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The limiting selectivity of active sites on vanadium oxide catalysts supported on silica for methane oxidation to formaldehyde

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Abstract

The selective oxidation of methane to formaldehyde is compared to a number of other selective oxidation reactions, primarily on the basis of its selectivity–conversion behavior and the data is presented for a range of promoted vanadium oxide catalysts supported on silica. The reaction mechanism involves activation of methane by an adsorbed oxygen species with subsequent generation of a CH_3 species. This species, in turn, reacts with lattice oxygen to form formaldehyde. Selectivity is determined by the ability of the activating species to discriminate between a C–H bond in methane and a similar, but much weaker C–H bond in formaldehyde. Conventional selective oxidation catalysts are not capable of selectively activating a C–H bond in a reactant in the presence of a similar C–H bond in a product when the bond dissociation enthalpy of the product is weaker by more than 30–40 kJ mol^{-1}. The C–H bonds in formaldehyde are 75 kJ mol^{-1} weaker than the corresponding C–H bonds in methane. The discriminating capacity of active sites on oxide catalysts has been exceeded in attempting to convert methane into formaldehyde, hence the poor selectivity observed. © 1998 Elsevier Science B.V.

1. Introduction

Direct oxidation of methane to formaldehyde occurs readily at ambient pressure over silica supported oxides of vanadium or molybdenum in the 773–923 K range [1–11]. High selectivities (up to 100%) are possible, but only at very low methane conversions using the range of catalysts tested to-date for this reaction. Over vanadium oxide catalysts supported on silica, in particular, the reaction network appears to involve only the sequential oxidation of CH_4 to HCHO, and eventually to CO_x, without the complication of a parallel route to CO_x [12–14]. Hence this system makes a good model for the determination of the underlying reason for poor selectivity, even at moderate conversions. Towards this end, the selectivity conversions for a range of silica supported and variously promoted vanadium oxide catalysts have been prepared and tested for the direct oxidation of methane to formaldehyde at ambient pressure. In addition, the TAP apparatus was applied to determine the overall reaction mechanism. Finally, methane conversion to formaldehyde is compared to 13 other selective oxidation reactions in an attempt to place it in the overall context of the limiting selectivity of active sites on selective oxidation catalysts [15].

2. Experimental

Catalysts comprising 1 wt% vanadium oxide on Cab-o-sil (1V-Cabosil) were prepared by wet impreg-

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nation [12–14]. Promoters in the form of iron, zirconium, molybdenum or niobium were added by co-impregnation. Testing was carried out in a standard flow quartz microreactor operating at ambient pressure, at 823 and 873 K.

In the TAP experiments, 100–150 mg of the catalyst 1V-Cabosil, was loaded into the reactor. A mixture of methane and/or oxygen and argon (9 : 1 : 1) (pulse size=3.6×10^{15} molecules) was passed through the reactor in the 300–900 K range. These conditions correspond to the Knudsen diffusion regime so that gas phase collisions were largely eliminated [13,14].

A series of sequential pulsing experiments were performed, in which a pulse of methane was passed over the catalyst (1.8×10^{15} molecules per pulse) followed at a precise delay by a pulse of oxygen (1.8×10^{15} molecules per pulse). The separation between the pulses, henceforth referred to as the pulse interval (PI), was varied between 0 and 5 s.

3. Results and discussion

Starting from the assumption that methane oxidation to formaldehyde proceeds on vanadium oxide supported on silica according to a series of pseudo-first-order reactions, with rate constants k_1 and k_2 (Eq. (1)):

$$CH_4 \xrightarrow{k_1} HCHO \xrightarrow{k_2} CO_x \tag{1}$$

it follows that the selectivity to the desired product, at a given conversion of methane, will depend greatly on the relative magnitudes of k_1 and k_2. Theoretical selectivity–conversion curves may be constructed, for various ratios of k_1/k_2, using Eq. (2)[16]:

$$\begin{aligned} S_{\mathrm{HCHO}} &\equiv \frac{[\mathrm{HCHO}]_t}{[\mathrm{CH_4}]_0-[\mathrm{CH_4}]_t}\times 100\% \\ &= \frac{[\mathrm{CH_4}]_0}{[\mathrm{CH_4}]_0-[\mathrm{CH_4}]_t}\left\{\frac{k}{k_2-k_1}\right\}(\mathrm{e}^{-k_1t}-\mathrm{e}^{-k_2t}) \\ &\quad\times 100\% \end{aligned} \tag{2}$$

Table 1
Measured values of k_1/k_2 for 1V-Cabosil promoted by the indicated metals and tested at 823 K in methane-lean conditions (0.1 g catalyst used, flow rate: 25 ml min^{-1}, methane-lean feed: 4 kPa CH_4, 97 kPa air)

Metal	Load (M-Cab)					
	0	0.1	0.2	0.5	1.0	0.2 [a]
Iron	0.004	0.007	0.003	0.001	0.002	0.004
Zirconium	0.004	0.015	0.03	0.006	0.001	—
Niobium	0.004	0.01	0.005	0.006	0.004	≪0.001
Molybdenum	0.004	0.004	<0.001	0.01	0.01	0.001

[a] Contains promoter oxide only.

Table 2
Measured values of k_1/k_2 for 1V-Cabosil promoted by the indicated metals and tested at 873 K in methane lean conditions (0.1 g catalyst used, flow rate: 25 ml min^{-1}, Methane lean feed: 4 kPa CH_4, 97 kPa air)

Metal	Load (M-Cab)					
	0	0.1	0.2	0.5	1.0	0.2 [a]
Iron	0.006	0.0025	0.015	0.01	0.015	0.015
Zirconium	0.006	0.02	0.05	0.015	0.004	0.03
Niobium	0.006	0.035	0.02	0.02	0.025	0.02
Molybdenum	0.006	0.008	0.008	0.035	0.03	0.015

[a] Contains promoter oxide only.

Values of k_1/k_2 have been determined for vanadium oxide catalysts supported on silica and promoted with iron, zirconium, molybdenum or niobium, in methane-lean (0.1 g catalyst used, flow rate: 25 ml min^{-1}, methane-lean feed: 4 kPa CH_4, 97 kPa air) and methane-rich conditions (0.1 g catalyst used, methane-rich feed: 81 kPa CH_4, 20 kPa air) at 823 and 873 K, by testing the catalysts and comparing the selectivity–conversion results with the theoretical curves indicated above. The results are presented in Tables 1–4 and clearly show that, in this study, no catalyst tested gave a reasonable selectivity–conversion behaviour. Dashes in Tables 1–4 represent values which could not be evaluated with any certainty. At higher temperatures, formaldehyde decomposition

Table 3
Measured values of k_1/k_2 for 1V-Cabosil promoted by the indicated metals and tested at 823 K in methane rich conditions (0.1 g catalyst used, flow rate: 25 ml min^{-1}, Methane rich feed: 81 kPa CH_4, 20 kPa air)

Metal	Load (M-Cab)					
	0	0.1	0.2	0.5	1.0	0.2 [a]
Iron	0.009	0.0015	0.0015	0.001	<0.001	≪0.001
Zirconium	0.009	0.004	0.0015	0.0015	<0.001	—
Niobium	0.009	0.0015	0.0025	0.002	0.002	—
Molybdenum	0.009	—	—	0.006	0.006	<0.001

[a] Contains promoter oxide only.

Table 4
Measured values of k_1/k_2 for 1V-Cabosil promoted by the indicated metals and tested at 873 K in methane rich conditions (0.1 g catalyst used, flow rate: 25 ml min^{-1}, Methane rich feed: 81 kPa CH$_4$, 20 kPa air)

Metal	Load (M-Cab)					
	0	0.1	0.2	0.5	1.0	0.2 [a]
Iron	<0.001	0.004	0.004	0.002	0.002	$\ll$0.001
Zirconium	<0.001	0.001	0.002	0.0015	0.001	—
Niobium	<0.001	0.001	0.001	0.001	0.001	0.001
Molybdenum	<0.001	0.004	0.003	0.006	0.004	0.001

[a] Contains promoter oxide only.

became more significant, in terms of observed production of HCHO over 1V-Cabosil.

In general, stronger promotional effects were noticed in methane-lean conditions than in methane-rich conditions. In terms of promotional effects, a definite relationship can be noted between the presence of a promoter and reaction conditions. For example, in methane-lean conditions, adding iron to 1V-Cabosil proved beneficial in preventing the sequential reactions of the partial oxidation product (formaldehyde), at 873 K (generally, larger k_1/k_2 values were observed when iron was present at 873 K). At 823 K, the optimum iron load was 0.1 wt%. All other amounts of iron, in 1V-Cabosil, gave lower k_1/k_2 ratios at that temperature.

The results of the present study, and a significant number of other studies on the selective oxidation of methane to formaldehyde have been gathered into a single selectivity–conversion plot which is shown in Fig. 1 [1–11] and generally confirm that to-date all oxide catalysts tested for this reaction have failed to breach a certain selectivity–conversion limit indicated by the solid line in Fig. 1. These data were generated without regard to reaction temperature, contact time, feed-gas composition or the nature of the catalyst used, but represent the upper performance limit which has been achieved to-date with oxide catalysts for this reaction.

In the TAP experiments, up to 2000 oxygen pulses were required to completely reoxidize a 1V-Cabosil sample which had been previously outgassed under vacuum in the TAP reactor in the 773–873 K range. By contrast, in the absence of gas-phase oxygen, methane acted like an inert gas; neither the pulse shape nor size changed on passage over the catalyst. Similarly, CO$_2$ did not interact in any way with the catalyst surface. These data were taken as an indication that lattice oxygen species on vanadium oxide alone supported on silica were not capable of activating methane, but that lattice oxygen in this system was readily removed and replaced [13,14].

The nature of the active oxygen species was further investigated by a series of sequential pulsing experiments in which the methane pulse preceded the oxygen pulse or vice versa. These experiments showed that formaldehyde was produced when a pulse of methane was passed through the reactor up to 60 s after the passage of an oxygen pulse. By contrast, formaldehyde was produced during passage of the oxygen pulse only if the interval to the preceding methane pulse was <2 s. These data indicate that the chemisorbed oxygen species had a lifetime on the vanadium oxide/silica surface, at 903 K, of the order of 60 s, but that hydrocarbon residues were much more rapidly removed.

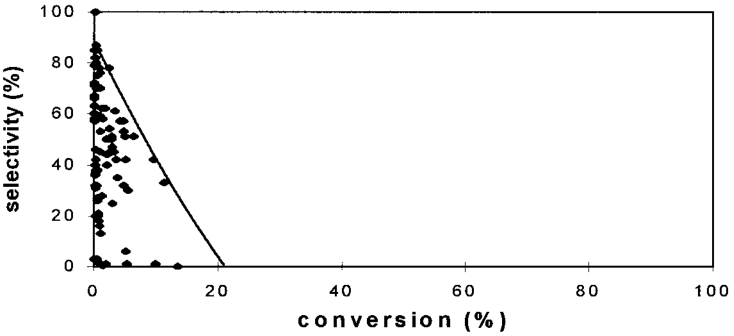

Fig. 1. Literature generated selectivity–conversion plot for methane oxidation to formaldehyde. The line represents the upper limit beyond which experimental studies for the reaction have not progressed.

When a mixture of CH_4 and $^{18}O_2$ was passed over 1V-Cabosil at 880 K, the only reaction products observed were $HCH^{16}O$, $C^{16}O$ and $C^{16}O_2$. H_2O exhibited a very long residence time (20 s) and its pulse shape could not be determined. The sequence, in which the reactants and products emerged from the TAP reactor, was CH_4 followed by O_2, thereafter the products HCHO, CO and CO_2. There is further mechanistic information contained in this sequence, based on the fact that CO_2 does not interact strongly with the catalyst. If CO_2 were formed directly from methane, corresponding to a parallel route not involving HCHO and CO, in the Knudsen diffusion regime HCHO and CO_2 should reach the MS detector with a time difference of $(44/30)^{1/2}=1.21$. The observed difference was much larger, indicating that CO_2 is a secondary product. Methanol was not detected, nor were $HCH^{18}O$, $C^{16}O^{18}O$ or $C^{18}O_2$.

One essential conclusion to be drawn from this work is that there is a very weak interaction between the catalyst surface and methane, whereas interaction with oxygen involves the formation of a surface species of lifetime <60 s which, in turn, were capable of activating the methane, ultimately resulting in the production of formaldehyde. Given that formaldehyde is not produced from methane pulses when 60 s is allowed for the flushing of oxygen species from the catalyst surface, it seems reasonable to conclude that methane is initially activated through interaction with a form of adsorbed oxygen, most likely O_2^- or O^-, with the formation of methyl radicals. Further reaction of this species, leading ultimately to the formation of formaldehyde, occurs via a reaction with lattice oxygen leading to its incorporation into the product.

The following sequence can be written to describe the steps involved:

$$CH_4 + {}^{18}O_{n(\mathrm{ads})} \rightarrow CH_3^{\bullet} + {}^{18}OH$$

$$CH_3^{\bullet} + {}^{16}O_{(\mathrm{latt})} \rightarrow CH_3^{16}O^{\bullet}$$

$$CH_3^{16}O^{\bullet} \rightarrow HCH^{16}O + H^{\bullet}$$

Furthermore, it can be argued that whereas the initial activation of the methane occurs via a short-lived adsorbed oxygen species, the subsequent interaction between the $CH_3^{\bullet}$ species and the lattice oxygen is rather non-specific in nature and the extent of incorporation of the ^{16}O is simply a function of the preponderance of lattice oxygen in the reactor, hence, available for reaction.

Under the applied conditions, the proposed intermediate gas phase radicals cannot couple. This was demonstrated on Sm_2O_3/MgO catalysts for the oxidative coupling of methane [17]. Additionally, the reaction temperature was rather low (<900 K). Experimental as well as simulation results for the pure gas-phase reaction demonstrated that, under these conditions, the formation of coupling products is small (selectivity <30%). Therefore, because 1V-Cabosil is a very bad coupling catalyst, it is rather unlikely that coupling products are formed.

In order to put the performance of methane oxidation catalysts in a broader context, selectivity–conversion plots have been generated from literature data for 13 other selective oxidation reactions, which are listed in the legend to Fig. 2. Each plot has a characteristic upper limit, ranging from very poor selectivity at all conversions for ethane oxidation to acetaldehyde to excellent selectivity performance for oxidative dehydrogenation of ethylbenzene to styrene. We have attempted to find the underlying reasons for the variable upper limits [15].

In our approach to this, we ask the question: How well does an active site distinguish between a C–H bond in a reactant, in this case CH_4 and a similar C–H bond in a product, namely formaldehyde. Generally, selectivity in oxidation catalysis involves activation of the reactant through rupture of a C–H bond, whereas diminishing selectivity is associated with rupture of any bond in the selective oxidation product. As a means of validating this hypothesis, the upper selectivity limit, attained at a fixed conversion, in all the reactions used in this study was plotted against the following function:

$$D^0H_{\mathrm{C–H(reactant)}} - D^0H_{\mathrm{C–H\ or\ C–C(product)}}$$

where $D^0H_{\mathrm{C–H\ (reactant)}}$ is the bond dissociation enthalpy of the weakest C–H bond in the reactant and $D^0H_{\mathrm{C–H\ or\ C–C\ (product)}}$ is the bond dissociation enthalpy of the weakest bond in the selective oxidation product. Full details of the individual bond dissociation enthalpies are presented elsewhere [15].

Fig. 2 shows the plot of the upper selectivity limit observed for the 14 selective oxidation reactions in question at a fixed conversion of 10% against the function listed in the previous paragraph. This figure

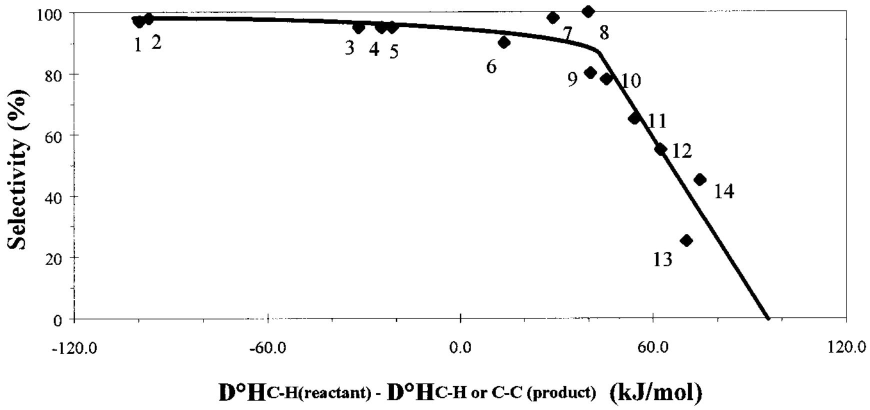

Fig. 2. Selectivity to product vs. $D^0H_{\text{C–H reactant}} - D^0H_{\text{C–H or C–C product}}$ at 10% conversion. 1, Ethylbenzene to styrene; 2, 1-butene to butadiene; 3, acrolein to acrylic acid; 4, ethane to ethylene; 5, *n*-butane to maleic anhydride; 6, propene to acrolein, 7, methanol to formaldehyde; 8, ethanol to acetaldehyde; 9, propane to propene; 10, *n*-butane to butenes; 11, propane to acrolein; 12, methane to ethane; 13, ethane to acetaldehyde; and 14, methane to formaldehyde [15].

shows that there is a clear relationship between limiting selectivities and the nature of the weakest C–H or C–C bonds in the reactants and products. Moreover, Fig. 2 indicates that active sites in oxide catalysts are capable of activating target bonds selectively, provided that the difference in bond dissociation enthalpies between the weakest bond in the reactant and the weakest bond in the selective oxidation product is not >30–40 kJ mol^{-1}. In the case of methane oxidation to formaldehyde, the weakest C–H bond in formaldehyde is 75 kJ mol^{-1} weaker than any of the C–H bonds in methane. This difference exceeds the discriminating capacity of active sites on oxide catalysts, hence the poor selectivity–conversion performance.

4. Conclusions

The primary mechanism of methane activation over vanadium oxide catalysts supported on silica involves an adsorbed oxygen species and gives rise to a CH_3 radical which, subsequently, reacts with lattice oxygen to form formaldehyde. However, the adsorbed oxygen species appears to discriminate between C–H bonds in CH_4 and HCHO, primarily on a bond strength basis and as such reacts much more readily with HCHO than with CH_4. This is not surprising in view of the inherently simple nature of adsorbed oxygen species and their reactivity towards most hydrocarbon species, but it makes progress towards improved selectivity unlikely on the basis of the current generation of catalysts.

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