A highly active silica(silicon)-supported vanadia catalyst for C_1 oxygenates and hydrocarbon production from partial oxidation of methane

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A very low surface area silica–silicon substrate has been used as a support for vanadium oxide and has been tested in the partial oxidation of methane. Use of a reactor with variable dead volume ahead of the bed of the catalyst allows determining the relevance of gas phase reactions in initiating methane conversion. Experimental evidence supports that at atmospheric pressure C_1 oxygenates are essentially produced on the catalyst surface rather than in the gas phase. Comparison with a high surface area silica-supported vanadium oxide catalyst clearly highlights the double role of surface area in promoting catalytic activity, but also in promoting non-selective further oxidation of reaction products. It is shown that a reaction system combining dead volume upstream the bed of the catalyst and a very low surface area is very promising to activate methane conversion to C_1 oxygenates and C_{2+} hydrocarbons at remarkable TOF number preventing further non-selective oxidation. In addition, production of C_{2+} hydrocarbons is observed at temperatures as low as 750 K.

Keywords: gas phase; methane partial oxidation; vanadia/silica–silicon; C_1 oxygenates; C_{2+} hydrocarbons

1. Introduction

The conversion of methane or natural gas to C_1 oxygenates is nowadays one of the most technologically important and challenging problems for catalysis [1,2]. Redox metal oxides have been frequently used for the direct conversion of methane to methanol and formaldehyde [3–7]. The maximum reproducible yields per pass with metal oxides are about 2–3%. Slightly better formaldehyde yields have been

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reported by Kastanas et al. [8] and by Baldwin et al. [9] using an empty Vycor and silica tube, respectively, at pressures above atmospheric, suggesting some participation of the homogeneous reaction and questioning the need of a catalyst. In general, the importance of the gas phase has been highlighted by several authors [10–13]. Here, we present a catalytic system that combines gas phase initiated reaction with a very low surface area catalyst. This configuration yields activities similar to conventional high surface area catalysts, but selectivities to partial oxidation products are remarkably enhanced. Here, we describe the partial oxidation of methane by oxygen at atmospheric pressure over a catalyst based on vanadium oxide deposited on a SiO_2–Si substrate. The contribution of the gas phase reaction, as evaluated in blank experiments, was rather small in the low temperature range. An evaluation of the role of the gas phase reactions and the role of catalyst surface area is proposed.

2. Experimental

A boron-doped (10^{16} B atoms/cm^3 Si) silicon (100) single crystal was used as a support. Prior to vanadia incorporation, this substrate was heated in an air atmosphere at 1000 K for 1.5 h, producing silica–silicon substrate (SS). Subsequently, vanadium was incorporated by wet impregnation with a solution of vanadium acetylacetonate in methanol. The impregnates were dried at 383 K for 12 h and then calcined at 823 K for 2 h. The silica–silicon supported vanadium oxide catalyst is denoted VSS. Vanadium oxide loading on SS support is 0.0021% V_2O_5/SiO_2–Si. For comparative purposes a conventional high surface area silica-supported vanadium oxide (HA-V_2O_5/SiO_2) catalyst was prepared. A commercial silica (Degussa Aerosil-200), particle size 12 nm, BET area ca. 200 m^2/g and composition $SiO_2 > 98.3\%$, $Al_2O_3 = 1.3\%$, $Fe_2O_3 < 0.01\%$, and Na_2O ca. 0.05% was used as a support. Vanadium was incorporated into the silica support by impregnation with an aqueous solution of ammonium metavanadate (NH_4VO_3, Merk reagent grade). Drying and calcination were the same as for VSS counterparts. All catalysts were pelletized and sieved in the particle size range from 60–120 mesh ASTM.

X-ray photoelectron spectra were obtained using a Fisons ESCALAB Mr II 200R spectrometer fitted with a hemispherical electron analyzer and a Mg anode X-ray exciting source (Mg $K_\alpha = 1253.6$ eV). The samples were pressed inside small aluminium cylinders and then mounted on a rod placed in the pretreatment chamber of the spectrometer. The samples were pumped to ca. 10^{-6} Torr (1 Torr = 133.33 $N m^{-2}$) before being transferred to the analysis chamber. The residual pressure in the ion-pumped analysis chamber was maintained below 3×10^{-9} Torr during data acquisition. 20 eV energy regions of the photoelectrons of interest at a pass energy of 20 eV were chosen for each sample. Each spectral region was signal averaged for a number of scans to obtain good signal to noise ratios. A binding energy (BE) of 103.4 eV, corresponding to the Si 2p peak, was used as an internal standard. The spectra were collected in a PDP computer and the peak areas measured assuming a curved background.

Electron microscopy pictures were taken in a Jeol equipment model JSM-840. Element analysis was carried out in a Perkin-Elmer 3030 atomic absorption spectrometer. The sample was prepared by dissolving in HCl, HF and HNO_3 solution and further treatment in a microwave oven at a power of 650 W. Surface areas were calculated by the BET method on a Micromeritics ASAP-2000.

Activity experiments have been performed in a flow quartz microreactor (9 mm i.d.) working at 1 bar (10^5 Pa) total pressure. The reactor is designed so that very low dead volume is present downstream of the catalyst bed to prevent further decomposition of partial oxidation products [8,14]. Two configurations were used, one with dead volume ahead of the bed and another with minimum dead volume upstream the bed (fig. 1). These configurations will be referred to as "dead-volume reactor" and "no-dead-volume reactor", respectively. The reaction mixture consisted of 67 vol% CH_4 and 33 vol% O_2 without diluent. Methane pseudo-residence time was 2 g h/mol. Blank reactions were performed for both configurations on SS substrate, inert packing SiC and on the empty reactor.

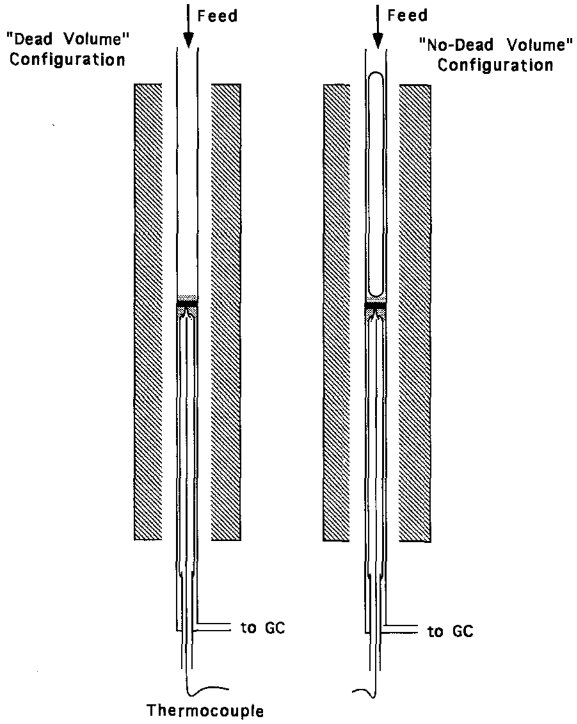


Fig. 1. Two configurations of the reactor. A quartz tube closed at both ends is used to eliminate dead volume upstream the bed of the catalyst.

3. Results

3.1. CATALYST CHARACTERIZATION

Vanadium loading on HA-V_2O_5/SiO_2 is 0.95% according to atomic absorption analysis. Vanadium loading on the VSS catalyst was prepared so that its surface vanadium loading was similar to that of the high surface area silica based catalyst. Since there is a significant difference in specific surface areas (180 m^2/g vs. ca. 1 m^2/g), determination of vanadium on the silica–silicon substrate was accomplished by XPS. Therefore, the vanadia loading was 1% in the final VSS catalyst according to photoelectron spectroscopy (XPS). However, the total vanadium oxide loading on VSS material is 0.0021% V_2O_5/SiO_2–Si. That big difference between the vanadium loading and XPS measurement of vanadium loading on VSS material originates from the very low surface area of SS support, which makes the surface vanadium concentration higher than the absolute mass ratio.

The XP spectra of SS and VSS materials after reaction show the existence of Si^{4+} species. No metallic silicon could be recorded. However, the material has a metallic appearance. Consequently, the bulk silicon substrate must remain essentially metallic while the outer layers are oxidized to Si^{4+}. The V $2p_{3/2}$ binding energy region shows a band at 517.0 eV, characteristic of V(V) species [15] and after reaction the V $2p_{3/2}$ core line exhibits an additional component at 516.0 eV, assigned to reduced V(IV) sites [15]. The presence of reduced vanadium sites suggests that redox property is involved in the partial oxidation of methane.

The picture obtained by SEM of the VSS catalyst (fig. 2) clearly shows the development of a (111) face of silica on top of the Si(100) substrate, as evidenced by the pyramids observed. Vanadium oxide deposits on the developed silica surface as essentially dispersed species, as evidenced by the absence of vanadia crystals. Vanadium species on HA-V_2O_5/SiO_2 material are also highly dispersed [16]. The small pieces observed are due to fragments generated during chopping of the original silicon tube.

3.2. CATALYTIC ACTIVITY

Table 1 presents the conversion of methane on both configurations of the reactor. For the dead-volume reactor upstream, the methane conversion increases drastically with temperature in the absence of catalyst. Furthermore, for the same reactor configuration, the comparison of the results obtained in the empty reactor with those obtained when the reactor is filled with an inert packing material or the SS substrate indicates that there is no substantial change in the methane conversion at a given temperature. The incorporation of vanadium oxide on SS support results in a reactive material. Its reactivity is more evident in the dead-volume reactor configuration. The conventional silica-supported vanadium oxide catalyst presents higher reactivities than the VSS catalyst in the no-dead-volume reactor configura-

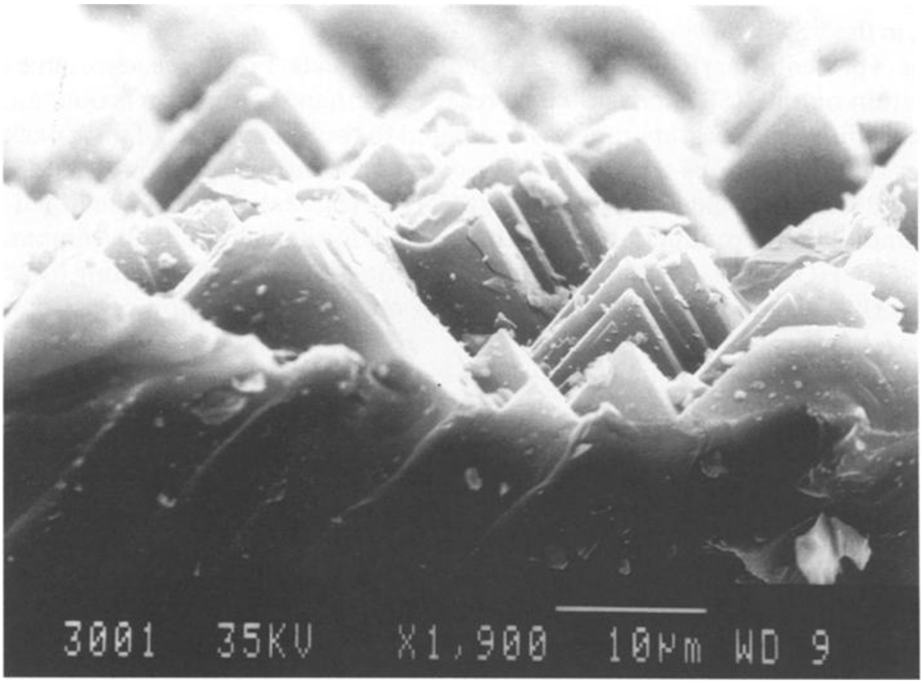


Fig. 2. SEM microphotograph of silica–silicon supported vanadium oxide (VSS) catalyst.

tion. The almost constant conversion values reported are due to the complete consumption of oxygen at the reported temperatures. The presence of dead volume does not significantly alter the conversion of methane on silica-supported vanadium oxide. It should be noted that the reactivity of VSS catalyst in the dead-volume reactor configuration is similar to that of the silica-supported vanadium oxide catalyst in either reactor configuration, despite of the huge difference in vana-

Table 1
Methane conversion on V_2O_5/SiO_2–Si catalyst and SiO_2–Si support as a function of temperature for two reactor configurations [a]

Catalyst	Dead volume			No dead volume		
	863 K	923 K	983 K	863 K	923 K	983 K
no catalyst	1.8	11.3	32.0	0.0	0.1	1.0
SiC	3.6	15.4	33.0	0.0	0.1	0.6
SS	2.0	11.6	30.0	0.0	0.2	1.8
VSS	21.6	25.0	35.0	0.1	0.4	2.9
HA-V_2O_5/SiO_2	26.9	26.9	26.9	26.8	26.8	26.8

[a] Reaction conditions: contact time, 2 g h mol^{-1}; methane/oxygen molar ratio in the feed, 2.0.

dium loading. There are 1.9 mg V_2O_5 in the HA-V_2O_5/SiO_2 bed and 0.042 mg V_2O_5 in the VSS bed.

Fig. 3 presents the yield of different kinds of products. For the dead-volume configuration on the VSS catalyst, the increase of methane conversion is outstanding in the medium temperature range as compared to the SS substrate of inert packing. Under these conditions the combined production of methanol and formaldehyde has a 2.2% molar yield on VSS catalyst at 793 K (fig. 3a). It should be noted that the simultaneous production of methanol and formaldehyde with comparable yields (HCHO to CH_3OH molar ratio is 0.83) (fig. 4a) is a differentiating aspect of this work with many other literature works on partial oxidation of methane at

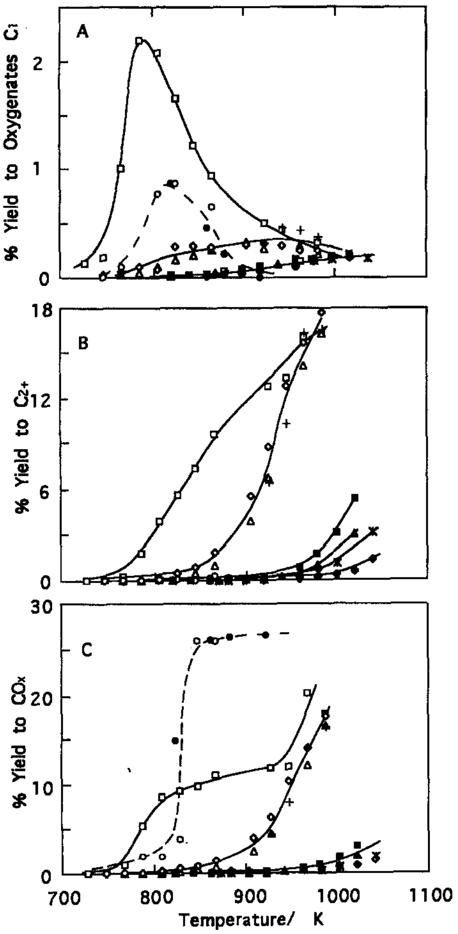


Fig. 3. (a) Yield of C_1 oxygenates (methanol and formaldehyde); (b) yield of CO_x products; and (c) yield of C_{2+} products. On dead-volume configuration: (□) VSS catalyst; (△) silica–silicon substrate; (◇) SiC; (+) no catalyst; (○) high surface area V_2O_5/SiO_2. On no-dead-volume configuration: (■) VSS; (▲) silica–silicon substrate; (◆) SiC; (∗) no catalyst; and (●) high surface area V_2O_5/SiO_2. Dotted lines are for high surface area V_2O_5/SiO_2 catalyst.

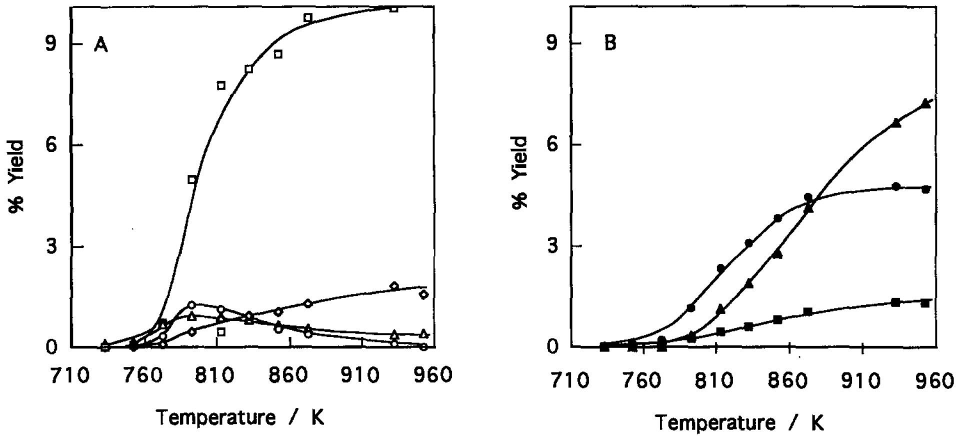


Fig. 4. Percent yield of oxygen-containing compounds (a) and of hydrocarbons (b) as a function of reaction temperature for reactor configuration with dead volume upstream of the catalyst bed: (□) CO; (◇) CO_2; (△) HCHO; (○) CH_3OH; (●) C_2H_6; (▲) C_2H_4; (■) C_3.

atmospheric pressure, as in the case of the conventional high surface area silica-supported vanadium oxide catalyst where mainly formaldehyde was produced and only trace amounts of methanol could be recorded. It is apparent from fig. 3a that production of C_1 oxygenates is essentially due to vanadium sites. Consequently, assuming that all vanadium sites were active, we can calculate that TOF for the production of C_1 oxygenates at 803 K is 12.7 s^{-1} on VSS materials with the dead-volume reactor configuration and 9.9×10^{-3} s^{-1} on silica-supported vanadium oxide catalyst. Consequently, the TOF to C_1 oxygenates is more than three orders of magnitude (ca. 1300 times) higher on VSS materials than on HA-V_2O_5/SiO_2 catalyst. As reaction temperature increases, formation of C_2 and C_3 hydrocarbons becomes predominant (fig. 4b) on SS series. For instance, on the VSS catalyst the production of C_{2+} at 923 K reaches 12.7%, of which 1.3% is propane (fig. 4b). In addition, higher temperature promotes dehydrogenation of ethane and propane to ethylene and propylene (fig. 4b), as evidenced by the presence of hydrogen in the reactor effluents. No significant catalyst deactivation was observed as the C_1 oxygenates and C_{2+} hydrocarbons yield remained essentially unchanged for periods on-stream of 100 h. The production of C_{2+} hydrocarbons as the major partial oxidation products after formaldehyde, and their increase with increasing reaction temperature, is not a new finding; however, yields reported here are substantially higher than those reported in literature [8,17]. Thus, in the work reported by Kastanas et al. [8] for the empty tube experiments using a diluted CH_4/O_2 mixture ($CH_4 : O_2 : Ar = 1.1 : 1 : 10$) at a total pressure of 205 kPa and at 928 K, a yield of formaldehyde of 0.31% and of C_{2+} hydrocarbons of 9.2% was observed. Simultaneous production of C_1 oxygenates and C_{2+} hydrocarbons (0.3% yield of formaldehyde and higher 3.3% yield of C_{2+} hydrocarbons) has been documented by Sun et al. [17] working with a double layered Sr/La_2O_3–MoO_3/SiO_2 catalyst at 103 kPa with CH_4 : air = 1.5 : 1 reactant at 903 K.

The HA-V_2O_5/SiO_2 catalyst activity is essentially associated to the non-selective oxidation products (fig. 3c) and trace amounts of C_{2+} products can be observed. It is noteworthy that the activity of the HA-V_2O_5/SiO_2 catalyst appears to follow essentially the same trend independently of whether dead volume is present or not upstream the bed of the catalyst. At reaction temperatures above ca. 850 K activity of silica-supported vanadium oxide catalyst on either configuration levels off due to complete consumption of oxygen. There is a clearly differentiated response to changes in dead volume on VSS and HA-V_2O_5/SiO_2 catalysts.

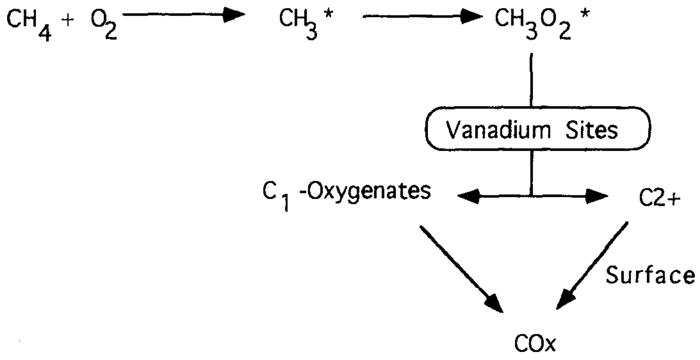
4. Discussion

Analysis of methane conversion using empty reactor, SiC, silica–silicon substrate and with the no-dead-volume reactor configuration shows very low reactivity. Presence of vanadium oxide in the dead-volume reactor does increase reactivity at the highest temperature, essentially leading to C_{2+} hydrocarbons. The presence of dead volume upstream of the bed of the catalyst drastically increases activity for all non-high surface area materials and empty reactor (table 1). There are two clearly differentiated catalytic behaviours characterized by temperature range (fig. 3). Above ca. 925 K, activity and product distribution appear to be independent of the nature of the material used, as long as they do not develop high surface area. Values recorded are extremely close to those in the absence of any catalytic material. Therefore, all activity observed above ca. 925 K must essentially be due to the gas phase reaction. When the reaction system is operating below ca. 925 K, significant differences can be observed in the low surface area materials. In the absence of vanadium, the materials do not show any appreciable activity, and only gas phase reactivity appears to be of relevance. However, the presence of remarkably low amounts of vanadium oxide clearly increases the catalytic activity to C_1 oxygenates and C_{2+} hydrocarbons.

Methane conversion is a radical process which can be initiated in the gas phase by reaction with oxygen to yield $CH_3\cdot$ radicals [1,2]. Doubtless, the increased activity is closely related to the mixing volume granted by the dead-volume configuration of the reactor, thus producing radicals. At low temperatures (below ca. 925 K), conversion to $CH_3O_2\cdot$ radicals by reaction with oxygen is very important [2]. The ratio of methylperoxy to methyl radicals under our experimental conditions is expected to be especially high at temperatures below ca. 925 K [2]. It is expected that there are ca. one order of magnitude more methylperoxy radicals than methyl radicals at temperatures where maximum yields to C_1 oxygenates are reported [2]. The high population of methylperoxy radicals must promote the propagation of oxygenate intermediates that will interact with vanadium sites, thus producing the observed products, as expected from the remarkable capacity of transition metal oxides to catch radicals [17,18]. Otherwise, radicals might revert to initial methane and oxygen molecules. Coupling of methyl radicals to produce C_{2+} hydrocarbons is essentially due to gas phase coupling of methyl radicals [19] and few methyl radicals are expected to be present at temperatures below ca. 925 K [2]. However, production of C_{2+} hydrocarbon increases on VSS materials at temperatures above ca. 750 K. Consequently, there must be an alternative low temperature route to produce them. It has been proposed that the interaction with surface can also revert the $CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$ reaction [9,20]. In addition, vanadium has a tendency to break homolytically peroxy radicals [21], thus providing a heterogeneous route to methyl radicals that may form C_{2+} hydrocarbons at temperatures below those reported for most OCS catalysts. This surface reaction must account for the production of C_{2+} hydrocarbons under reaction conditions where few available methyl radicals are expected to be present if only gas phase reactions are considered. A similar increase in both C_1 oxygenates and C_{2+} hydrocarbons has also been observed by Sun et al. [17] in an experiment where radical production is also induced by other means prior to the bed of a catalyst with a transition metal oxide. Nevertheless, the selectivity to CO_x products was higher in Sun's work than on our low surface area VSS materials, where further decomposition of selective oxidation products appears to be discouraged by the lower specific area.

The role of surface area on the catalysts appears to be dual. On the one hand, it promotes reactivity by surface initiated reactions [1,18,22,23], but also promotes non-selective termination reactions [9,24]. Consequently, catalytic activity on high surface area silica-supported vanadium oxide catalyst is essentially unaffected by promotion of gas phase initiated reactions produced in the dead-volume reactor, since interaction of methane with surface in the presence of oxygen can also produce methyl radicals. Whilst conversion of HA-V_2O_5/SiO_2 is similar to that recorded in the dead-volume configuration reactor with VSS catalyst, the production of C_{2+} hydrocarbons is minimal and a complementary increase in the production of non-selective oxidation CO_x products can be observed. Since C_{2+} hydrocarbons are more reactive than methane in oxidative conditions [1], it appears that C_{2+} hydrocarbons are indeed formed on HA-V_2O_5/SiO_2, but they must further react yielding non-selective CO_x products. It should be reminded that the plateau reached at ca. 825 K in CO_x production and methane conversion is due to the almost complete consumption of oxygen in HA-V_2O_5/SiO_2 catalyst. Production of C_1 oxygenates is essentially due to formaldehyde on HA-V_2O_5/SiO_2 catalyst and few or no methanol can be observed, as opposed to VSS catalyst where formaldehyde and methanol production are similar. Burch et al. showed the high stability of methanol in an empty reactor under methane conversion conditions [20]. It appears that the reason for the negligible presence of methanol on HA-V_2O_5/SiO_2 material must be related to its high surface area that will promote further oxidation of methanol to formaldehyde.

All these results are consistent with the route of the conversion of methane on vanadium oxide catalysts given in scheme 1.



Scheme 1.

5. Conclusion

The strong inhibition of methane conversion for no-dead-volume configuration with empty reactor and when filled with the inert SiC packing or the SS support points out the relevance of gas phase reactions [8–13,25]. The whole data suggests that methyl radicals are formed in the gas phase and then are either oxidized to methanol and/or formaldehyde over the vanadium sites or coupled to form C_{2+} hydrocarbons, the extent of the latter reaction increasing with increasing reaction temperature. A low temperature route to C_{2+} hydrocarbons is provided by the vanadium sites. High temperature production of C_{2+} products has a homogeneous character. The higher surface area of silica-supported vanadium oxide catalyst must account for methane activation and lower yield to selective oxidation products.

These results on the partial oxidation of methane by molecular oxygen on the VSS catalyst using a reactor with dead volume upstream of the catalyst bed indicate that this configuration is critical in its functioning. This would enable selective oxidation of methane to C_1 oxygenates and low molecular weight (C_2 and C_3) hydrocarbons, at a good and constant yield using loadings of active phase in the level of ppm amounts. Very low area is a strong requirement to promote selective oxidation products. These experiments support the proposal that the formation of methanol and formaldehyde at atmospheric pressure occurs on the catalyst surface rather than in the gas phase. Further work in this direction aimed at elucidating more precisely the type of surface sites responsible for the formation of oxygenates and hydrocarbons on the VSS catalysts is in progress.

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