# $BaCO_3$-supported vanadium oxide catalysts for the oxidative coupling of methane

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**$BaCO_3$-supported vanadium oxide catalysts, which consist of $BaCO_3$ and small amounts of a barium orthovanadate $Ba_3(VO_4)_2$ phase, exhibit high catalytic activity for oxidative coupling of methane, with particularly high activity for ethene and ethane production.**

Vanadium oxide-based catalysts have become an important class of catalytic materials because of their numerous industrial applications in heterogeneous catalytic selective oxidation reactions and use as model systems for fundamental studies of catalysts.[1–3] Recently, a review article has demonstrated that certain types of vanadium oxide-based catalysts, particularly those containing orthovanadate, pyrovanadate or metavanadate crystalline phases, exhibit significant catalytic activity for the oxidative dehydrogenation of light alkanes.[3] For instance, the VMgO catalysts, consisting of MgO and $Mg_3(VO_4)_2$ phases, are particularly active in the oxidative dehydrogenation of ethane, propane and butane.[4] One can deduce that this type of catalyst should be active for oxidative coupling of methane at a relatively high reaction temperature. However, to our knowledge, there has been no report on the use of this type of vanadium oxide-based catalyst for oxidative coupling of methane to produce ethene or ethane although many types of catalysts have been developed for this reaction[5] since the early work of Keller and Bhasin on oxidative coupling of methane.[6] Here, we report a successful application of $BaCO_3$-supported vanadium oxide catalysts, containing barium orthovanadate $Ba_3(VO_4)_2$ and $BaCO_3$ phases, for oxidative coupling of methane, with a particularly high activity for ethene and ethane production.

**Table 1** Identification of $BaCO_3$-supported vanadium oxide catalysts by X-ray diffraction

| V/Ba atomic ratio | Phase identified | $I_V/I_{Ba}$[a] |
|---|---|---|
| 0.00 | $BaCO_3$ | 0.0 |
| 0.05 | $BaCO_3 + Ba_3(VO_4)_2$ | 0.16 |
| 0.10 | $BaCO_3 + Ba_3(VO_4)_2$ | 0.22 |
| 0.25 | $BaCO_3 + Ba_3(VO_4)_2$ | 0.31 |
| 0.50 | $Ba_3(VO_4)_2 + BaCO_3\ (Ba_2V_2O_7)$[b] | 1.25 |
| 0.70 | $Ba_3(VO_4)_2 + BaCO_3 + Ba_2V_2O_7$ | 2.05 |
| 1.00 | $Ba_2V_2O_7\ (BaCO_3)$[b] | — |

[a] The ratio of $I_{Ba_3(VO_4)_2}(110)$ to $I_{BaCO_3}(111)$. [b] Very weak diffraction patterns were detected.

The catalysts with nominal V/Ba atomic ratio varying from 0.0 to 1.0 were prepared by a conventional impregnation method: *i.e.* $BaCO_3$ powder was added to a hot aqueous solution containing an appropriate amount of $NH_4VO_3$ with constant stirring for 1 h, then evaporated to dryness and dried at 110 °C, and finally calcined at 820 °C in air for 4 h. The phase identification of the catalysts was performed by X-ray diffraction on a D/MAX-RB Rigaku powder diffractometer using Cu-Kα radiation. The characterisation results of the catalysts by XRD are shown in Table 1. Three phases are identifiable: $BaCO_3$, $Ba_3(VO_4)_2$ and $Ba_2V_2O_7$. The ratio $I_{Ba_3(VO_4)_2}(110)/I_{BaCO_3}(111)$ is used to indicate the relative amounts of the $BaCO_3$ and $Ba_3(VO_4)_2$ phases. For activity measurements, 0.4 $cm^3$ of catalyst (30–60 mesh) was placed in a flow microreactor equipped with vertical quartz tubes as described in ref. 7; the internal diameter of the external tube is 8 mm and the external diameter of the internal tube is 4 mm. The reaction temperature was monitored by a thermocouple adjacent to the quartz tube. All reactants and products were analysed using two gas chromatographs containing a Poropak QS column and a carbon molecular sieve column, respectively, equipped with thermal conductivity detectors (TCD). The catalysts were allowed to equilibrate under the reaction conditions for at least 30 min.

The results of catalytic activity of the catalysts in oxidative coupling of methane are presented in Table 2. It is clear that under the condition used, the catalysts are catalytically active for oxidative coupling of methane, but that the activity decreases with increasing V/Ba atomic ratio. When the V/Ba atomic ratio is in the range 0.05–0.5, the catalysts have only a small amount of the $Ba_3(VO_4)_2$ phase together with are much larger amount of $BaCO_3$, and show a particularly high activity for ethene and ethane production with a high ratio of ethene to ethane being observed. The activity of these catalysts is comparable with other well known oxide catalysts such as Li/MgO, $La_2O_3/BaCO_3$ and $MgO/BaCO_3$.[5] When the V/Ba atomic ratio is >0.5, a large amount of $Ba_3(VO_4)_2$ is present together with only a small amount of the $BaCO_3$ phase, and a new phase of barium pyrovanadate $Ba_2V_2O_7$ is observed. These catalysts are relatively inactive for methane conversion. By comparison, the pure $BaCO_3$ catalyst shows some activity for ethane

**Table 2** The results of the catalytic activity of $BaCO_3$-supported vanadium oxide catalysts in oxidative coupling of methane[a]

| V/Ba atomic ratio | $CH_4$ conv. (mol %) | Product selectivity (mol%) | | | | | $C_2$ yield (mol %) |
|---|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $C_2H_4$ | $C_2H_6$ | $C_2$ | |
| 0.00 | 3.0 | 21.1 | 23.5 | — | 55.4 | 55.4 | 1.7 |
| 0.05 | 24.3 | 9.6 | 29.7 | 35.5 | 25.2 | 60.7 | 14.8 |
| 0.10 | 25.0 | 9.6 | 29.4 | 37.2 | 23.8 | 61.0 | 15.2 |
| 0.25 | 24.4 | 10.2 | 29.2 | 36.6 | 23.4 | 60.0 | 14.7 |
| 0.50 | 16.8 | 13.4 | 27.0 | 31.2 | 28.0 | 59.2 | 10.0 |
| 0.70 | 3.8 | 32.4 | 28.4 | — | 39.2 | 39.2 | 1.5 |
| 1.00 | 1.0 | 41.0 | 34.2 | — | 24.8 | 24.8 | 0.2 |

[a] *Reaction conditions*: $T$ = 820 °C; $CH_4$ GHSV = $12 \times 10^3\ h^{-1}$; $CH_4/O_2$ = 4.25.

production accompanied by considerable amounts of combustion products with very low conversion of methane.

The activity and selectivity of a $BaCO_3$-supported vanadium oxide catalyst with a V/Ba atomic ratio of 0.25 for oxidative coupling of methane as a function of reaction temperature is presented in Fig. 1. As expected, the reaction temperature has a marked effect on the catalytic activity and product distribution. At low temperatures ($<750$ °C), methane conversion is low, considerable amounts of combustion products are formed and almost no useful products are formed. Significant conversion of methane takes place at *ca.* 780–850 °C, leading to the high activity for ethene and ethane production with a total $C_2$ selectivity of $>60$ mol%; the optimum temperature range for selective production of ethene and ethane is 780–820 °C.

The VMgO catalysts have been proposed to be efficient for the oxidative dehydrogenation of light alkanes.[2–4,8–10] Three magnesium vanadate phases, *i.e.* orthovanadate, pyrovanadate and metavanadate, are found in the working catalysts depending on the vanadium concentration and calcination temperature. Although two isolated phases have been proposed to be responsible for the selective oxidation of light alkanes,[8,9] one can note from these studies that in the VMgO catalysts, the coexistence of more than one phase has been identified. Thus it is reasonable to suggest that the active phases for oxidative dehydrogenation of light alkanes would be attributable to at least two phases. This conclusion has been further proved by the work of Gao *et al.*[10] However, in the present studies, the $BaCO_3$-supported vanadium oxide catalysts which consist of $BaCO_3$ and $Ba_3(VO_4)_2$ phases resemble the VMgO working catalysts which consist of MgO and $Mg_3(VO_3)_2$ phases.[8] Thus it is reasonable to expect that the $BaCO_3$ and $Ba_3(VO_4)_2$ phases are the active phases for oxidative coupling of methane, as proposed in the VMgO catalysts.[8] The present results indicate that the presence of a relatively large amount of the $Ba_3(VO_4)_2$ and $Ba_2V_2O_7$ phases leads to low activity for methane conversion, but that $BaCO_3$-supported vanadium oxide catalysts, consisting of $BaCO_3$ and small amounts of $Ba_3(VO_4)_2$, exhibit particularly high activity for oxidative coupling of methane. Therefore, it is concluded that the active phases for oxidative coupling of methane arise from the cooperation of $BaCO_3$ and small amounts of the $Ba_3(VO_4)_2$ phase.

In comparison, it is interesting that the $BaCO_3$-supported vanadium oxide catalysts are very different from $TiO_2$-, $Al_2O_3$- and $SiO_2$-supported $V_2O_5$ catalysts, which have been also applied to the selective oxidation of light alkanes,[1–3] such as partial oxidation of methane to formaldehyde and methanol, and oxidative dehydrogenation of ethane and butane. It has been established that $V_2O_5$ forms a layer structure on these supports with a high density of reactive V=O groups which show a characteristic IR stretching vibration at *ca.* 1000 cm.[1] The V=O groups on the surface of these catalysts, which tend to form C–O bonds during reaction due to their stronger nucleophilicity,[11] have been proposed to be responsible for selective oxidation to oxygenation or combustion products. By contrast, the $BaCO_3$-supported vanadium oxide catalysts contain the $Ba_3(VO_4)_2$ phase in which there are only isolated tetrahedral $VO_4$ groups and no V=O or V–O–V groups, and are relatively basic, as observed in the $Mg_3(VO_4)_2$ phase.[8] Thus, the lattice oxygen ions in the V–O–Ba bridging bonds are relatively less reactive, and the tendency for the formation of C–O bonds is reduced. Consequently, products *via* oxidative coupling of methane are dominant on this catalyst.

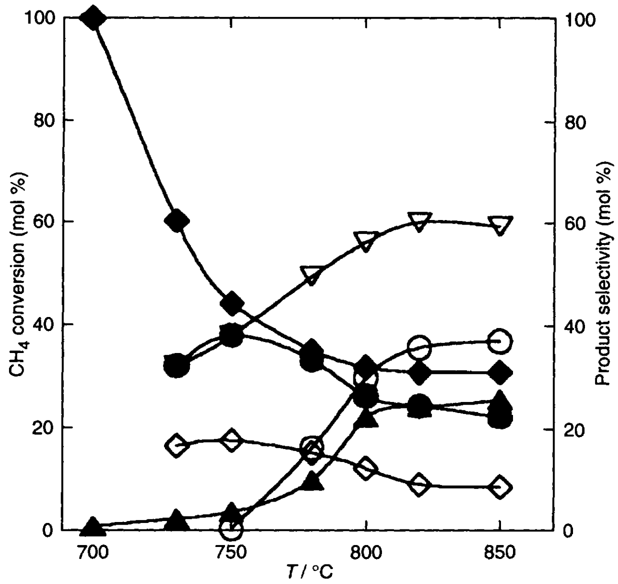

**Fig. 1** Activity and selectivity of $BaCO_3$-supported vanadium oxide catalysts (V/Ba = 0.25) for oxidative coupling of $CH_4$. *Conditions*: $CH_4$ GHSV = $1 \times 10^4$ $h^{-1}$; $CH_4/O_2$ = 4.25, no inert gas employed; (▲), $CH_4$ conversion. Selectivity for (▽): total $C_2$, (○) ethene, (●) ethane, (◆) $CO_2$, (◇) CO.

## References

1 G. Deo, I. E. Wachs and J. Haber, *Crit. Rev. Surf. Chem.*, 1994, **4**, 141.

2 G. C. Bond and S. F. Tahir, *Appl. Catal.*, 1991, **71**, 1; P. J. Gellings, *Specialist Periodical Reports - Catalysis*, ed. G. C. Bond and G. Webb, Royal Society of Chemistry, London, 1985, vol. 7, p. 105; M. S. Wainwright and N. R. Foster, *Catal. Rev. Sci. Eng.*, 1979, **19**, 211; A. Bielanski and J. Haber, *Catal. Rev. Sci. Eng.*, 1979, **19**, 1; D. B. Dadyburjor, S. S. Jewur and E. Ruckenstein, *Catal. Rev. Sci. Eng.*, 1979, **19**, 293; J. Villadsen and H. Livbjerg, *Catal. Rev. Sci. Eng.*, 1978, **17**, 203.

3 E. A. Mamedov and V. Cortes Corberan, *Appl. Catal.*, 1995, **127**, 1.

4 P. M. Michalakos, M. C. Hung, I. Jahan and H. H. Kung, *J. Catal.*, 1993, **140**, 226.

5 J. S. Lee and S. T. Oyama, *Catal. Rev. Sci. Eng.*, 1988, **30**, 249; G. J. Hutchings, M. S. Scurell and J. R. Woodhouse, *Chem. Soc. Rev.*, 1989, **18**, 251; Y. Amenomiya, V. I. Birss, M. Goledzinowski, J. Galuska and A. R. Sanger, *Catal. Rev. Sci. Eng.*, 1990, **32**, 163; J. L. Dubois and C. J. Cameron, *Appl. Catal.*, 1990, **67**, 46.

6 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.

7 Y. Chu, S. Li, J. Lin, J. Gu and Y. Yang, *Appl. Catal.*, 1996, **134**, 67.

8 M. A. Chaar, D. Pater, M. C. Kung and H. H. Kung, *J. Catal.*, 1987, **105**, 438.

9 D. Siew Hew Sam, V. Soenen and J. C. Volta, *J. Catal.*, 1990, **123**, 417.

10 X. Gao, P. Ruiz, Q. Xin, X. Guo and B. Delmon, *J. Catal.*, 1994, **148**, 56.

11 J. Haber, in *Solid State Chemistry in Catalysis*, ed. R. K. Grasselli and J. F. Breazdil, *ACS Symp. Ser.*, 1985, **279**, 1.

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