pump and a liquid product condenser placed downstream of the reactor and maintained at -15 °C which traps the oxygenated products and prevents their further oxidation, or a conventional flow reactor. The reactors permit operation in differential (quasi zero conversion per pass) or integral mode, respectively. In both cases the reaction mixture consisted of 18.4 vol% CH<sub>4</sub>, 9.2 vol% O<sub>2</sub>, 18.4 vol% N<sub>2</sub> (as an internal standard for gas chromatographic analysis) and 54 vol% He with a total reaction pressure of 1.7 bar (1 bar = 10<sup>5</sup> Pa).

Appropriate blank runs have shown that, under our experimental conditions, the contribution of the gas phase reaction up to 650 °C is negligible. Catalytic data are reported in Table 1.

The results indicate that formaldehyde selectivity falls with increasing reactor temperature with a concomitant increase in CO selectivity, but that, overall the space time yield of formaldehyde rises. Comparison of the sets of data obtained at 650 °C for operation of the reactor in differential and integral mode clearly shows comparable product selectivities and formaldehyde STYs.

Table 2 compares STY values obtained for SiO<sub>2</sub> and 5% V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalysts with those reported by others.

As can be seen from Table 2 our SiO<sub>2</sub> samples give remarkably high STY values, but the activity is enhanced in the case of V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalysts. The activity of the bare SiO<sub>2</sub> is likely due to some specific surface sites possessing donor properties to activate molecular oxygen. We have proposed elsewhere<sup>15</sup> that the enhancing effect of V<sub>2</sub>O<sub>5</sub> can be attributed to the increase in the number of such specific sites on the catalysts capable of chemisorption of oxygen and of such a nature that formaldehyde is produced as a partial oxidation product.

The formation of formaldehyde as a partial oxidation product over silica is not a new finding.<sup>1,4</sup> However, in general, silica is not associated with such high activities as reported here, though specific silicas examined by Guliev *et al.*<sup>16</sup> also seem to exhibit comparatively high rates and selectivities. It must be emphasised that not all silica samples are equally active, with 'pyrolytic' or 'fumed' silicas being very much less active than 'precipitated' silicas.<sup>4,14</sup> However, the present work clearly demonstrates that the relatively high activity of silica type Si4-5P previously noted for reaction temperatures of 520 °C is at the higher temperature of 650 °C remarkably high in absolute terms (STY basis). What is also apparent is that the high values of STY associated with SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalysts are not confined to the use of a reactor system with external recycle incorporating a condensation unit for removal of formaldehyde, since use of a reactor in an integral mode leads to essentially identical space time yields and selectivities (Table 1). It might otherwise have been inferred that the high STY values could be obtained only if methane conversions per pass were extremely low (<0.2 mol%). In fact the high STY value has been seen for methane conversion per pass of 13.5 mol%.

In absolute terms, the high STY values reported here are comparable with those associated with copper-based commercial catalysts used for the synthesis of methanol from carbon monoxide and hydrogen mixtures.<sup>17</sup> The only comparable

STY values so far reported for direct partial oxidation of methane appear to be those obtained by ICI workers on MoO<sub>3</sub> containing catalysts but at high pressures (ca. 50 bar), high methane: O<sub>2</sub> ratios (ca. 30:1) and low (ca. 2–3 mol%) methane conversion levels.<sup>18</sup>

Further investigations aimed at elucidating more precisely the nature of the sites responsible for the high rate of generation of formaldehyde on SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> catalysts are in progress.

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## References

- 1 M. J. Brown and N. D. Parkyns, *Catal. Today*, 1991, **8**, 305.
  - 2 T. R. Baldwin, R. Burch, G. D. Squire and S. C. Tsang, *Appl. Catal.*, 1991, **74**, 137.
  - 3 J. S. J. Hargreaves, G. J. Hutchings and R. W. Joyner, *Appl. Catal.*, 1991, **77**, N18.
  - 4 A. Parmaliana, F. Frusteri, D. Miceli, A. Mezzapica, M. S. Scurrell and N. Giordano, *Appl. Catal.*, 1991, **78**, L7.
  - 5 K. J. Zhen, M. M. Khan, C. H. Mak, K. B. Lewis and G. A. Somorjai, *J. Catal.*, 1985, **94**, 501.
  - 6 M. Kennedy, A. Sexton, B. Kartheuser, E. MacGiolla Coda, J. B. McMongale and B. K. Hodnett, *Catal. Today*, 1992, **13**, 447.
  - 7 S. Kasztelan and J. B. Moffat, *J. Catal.*, 1987, **106**, 512.
  - 8 K. Otsuka and M. Hatano, *J. Catal.*, 1987, **108**, 252.
  - 9 Z. Sojka, R. G. Herman and K. Klier, *J. Chem. Soc., Chem. Commun.*, 1991, 185.
  - 10 N. D. Spencer and C. J. Pereira, *J. Catal.*, 1989, **116**, 399.
  - 11 V. Amir-Ebrahimi and J. J. Rooney, *J. Mol. Catal.*, 1989, **50**, L17.
  - 12 N. D. Spencer, *J. Catal.*, 1988, **109**, 187.
  - 13 J. S. J. Hargreaves, G. J. Hutchings and R. W. Joyner, *Nature*, 1990, **348**, 428.
  - 14 Q. Sun, R. G., Herman and K. Klier, *Catal. Lett.*, 1992, **16**, 251.
  - 15 A. Parmaliana, V. Sokolovskii, D. Miceli, F. Arena and N. Giordano, *Preprints, Petroleum Chemistry Division Inc., Symposium on 'Catalytic Selective Oxidation'* ACS, 1992, **37**, 1076.
  - 16 I. A. Guliev, A. Kk. Mamedov and V. S. Aliev, *Azerbaijan Khim. Zhur.*, 1985, 35.
  - 17 G. C. Chinchin, P. J. Denny, J. R. Jennings, M. S. Spencer and K. C. Waugh, *Appl. Catal.*, 1988, **36**, 1.
  - 18 D. A. Dowden and G. T. Walker, UK Patent 1,244,001 (Aug. 25, 1971) to ICI Ltd.
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