NOTE

Partial Oxidation of Methane over Silica- and Alumina-Supported Vanadia Catalysts

A considerable effort has been made to study catalysts which are active and selective for the partial oxidation of methane to oxygenates primarily because of the need to convert surplus natural gas, mainly methane, to value added products (1, 2). Among the catalysts active and selective for partial oxidation, supported vanadia and molybdena catalysts have been shown to be the most promising (2–7). Although there have been a number of studies reporting on the influence of different vanadia species on the activity and selectivity for the partial oxidation of higher hydrocarbons (8–12), including ethane (13, 14), such investigations have not yet been made for the partial oxidation of methane. In a companion article we reported on the nature of the vanadium species and the dispersion of vanadia found on V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts as determined by TPR and solid-state ^{51}V NMR (15). In this note, we report on the influence of the nature of these species and the effect of vanadia disperison on the activity and selectivity for the partial oxidation of methane.

V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalyst having a loading of 1.5–25 wt% V_2O_5 were prepared by standard wet impregnation starting from ammonium metavanadate. A detailed description of this preparation can be found elsewhere (15). After impregnation, the catalysts were ground to <400 mesh, dried overnight at 100°C, and calcined at 550°C for 8 h. The pure supports, SiO_2 (Cab-O-Sil, Cabot Corp.) and γ-Al_2O_3 (Vista Chemicals), were subjected to a similar preparation treatment. Bulk V_2O_5 was bought from Aldrich and used as received. Dispersions of vanadia on silica- and alumina-supported V_2O_5 catalysts, as estimated by TRP and reported in a separate publication, are given in Tables 1 and 2 (15).

The partial oxidation of methane was carried out in a quartz microreactor system described elsewhere (16). The reaction conditions used were $P = 1$ atmosphere, $T = 500$–650°C, catalyst weight = 100–200 mg, total flow rate = 150 cm^3/min, CH_4 flow rate = 108 cm^3/min, $CH_4/O_2 = 10$, and balance He. The catalyst was pretreated for 1 h in O_2 at 550°C before starting the flow of methane in the system. All effluent lines were heat traced to 150°C in order to prevent the polymerization of formal-

dehyde. The products were analyzed by online gas chromatography.

Bulk SiO_2 and V_2O_5 exhibited negligible activities in the temperature range (500–650°C) studied. Al_2O_3 exhibited measurable activity for methane oxidation to CO and CO_2 only above 600°C with CO and CO_2 being the only products detected (see Table 2).

Formaldehyde, CO, and CO_2 were the main products observed over the V_2O_5/SiO_2 catalysts with CH_3OH and C_2H_6 detected only in trace amounts. The methane conversion, selectivities, and reaction rates of the V_2O_5/SiO_2 catalysts at 580°C are listed in Table 1. In all cases the conversions were limited to less than 5% in order to maintain differential conditions. Reaction rates on a total catalyst weight basis increased initially with increasing vanadia loading and then decreased. The same behavior was observed at all temperatures studied.

Based on the V_2O_5 dispersion estimated by TPR (see Table 1), turnover frequencies (TOFs) were calculated. These are given in the form of an Arrhenius plot, shown in Fig. 1. Although some variations exist in the TOFs with a change in the loading, these are within experimental error. An apparent activation energy of 190 ± 20 kJ/mol was determined. Thus the total rate of methane conversion based on surface V can be considered to be similar for all the V_2O_5/SiO_2 catalysts. Similar observations have been reported for the oxidation of ethane over V_2O_5/SiO_2 (13).

Figure 2 shows the HCHO selectivities as a function of methane conversion for the V_2O_5/SiO_2 catalysts. In all cases, HCHO selectivity decreased with an increase in methane conversion and only approached 100% at very low conversions. Such behavior is typical of partial oxidation reactions where the selective products are the primary reaction products and the nonselective products are the result of secondary reactions (4, 17). For a given conversion, HCHO selectivity also decreased with an increase in V_2O_5 loading above 4% vanadia loading. The difference in selectivity with V_2O_5 loading may be attributed to changes in the structure of vanadia. We have shown earlier that the dispersion of vanadia decreased

TABLE 1

Conversions and Selectivities for the Partial Oxidation of Methane over V_2O_5/SiO_2 Catalysts at 580°C

Catalyst	Dispersion estimated by TPR[a]	CH₄ Conv. (%)[b]	Selectivity (%)		Rate (μmol/g s)[c]
			HCHO	CO_x	
1.6% V₂O₅/SiO₂	60	0.5	75	25	4.0
4.0% V₂O₅/SiO₂	38	2.6	45	55	20.0
8.2% V₂O₅/SiO₂	17	1.3	28	72	10.4
25.0% V₂O₅/SiO₂	6	0.7	21	79	5.8

[a] From Ref. (15).
[b] For 100 mg of catalyst.
[c] Based on per gram of catalyst.

with an increase in the vanadia loading (15). This was due to an increase in the amount of bulk-like vanadia, whereas the amount of surface vanadia remained essentially constant for all the V_2O_5/SiO_2 catalysts, on a constant total catalyst weight basis (15). Thus the decrease in the HCHO selectivity with an increase in vanadia loading may be attributed to a secondary reaction of formaldehyde on bulk-like vanadia. Recently, Bars et al. (14) reported a similar trend for the oxidation of ethane over V_2O_5/SiO_2 catalysts wherein the nonselective products were favored at higher vanadia loadings.

In contrast with the silica-supported catalysts, the oxidation of methane over V_2O_5/Al_2O_3 catalysts produced only CO and CO_2. No HCHO or CH_3OH could be detected under any of the conditions used in these experiments. Table 2 shows the methane conversion, selectivities, and the reaction rates at 560°C for this series of catalysts. In this case, the total rate of methane oxidation on a total catalyst weight basis increased with an increase in vanadia loading. When the rates are expressed in terms of a TOF (see Fig. 3) the 2% V_2O_5/Al_2O_3 catalyst is noted

TABLE 2

Conversions and Selectivities for the Partial Oxidation of Methane over V_2O_5/Al_2O_3 Catalysts at 560°C

Catalyst	Dispersion estimated by TPR[a]	CH₄ Conv. (%)[b]	Selectivity (%)		Rate (μmol/g s)[c]
			HCHO	CO_x	
Al₂O₃[d]	—	0.6	—	100	2.0
2.0% V₂O₅/Al₂O₃	100	1.0	—	100	7.2
4.8% V₂O₅/Al₂O₃	100	1.1	—	100	8.0
8.9% V₂O₅/Al₂O₃	85	2.0	—	100	15.2

[a] From Ref. (15).
[b] For 100 mg of catalyst weight.
[c] Based on per gram of catalyst.
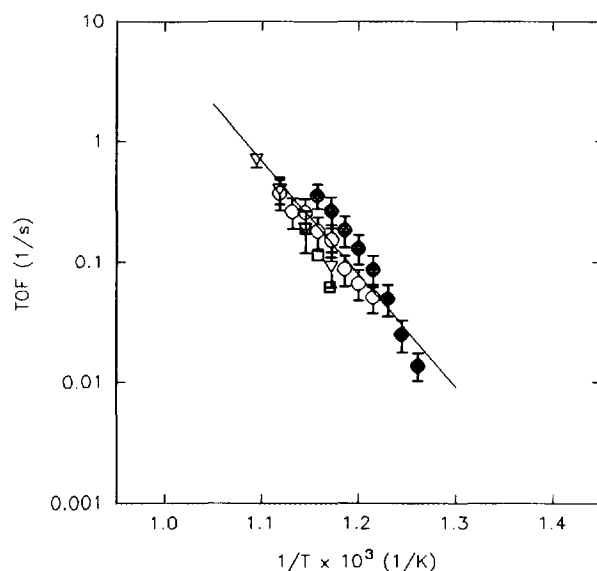[d] At $T = 600°C$ and wt of catalyst = 200 mg.

FIG. 1. Activity for the partial oxidation of methane over V_2O_5/SiO_2 catalysts. (∇) 1.6%, (●) 4.0%, (○) 8.2%, and (□) 25% V_2O_5/SiO_2.

to be more active on a surface vanadia basis than either the 4.8 or the 8.9% loading catalysts. The activation energy for methane oxidation on the V_2O_5/Al_2O_3 catalysts was calculated to be 210 ± 6 kJ/mol.

The differences in the activities seen for these catalysts may be due to the differences in the types of V species present on the surface. Tetrahedral monomeric vanadia species tend to predominate at low vanadia loadings for the V_2O_5/Al_2O_3 catalysts (18, 19). As the vanadia loading is increased, the vanadia species tends to polymerize, yielding dimeric, tetrameric, and finally polymeric surface species (15, 18, 19). Since the TOF for the 2% V_2O_5/Al_2O_3 catalysts is higher than that for the higher loading catalysts, it is proposed that the monomeric vanadia present on the 2% V_2O_3/Al_2O_3 catalyst is more active toward
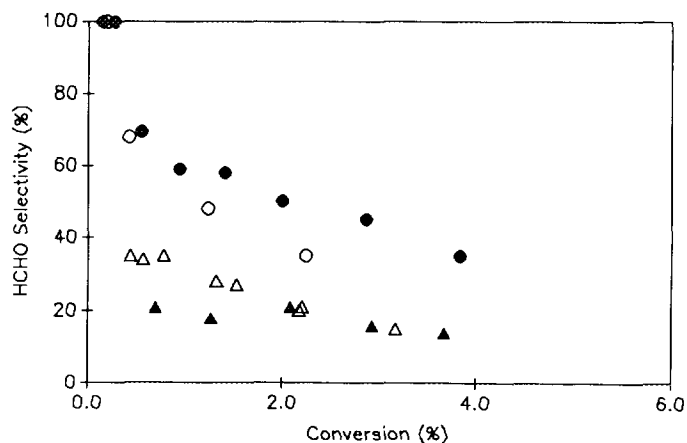

FIG. 2. CH₄ conversion vs HCHO selectivity for V_2O_5/SiO_2 catalysts. (○) 1.6%, (●) 4.0%, (△) 8.2%, and (▲) 25% V_2O_5/SiO_2.

methane oxidation than other surface forms of vanadia which can exist at higher loading. Indeed, Haber *et al.* (20) have reported that monomeric vanadia species are more easily reduced than dimeric forms which would suggest that the former is more active for methane oxidation.

The negligible activity exhibited by bulk V_2O_5 cannot be simply attributed to its low surface area since the 25% V_2O_5/SiO_2 catalyst, which has a similar V_2O_5 surface area (15), was shown to be active for methane oxidation. This suggests that the active sites necessary for methane oxidation are somehow related to the structure of vanadia. Bulk V_2O_5 is known to have an octahedral structure, whereas tetrahedral vanadia is present on silica- and alumina-supported vanadia (15, 18, 21). Thus it is proposed that a tetrahedral V species is an active site for methane oxidation on the supported catalysts. This is also confirmed by the fact that the TOF for V_2O_5/SiO_2 was essentially invariant with V_2O_5 loading. TOF was calculated based on a measurement of amount of surface vanadia estimated by TPR. That measurement correlated well with the amount of tetrahedral vanadia determined by NMR (15).

On the V_2O_5/Al_2O_3 catalysts, no HCHO or CH_3OH was detected. This can be attributed either to differences in the nature of the V_2O_5 sites or to active sites on the surface of the alumina. It was shown earlier that the nature of the surface vanadia is similar for silica- and alumina-supported vanadia as determined by NMR and TPR (15) and that on V_2O_5/Al_2O_3 no bulk-like vanadia is present at low loadings. However, reduction during TPR of the surface vanadia on alumina appears to begin 20°C lower than that on SiO_2. This suggests that V_2O_5/Al_2O_3 may be more prone to form the more oxidized products (CO_x) than

FIG. 4. Generalized reaction pathway for the partial oxidation of methane.

V_2O_5/SiO_2. However, some formation of HCHO on the active vanadia sites cannot be completely ruled out. In order to test this hypothesis, dual bed experiments similar to those of Spencer and Pereira (4) were carried out in which the feed contacted first a bed of V_2O_5/SiO_2 followed by a V_2O_5/Al_2O_3 bed and vice versa. No HCHO was detected in the former case, whereas HCHO was readily detected in the latter. Similar observations were noted when plain Al_2O_3 was used in place of the V_2O_5/Al_2O_3. Thus it is likely that, even if HCHO is initially formed on the tetrahedral vanadia sites on V_2O_5/Al_2O_3, it is further oxidized by acid sites on the alumina.

Based on these observations a generalized reaction pathway for V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts as shown in Fig. 4 can be written. H abstraction and oxygen insertion leading to the selective partial oxidation product, HCHO, appears to take place on a tetrahedral vanadia site. The HCHO so formed can then undergo secondary reaction on either bulk-like vanadia or on alumina acid sites resulting in the formation of the nonselective products, CO and CO_2. Thus proper control over readsorption sites is the key to controlling the selectivity in the partial oxidation of methane.

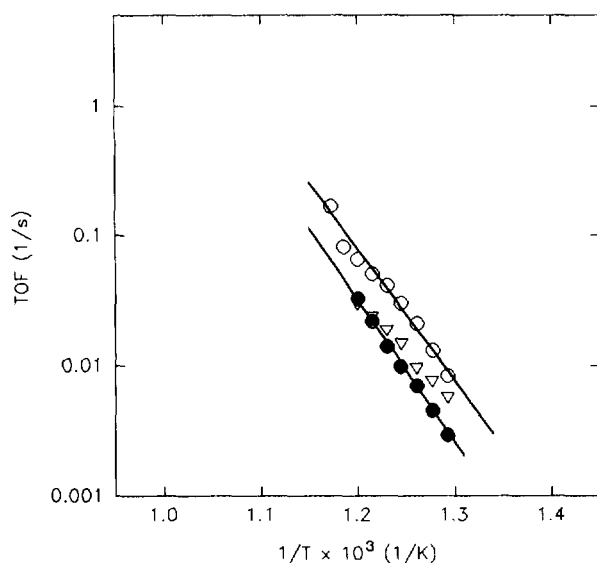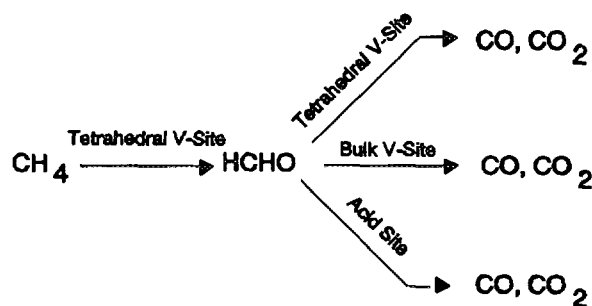FIG. 3. Activity for the partial oxidation of methane over V_2O_5/Al_2O_3 catalysts. (Error bars are proportional to the size of the symbols.) (▽) 2.0%, (●) 4.8%, and (○) 8.9% V_2O_5/Al_2O_3.

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