

PARTIAL OXIDATION OF METHANE ON SILICA-SUPPORTED VANADIA CATALYSTS. THE RELEVANCE OF CATALYST BET AREA AND GAS-PHASE ACTIVATION

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Silica-supported vanadium oxide catalysts with different BET areas have been used in partial oxidation of methane to formaldehyde. The BET area of the silica support not only plays an important role in the activation of methane but also in promoting the degradation of reaction intermediates. A reaction scheme is proposed where HCHO and CO₂ are primary products, whereas CO is a secondary product from the degradation of formaldehyde and hydrocarbons. A large BET area led to degradation of hydrocarbons to CO, whereas on low-BET-area catalysts, this side reaction is partially inhibited with the simultaneous formation of C₂ hydrocarbons. The general trend observed is that the activity decreases with decreasing BET areas. Gas-phase reactivity increases the initial activation of methane, but does not increase the degradation of reaction intermediates as much as surface area does thus providing a selective activation for methane.

Key words: Methane; Vanadia; Gas-phase reaction; Coupling; Oxygenates; BET area; Heterogeneous catalysis.

The direct conversion of methane into more valuable C1 oxygenates is a very appealing route to convert the large reserves of natural gas (>90% CH₄) (refs^{1,2}), although the results reported so far have not been always encouraging. The need for a solid catalyst for this reaction at high pressure has been seriously questioned since the yields to C1 oxygenates are lower than those obtained from homogeneous gas phase^{3,4}. At low pressure, the presence of a catalysts affecting the activity and selectivity of the system is required. In any case, the oxidative nature of a catalyst capable of activating methane conversion, will promote further degradation of partial oxidation products (C1 oxygenates). It has been shown that the rate of decomposition of HCHO on catalyst surface

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is higher than in the gas phase⁵. We have recently reported that product distribution not only depends strongly on the type of the redox oxide⁶, but also depends on the BET area of the support⁷. Participation of both homogeneous and heterogeneous reactions in the methane activation has been evidenced by different means⁸⁻¹¹. An increase in the generation of radicals is expected to increase the yield to oxidative coupling products¹². Generation of methyl radical on redox catalysts has certainly increased reactivity and partial oxidation products^{5,7,13}.

In the present work, thermal gas-phase and heterogeneous activation of methane have been evaluated in a series of silica-supported vanadium oxide catalysts with BET areas ranging from 174 to *ca* 1 m²/g. A reactor with variable void volume before the catalyst bed was used to control the gas-phase activation of methane. The role of different BET areas of the catalyst, the CH₄ + O₂ mixing volume and nitric oxide, as a radical initiator, are discussed in the frame of a heterogeneous-homogeneous reaction scheme.

EXPERIMENTAL

A commercial non-porous silica (Aerosil 200, BET area 174 m²/g, particle size *ca* 14 nm) was used as a starting carrier. Silica samples with lower BET areas were prepared by calcining various aliquots of the starting silica at temperatures of 1 273–1 423 K, for a period ranging from 3 to 9 h. The carriers were labeled as “Sy”, where “y” refers to the BET area of the carrier.

Silica supports with various surface areas were impregnated with an aqueous solution of ammonium metavanadate (Aldrich) and hydrogen peroxide in a rotary evaporator at 343 K. The vanadium oxide concentration was *ca* 0.8 V atoms/nm² of the silica support in order to obtain a constant surface coverage of vanadium. The impregnates were dried at 383 K and calcined in two steps: 623 K for 2 h and 923 K for 5 h. After calcination they were sieved to particles size range of 0.125–0.250 mm. Similarly to the supports, the catalysts are referred to as “Vy”.

The vanadium concentration for each sample was determined by atomic absorption spectrophotometry on a Perkin–Elmer 3030 instrument. The BET surface area of the catalysts was calculated by the BET method from N₂ adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2000 apparatus. Pore size distributions were determined by Hg intrusion porosimetry on a Micromeritics equipment. XRD measurements were taken with a Seifert diffractometer and CuK α radiation. Raman spectra were measured on a Renishaw System 1000 spectrometer with a Ar⁺ laser as excitation source at 514 nm, with a resolution better than 2 cm⁻¹. The spectra were recorded from dehydrated samples. XPS spectra were obtained using a ESCALAB 200R spectrometer fitted with a hemispherical electron analyzer and a Mg anode X-ray exciting source (MgK α = 1 253.6 eV) powered at 120 W. All binding energies (BE) were referenced to the Si 2p peak at 103.4 eV.

The steady-state reaction studies were carried out at atmospheric pressure in a 4-mm i.d. quartz fix-bed microcatalytic reactor, designed to minimize the dead volume upstream and downstream the bed of the catalyst. The minimum volume upstream decreases the reaction of methane in the gas phase^{7,14} so that all the activity originates from the catalyst alone, whereas the minimum volume downstream prevents further decomposition of partial oxidation products. In another set of experiments, a 10-mm i.d. quartz fix-bed microcatalytic reactor was used in order to investigate the gas-phase reaction of methane with oxygen upstream from the bed of the catalyst. The runs with the mixing volume upstream the catalyst bed will be referred to as the “mixing-volume” reactor configuration. The surface to volume ratio (S/V) of the reactor (2 cm⁻¹), is low to quench the radical, since Baiker and co-workers observed wall effects at higher S/V ratios¹⁵. The reactor feed was CH₄ (99.95 vol.%)

and O₂ (99.98 vol.%) without diluent. The CH₄/O₂ molar ratio was adjusted to 2 by means of mass-flow controllers (Brooks). The methane pseudo-residence time was kept in the range of 0.3–2.0 g h/mol, and reaction temperatures in the range 783–983 K. No deactivation of the catalysts was observed during time-on-stream experiment. The reactor exit stream was heated in order to avoid condensation of products and polymerization of formaldehyde. The reactor effluents were analyzed by on-line gas chromatography (HP 5890 II) with a thermal conductivity detector, a Chromosorb 107 column and a 4A molecular sieve column, using helium as the carrier gas. Three reaction feeds were used if nitric oxide was added: (i) CH₄ + O₂, (ii) CH₄ + O₂ + He and (iii) CH₄ + O₂ + NO in N₂. Since NO is supplied as 935 ppm NO in N₂, the addition of NO implies a dilution of the reaction feed. Consequently, a third reaction feed diluted in helium to the same extent as in the case of the NO reaction feed was also run for comparative purposes. A clean new quartz microreactor was used in each experiment to avoid contributions of small amounts of catalyst impurities on the catalytic performance. The experiments were repeated to check their reproducibility. Blank reaction for dead-volume and no-dead-volume reactor configuration on inert packing CSi and in empty reactors have been reported elsewhere⁷.

RESULTS

The Raman spectrum of the representative V25 and V174 catalysts show bands at *ca* 495, 606, 802 and 970 cm⁻¹, which are characteristic of an amorphous silica support. Despite of the high calcination temperatures of the silica used, no evidence of an extended crystallization is observed by Raman spectroscopy or X-ray diffraction. The sharp Raman band at 1 037 cm⁻¹ is characteristic of the vanadyl bond of surface-isolated vanadia species¹⁶. Irrespective of the silica area, all the catalysts show the same Raman bands for the support at *ca* 495, 606, 802 and 970 cm⁻¹. The presence of the same surface vanadium oxide species is evidenced in all the series by the presence of the Raman band at 1 037 cm⁻¹. This is indicative of a dispersion of vanadium species despite of the large V loading range used, which is compensated by a parallel change of the area of the support, thus keeping the vanadia loading per surface area at comparable values. Trace amounts of crystalline V₂O₅ are also detected as evidenced by weak features near 146, 284, 702 and 994 cm⁻¹. Tables I and II summarize the characterization of the silica supports and V₂O₅/SiO₂ catalysts. As a consequence of the thermal treatment, the BET area decreases from 174 to *ca* 1 m²/g, while no changes in the structural density can be observed by helium pycnometry, presenting values in the range 2.2–2.5 for all the samples. In addition, no X-ray diffraction patterns are observed for different supports or catalysts, although mercury intrusion evidences significant changes of the bulk density, increasing continuously from 0.4 mg/ml for S174 to 2.0 mg/ml for S1. The change in density arises from different aggregation of large silica particles in the micrometer range as evidenced by the average pore diameter, determined by mercury intrusion (Table I). The V-containing samples show a continuous decrease in the BET area, in parallel with that of the corresponding supports, though lower than those of their V-free counterparts (Table II). The V 2p core level spectra of the catalysts show the characteristic spin-orbit splitting in the 520–516 eV

binding energy range (BE), with the most intense V 2p_{3/2} peak at approximately 517.2 eV, which indicates that V^(V) species is present. Some reduction to V^(IV) is also observed, most probably due to photoreduction of vanadium oxide under the X-ray irradiation of the sample under vacuum during the measurement. No significant changes in BE values can be observed after time-on-stream operation. The V/Si atomic ratio determined by XPS does not show a clear trend, but shows values close to 0.04 which is indicative of all the samples having a similar surface coverage. This result is expected since the vanadium oxide loading was selected to keep a surface coverage near 0.8 V atom/nm² for all the samples. As this coverage is below the real monolayer coverage, the vanadium oxide species are expected to be highly dispersed. This is confirmed by the ab-

TABLE I
Surface and textural characterization of the supports

Support	Nitrogen isotherm		Hg Porosimetry	
	BET m ² /g	pore diameter nm	bulk density mg/ml	pore diameter μm
S174	174	8	0.4	0.12
S95	95	28	0.5	0.11
S25	25	23	0.9	0.09
S1	ca 1	20	2.0	0.04

TABLE II
Chemical, textural and surface characterization of the catalysts

Catalyst	V ₂ O ₅	BET	XPS	
	wt.%	m ² /g	BEV 2p _{3/2}	(V/Si) atomic
V174	2.24	125	515.4 (45)	0.03
V95	1.29	80	515.8 (47) 517.3 (53)	0.07
V25	0.41	22	515.6 (63) 517.1 (37)	0.05
V1	0.01	1	515.4 (76) 516.8 (24)	0.02

sence of X-ray diffraction patterns from three-dimensional V_2O_5 aggregates and also by the absence of a significant presence of Raman bands of crystalline vanadia (Fig. 1).

The oxidation of methane yields ethane, ethene, formaldehyde, methanol, CO and CO_2 , along with water and small amounts of hydrogen. The reactivity of the supports and catalysts is presented in Fig. 2. Due to the large differences in reactivity caused by the large differences in BET, a logarithmic scale has been adopted to compare all the catalysts. Silica supports have very low activity except the silicas with very high BET areas. The incorporation of vanadium oxide has a negligible effect on S1 when using the 4-mm i.d. quartz microreactor. The activity of S25 shows a moderate increase after incorporation of vanadium oxide. The effect of vanadium oxide is most evident on the high surface area catalysts, where the activity increases by about one order of magnitude for S95 and two orders of magnitude for S174 in the 4-mm i.d. quartz microreactor. Blank tests of the corresponding silicas clearly indicate that only the silicas with high surface area show some activity.

FIG. 1

Raman spectra of the representative V174 and V25 catalyst under dehydrated conditions at 573 K in dry air (* indicates the Raman bands of traces of crystalline V_2O_5)

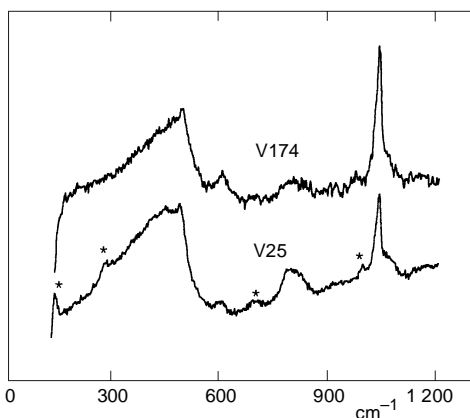
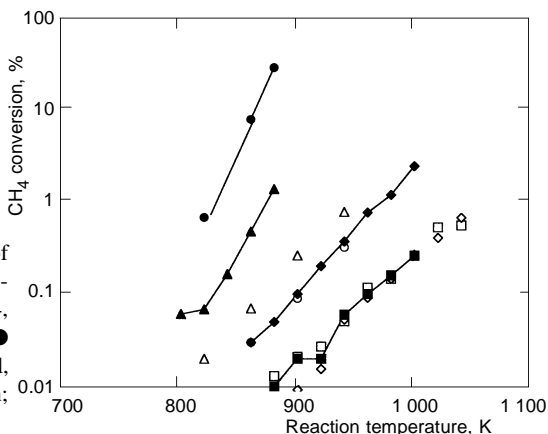


FIG. 2

Semilogarithmic plot of the conversion of methane vs reaction temperature for supports \square S1, \diamond S25, Δ S95 and \circ S174, and catalysts \blacksquare V1, \blacklozenge V25, \blacktriangle V95 and \bullet V174 (reaction conditions: $W/F = 2$ g h/mol, $CH_4/O_2 = 2$ mol/mol; reactor i.d.: 4 mm; catalyst weight: 100 mg)



The selectivity vs conversion plots for the 4-mm i.d. quartz microreactor configuration reveal some general trends for all catalysts (Fig. 3). As can be seen, the selectivity to formaldehyde decreases with conversion, whereas the selectivity to CO increases, suggesting that CO is a secondary product originating from the deep oxidation of HCHO. Moreover, the selectivity to CO₂ does not tend to zero at zero methane conversion, except for catalyst V1, indicating that CO₂ is a primary product. The very low selectivity to CO₂ on catalyst V1 suggests that its low BET area does not facilitate the heterogeneous oxidation of methane. CO selectivity tends to stabilize with the conversion of methane to different values following the order V174 > V95 ≈ V25 > V1. The presence of C₂ hydrocarbons is only observed for the catalysts V25 and V1; furthermore the selectivity to C₂ appears to follow a trend opposite to that of CO. We showed

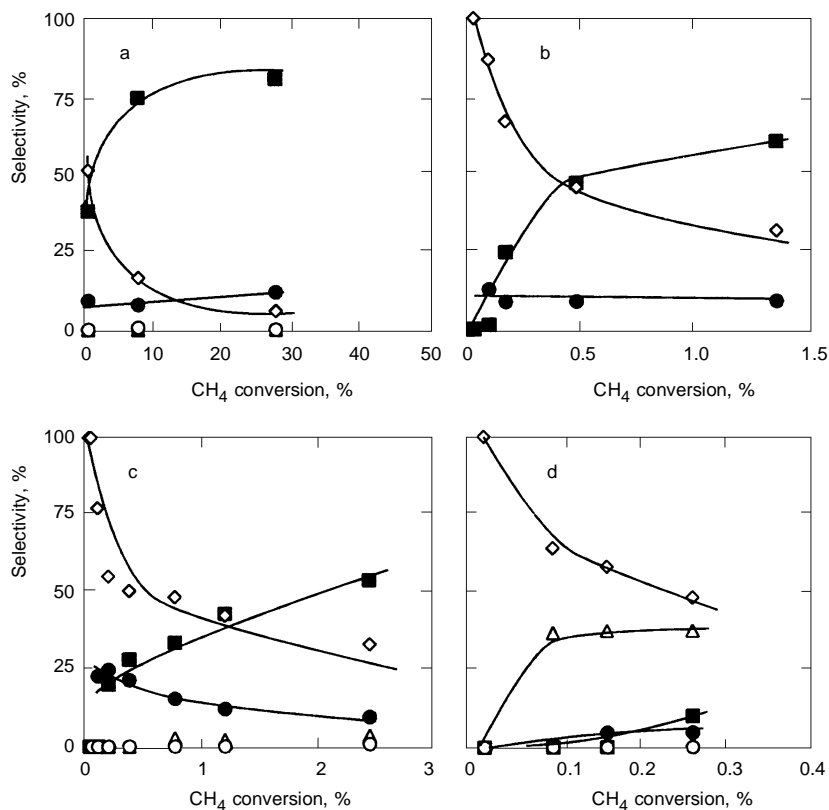


FIG. 3

Selectivity vs conversion plots of the catalysts V174: ■ CO, ● CO₂, Δ C₂, ◇ HCHO, ○ CH₃OH (a), V95 (b), V95 (c), and V1 (d) (reaction conditions: W/F = 2 g h/mol, CH₄/O₂ = 2 mol/mol; reactor i.d.: 4 mm (without mixing volume reactor configuration); catalyst weight: 100 mg)

by *in situ* DRIFTS spectroscopy–mass spectrometry that silica-supported vanadium oxide catalysts produce non-oxygenated intermediates⁶. These trends suggest that CO does not originate only from formaldehyde degradation, but also from a common intermediate with C₂ hydrocarbons. It was proposed that, for a given BET area of the support (*ca* 200 m²/g), the use of an appropriate oxide improves the selectivity to partial oxidation products (C1 oxygenates and C₂ hydrocarbons) *vs* non-selective CO_x. It also appears that for a specific oxide (vanadium oxide) the decrease in surface area improves the selectivity to partial oxidation products while the CO_x selectivity follows an opposite trend. Therefore, in order to improve this selectivity, it is imperative to find alternative ways of methane activation that take advantage of the low degradation activity of the catalysts with very low surface area. Since the heterogeneous-homogeneous nature of methane activation has a great relevance to the total activity^{9,10} and product distribution, the generation of radicals, either in the gas phase or on the catalyst surface is a key method to activate this molecule^{8,12,13,17}. Nitric oxide is a chemical initiator of radicals, which has proved to activate methane^{5,14}. The presence of void volume upstream the catalyst bed allows the activation of methane by oxygen in the gas phase so that the stream that reaches the catalyst bed contains CH₃• radicals^{7,18}. Both options have been evaluated in this work. The effect of NO additive is presented in Fig. 4, where the yields of the different products of the reaction for catalyst V1 in a 4-mm i.d. quartz microreactor are presented. Catalyst V1 using the 4-mm i.d. reactor shows very low activity. Dilution of the reaction feed (CH₄ + O₂ + He) led to an activity decrease; however, if 0.03% NO is added into the feed stream, the activity increased by a factor *ca* 6. The increase of reactivity observed upon addition of NO is essentially due to C1 oxygenates and, to a lesser extent, to C₂ hydrocarbons. However, nitric oxide is not an attractive additive from the environmental point of view, which is not the case of the

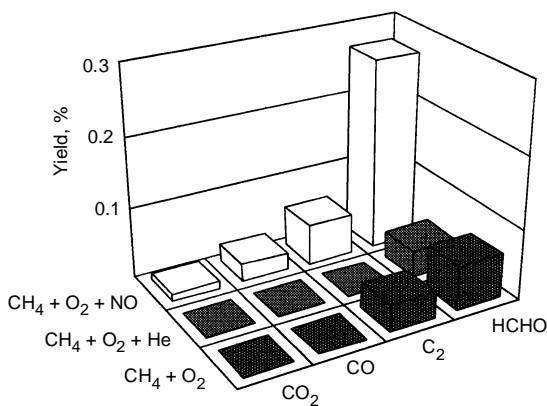


FIG. 4

Yield to the different products on V1 catalyst under three reaction feeds: CH₄ + O₂ + NO, CH₄ + O₂ + He and CH₄ + O₂ (reaction conditions: W/F = 2 g h/mol, reactor i.d.: 4 mm (without mixing volume reactor configuration); catalyst weight: 100 mg)

generation of radicals by providing a $\text{CH}_4 + \text{O}_2$ mixing volume. As illustrated in Fig. 5, the presence of a $\text{CH}_4 + \text{O}_2$ mixing volume upstream the catalyst bed affords a significant increase in methane conversions. The supports and catalysts with very low BET areas show negligible activity in the 4-mm i.d. quartz microreactor configuration, however, the activity increases to a certain extent in the 10-mm i.d. quartz microreactor with no void volume upstream from the bed of the catalyst. This must be due to a lowered linear speed of the molecules, which increases their chances to be activated. The conversion of methane is an order of magnitude higher on a 10-mm i.d. quartz microreactor with a void volume (9 ml) in the absence of a catalyst, and it increases almost another order of magnitude if the reactor is loaded with catalyst V1. This conversion level of methane is comparable to that of the high-BET-area catalyst V174 in the 4-mm i.d. quartz microreactor with no void volume present. Thus, similar conversion levels can be attained by a high-BET-area catalyst in a reactor with no void volume or by a very-low-BET-area catalyst in a reactor with void volume prior to reaching the catalyst bed. We have also observed that very-high and very-low-area catalysts show comparable activities in the "mixing volume" reactor configuration.

If the $\text{CH}_4 + \text{O}_2$ mixing volume affords methane conversion comparable with that of a high BET area, it is necessary to compare the product distribution for both configurations: high BET area alone and low BET area with the $\text{CH}_4 + \text{O}_2$ mixing volume. The selectivity of the three groups of products at 15% methane conversion in the $\text{CH}_4 + \text{O}_2$ mixing volume reactor configuration is presented in Fig. 6 for different catalyst series.

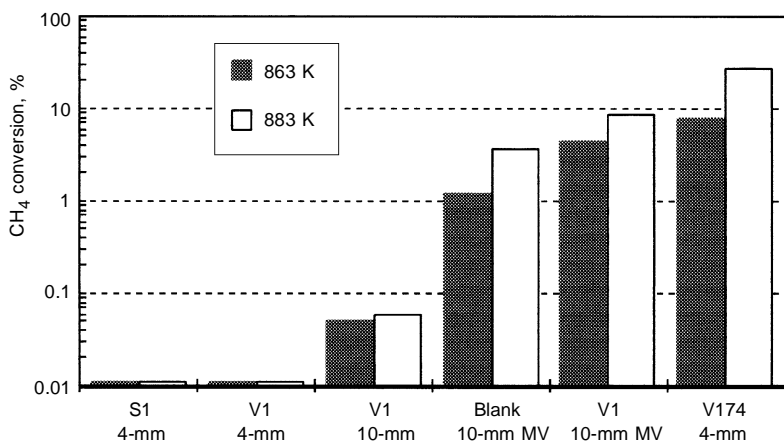


FIG. 5

Methane conversion on different catalyst in different reactor configuration: 4-mm, means the 4-mm i.d. quartz microreactor with no mixing volume; 10-mm MV, reactor with mixing volume configuration (9 ml) in a 10-mm i.d. quartz microreactor; 10-mm, means the 10-mm i.d. reactor with no mixing volume (reaction conditions: $W/F = 2$ g h/mol, $\text{CH}_4/\text{O}_2 = 2$ mol/mol; catalyst weight: 100 mg)

C1 oxygenate formation appears to have little dependence on the surface area of the catalysts in the $\text{CH}_4 + \text{O}_2$ mixing volume reactor configuration. On the other hand, CO_x formation which increases at the expense of C_2 hydrocarbons has a strong dependence on the surface area value of the catalyst. This trend suggests that C_2 hydrocarbons and oxygen-containing products may have a common intermediate

DISCUSSION

We have already shown that gas-phase activation of methane by means of a $\text{CH}_4 + \text{O}_2$ mixing volume upstream the bed, using very-low-BET-area catalysts converts methane to a similar extent as in high-BET-area V/SiO_2 catalysts^{7,14}. However, in these investigations, the very-low-BET-area catalysts were prepared from a silicon substrate on which a silica layer was developed by thermal treatment in air and no information could be reported on the effect of intermediate surface area values. To cover this gap in BET area values, the progressive decrease in the BET area of the original SiO_2 (Degussa Aerosil-200) allows a systematic study of the effect of the surface area on the catalytic performance of V/SiO_2 using a silica support of the same chemical nature. The use of silicas of different BET areas provided by different suppliers was ruled out since the level of impurities changes and it is well known that impurities in the ppm level lead to important differences in the structure of the supported oxide and also in the catalytic performance. Degussa Aerosil-200 is a good candidate for this purpose due to its high purity, and high surface area. For this carrier, the BET area can significantly decrease upon calcination at very high temperatures. The parallel evolution of the pore structure, as revealed by mercury porosimetry suggests that the BET-area changes must be related to the densification of the silica, since according the Raman and XRD techniques no structural modification of the amorphous silica support appears to take place.

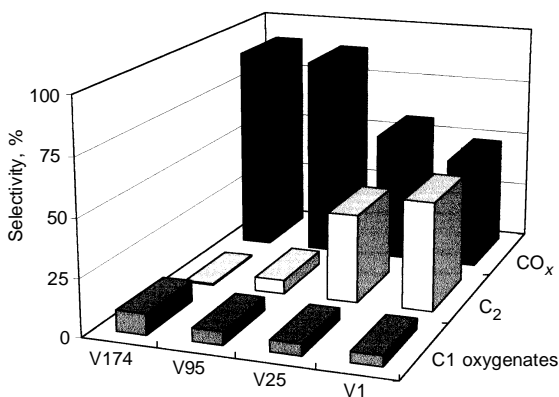


FIG. 6

Selectivity at 15% conversion vs the specific surface area of the catalysts (reaction conditions: $W/F = 2 \text{ g h/mol}$; catalyst weight: 100 mg in the $\text{CH}_4 + \text{O}_2$ mixing volume reactor configuration)

It should be also remembered that Degussa Aerosil-200 is a fumed silica, prepared at temperatures beyond its melting point, thus, no change of impurity levels on the surface is expected due to the temperature treatment used to decrease its area.

The vanadium oxide species do not generate any diffraction pattern since they are highly dispersed, as evidenced by Raman spectroscopy. All the catalysts are essentially oxidized and the V/Si atomic ratio determined by XPS is around 0.04. This value is equivalent to those observed on silica-supported vanadium oxide with vanadium oxide loading below the monolayer coverage^{16,19}, thus suggesting that the surface coverage of the silica-supported vanadium oxide species is comparable in the series. Consequently, the same surface vanadium oxide species is present on all the catalysts and any difference in catalytic performance must then originate from different BET areas of the catalysts.

The BET area of the catalysts plays a key role in the initial activation of methane. It has an intense effect on methane conversion in the absence of the $\text{CH}_4 + \text{O}_2$ mixing volume, since it increases the conversion of methane by several orders of magnitude. Surface vanadium oxide species interact with oxygen thus promoting its activation^{7,16,19} which will increase the activation of methane by oxygen. However, the BET area not only promotes methane activation, but also degradation of reaction intermediates since the selectivity to CO tends to stabilize at higher values as the area increases²⁰. Due to the radical nature of this reaction, the use of radical initiators must increase the activity. If the activation of methane on large BET areas is replaced by the radical initiator NO, this can compensate the low activity of low-surface-area catalysts and shift the product distribution towards oxygen-containing species, like methanol and formaldehyde. The presence of NO must shift the equilibrium between methyl and methylperoxy radicals towards the latter¹⁰. The interaction between the molecules of the reactants (O_2 and CH_4) to initiate the reaction is decreased upon dilution by helium, thus decreasing the probability of reactive collisions between O_2 and CH_4 to generate radicals. Despite the relevance of dilution of the homogenous activation, the presence of NO is capable to activate methane by production of radicals. The activation can also be granted by the homogenous reaction of oxygen with methane, which can be accomplished by providing a $\text{CH}_4 + \text{O}_2$ mixing volume upstream the catalyst bed. Under this configuration, the activity of all the catalysts is triggered to values comparable with those of the high-BET-area catalyst (V174) in the 4-mm i.d. quartz microreactor. In contrast to the use of nitric oxide, the use of $\text{CH}_4 + \text{O}_2$ mixing volume appears to shift the equilibrium to ethane and ethene. This trends are also affected by the area of the catalysts. As the BET area increases, the content of carbon monoxide increases at the expense of C_2 , thus, the C_2/CO yield ratio tend to lower values. The strong dependence of C_2 on the catalyst surface area suggests that non-oxygenated intermediates may form on V/SiO₂ catalysts, but they are oxidized near the surface before leaving the catalyst bed; the extent of this reaction is clearly determined by the BET area of the catalyst.

CONCLUSIONS

The catalysts prepared using the silica supports with variable areas allow to study the relevance of the BET area to the activation of methane and to the product distribution. The area not only increases the methane conversion, but also promotes further degradation of reaction intermediates. The selectivity to partial oxidation products is favored with respect to that to non-selective CO_x by decreasing the area of the catalysts. The study of the selectivity trends in dependence on the surface area suggests that non-oxygenated intermediates are present during the partial oxidation of methane on silica-supported vanadium oxide catalysts. On the high-BET-area catalysts, C_2 hydrocarbon intermediates are readily oxidized to CO and therefore no hydrocarbons are observed, thus, the non-selective degradation must be directly related to the BET area. The low activity of the catalyst V1 and V25 is compensated by an alternative activation, granted by the heterogeneous-homogeneous nature of methane activation. The generation of gas-phase radicals triggers initial activation of methane but does not increase the degradation of the reaction intermediates as much as the surface area does, thus yielding more selective catalytic systems if low-BET-area catalysts are used. The production of radicals can be achieved by chemical additives or by using an appropriate reactor configuration that promotes the reaction of methane with oxygen in the gas phase. The use of nitric oxide as a radical initiator shifts the product distribution towards C1 oxygenates, while the $\text{CH}_4 + \text{O}_2$ mixing volume shifts the selectivity towards C_2 hydrocarbons. The reactor configuration has an enormous effect on the catalytic performance. Even in the absence of void volume, as the cross section of the reactor increases, the linear speed of the gases decrease and the chances to have effective collisions increase.

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