

## Relationship between Dispersion of Vanadia on Silica Catalysts and Selectivity in the Conversion of Methane into Formaldehyde

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A relationship was observed between selectivity to formaldehyde in the conversion of methane at 550 °C over a series of silica supported vanadium oxide catalysts and the dispersion of the oxide on the support.

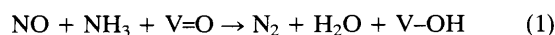
It has been known for some years that vanadium oxide catalysts supported on silica are active and selective in the oxidation of methane into formaldehyde at ambient pressure in the temperature range 450–650 °C.<sup>1–3</sup> Most of this work has been carried out with methane rich feeds. Previous work has also demonstrated that the most selective catalysts are those where the vanadium loading is less than 2 wt%.<sup>4,5</sup> A second feature to emerge is that there is a very strong relationship between selectivity to formaldehyde and the conversion of available methane. Selectivities of close to 100% have been reported over a number of catalyst systems (silica supported molybdenum oxide or vanadium oxide) at very low methane conversions, *i.e.* below 0.05%.<sup>1,2,6</sup> Very high space time yields of formaldehyde are possible on this basis, simply by reducing the contact time to a minimum value.<sup>7</sup> However, selectivity to formaldehyde decreases almost exponentially as the percentage conversion of available methane increases, so that selectivities of *ca.* 30% have been commonly reported at about 1% methane conversion.<sup>1,4,6</sup> This fact can be readily explained in terms of the relative stabilities of methane (C–H bond strength 438 kJ mol<sup>-1</sup>) and formaldehyde (C–H bond strength 364 kJ mol<sup>-1</sup>).<sup>8</sup> The latter decomposes readily once formed.

Here we make a preliminary report of a correlation between the dispersion of a range of vanadium oxide catalysts on silica as measured by the rectangular pulse technique<sup>9–13</sup> and the selectivity to formaldehyde from methane measured at a constant methane conversion.

A series of vanadium oxide catalysts supported on silica were prepared by impregnating silica (Cab-o-sil) with aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>VO<sub>4</sub> to yield catalysts with vanadium loadings in the range 0.4–8 wt%. These catalysts were calcined at 550 °C and tested for methane oxidation in a fixed bed reactor by passing a mixture of methane (0.8 atm) and air (0.2 atm) at 25 ml min<sup>-1</sup> at ambient pressure over catalyst

(0.1 g) held at 550 °C. Reaction products were analysed by on-line gas chromatography.<sup>4</sup>

Vanadium oxide dispersion on the support was measured by the method developed by Miyamoto *et al.*<sup>9–13</sup> in which a mixture of 1000 ppm NO and 20 000 ppm NH<sub>3</sub> was passed at 60 ml min<sup>-1</sup> as a pulse (duration 1 min) over 6–20 mg of the catalyst at 200 °C. The N<sub>2</sub> which evolved was detected by mass spectrometry. The initial sharp burst of N<sub>2</sub> was associated with surface V=O species. Eqn. (1) describes the surface reaction. This dispersion could be calculated by eqn. (2).



$$D(\%) = (\text{mol V}=\text{O}_{\text{surf}}/\text{mol V}_2\text{O}_5) \times 100 \quad (2)$$

Fig. 1 presents variations in percentage methane conversion and selectivity to formaldehyde for the full range of catalysts tested at 550 °C. Percentage conversion was approximately constant, in the range 1.3 to 1.5% of available methane, for vanadia loadings of *ca.* 1 wt% and above. Lower loadings were not as effective in converting methane. Effectively, the higher selectivity to formaldehyde observed with a catalyst comprising 0.5 wt% vanadium was primarily a consequence of the lower conversion rather than any intrinsic property of the catalyst. At vanadium loadings above 2 wt% a significant lowering in selectivity to formaldehyde was observed, in spite of the fact that CH<sub>4</sub> conversion was constant, or falling marginally as the loading was increased. Percentage yields to formaldehyde fell as vanadium loading was increased, as a consequence of the declining selectivity.

When dispersions were measured for loadings of 1 wt% vanadium and above, values in the range 10–30% were recorded, with dispersion lessening as the vanadium loading increased. These values are quite low by comparison with vanadium oxide supported on TiO<sub>2</sub> but are in the normal range expected for vanadium oxide on SiO<sub>2</sub>.<sup>14</sup> Selectivities to formaldehyde and rates of conversion into formaldehyde for conversions of methane in the range 1.3–1.5%, all measured at 550 °C, are plotted in Fig. 2 against the dispersion of the

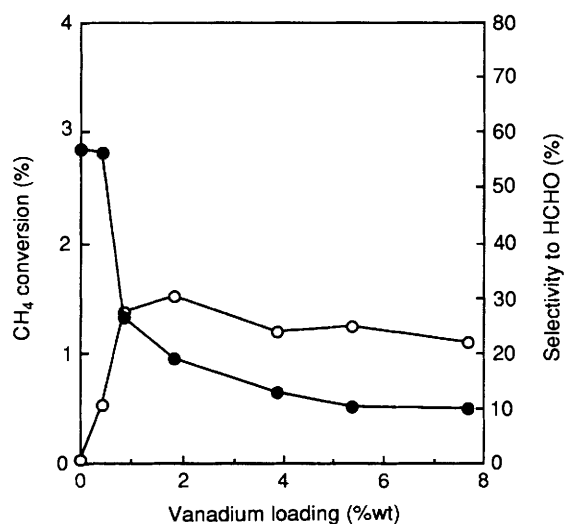


Fig. 1 Conversion of methane and selectivity to formaldehyde for the vanadium loadings indicated:  $T = 550\text{ }^\circ\text{C}$ ;  $p_{\text{CH}_4} = 0.8\text{ atm}$ ;  $p_{\text{air}} = 0.2\text{ atm}$ ;  $W/F = 0.24\text{ g s ml}^{-1}$  ( $W = \text{catalyst mass}$ ;  $F = \text{volumetric flow rate}$ );  $\circ$ , conversion;  $\bullet$ , selectivity

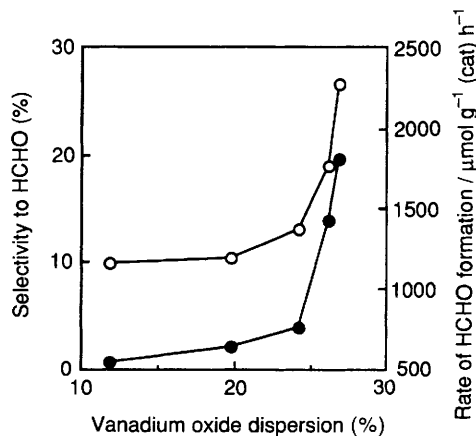


Fig. 2 Influence of vanadium oxide dispersion on selectivity and rate of formaldehyde formation for methane conversions in the range 1.3–1.5%:  $T = 550\text{ }^\circ\text{C}$ ;  $p_{\text{CH}_4} = 0.8\text{ atm}$ ;  $p_{\text{air}} = 0.2\text{ atm}$ ;  $W/F = 0.24\text{ g s ml}^{-1}$ ;  $\circ$ , selectivity;  $\bullet$ , rate

vanadium oxide. This figure shows the high selectivities to occur over those catalysts where the vanadium is most highly dispersed. An alternative statement is that for equivalent conversions selectivity is highest over the smallest vanadium oxide particles. An alternative explanation, namely that the diminishing selectivity was due to pore blocking by  $V_2O_5$  as the vanadium loading increases, was considered. However, pore size distribution analysis of these catalysts indicated that there was no change in pore size distribution (mean pore diameter = 300 Å) or in pore volume as the vanadium loading was increased.

The overriding factor in determining selectivity to formaldehyde in this system is the percentage conversion of methane, with selectivity decreasing as conversion increases.<sup>1-3</sup> Evaluation of other factors such as, in this case, supported phase dispersion is meaningful only if comparisons are made at constant conversion. Within these constraints the results presented in Fig. 2 clearly show a particle size effect, which can be rationalised in terms of the extreme instability of formaldehyde in the reaction conditions. Smaller particles lead to higher selectivities, and we postulate that this is because there is a greater probability that the formaldehyde product can more readily leave the active part of the catalyst surface, namely that part of the support covered by vanadium oxide. With larger particles the possibility of multiple collisions of formaldehyde with the vanadium oxide surface is enhanced, leading to lower selectivities. Reducing the vanadium loading on silica to below 1 wt% did not result in increased dispersion. In fact, the value for the vanadium oxide dispersion recorded for the 0.4 wt% vanadium sample was 28%, identical to that recorded for the 1 wt% sample. This value probably no longer indicates the true dispersion of the vanadium oxide phase, since the rectangular pulse technique

does not appear to detect single vanadium oxide atoms on the support surface.<sup>15</sup>

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