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Selective oxidation of methane with air over silica catalysts

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Partial oxidation of methane by oxygen to form formaldehyde, carbon oxides, and C_2 products (ethane and ethene) has been studied over silica catalyst supports (fumed Cabosil and Grace 636 silica gel) in the 630–780°C temperature range under ambient pressure. The silica catalysts exhibit high space time yields (at low conversions) for methane partial oxidation to formaldehyde, and the C_2 hydrocarbons were found to be parallel products with formaldehyde. Short residence times enhanced both the C_2 hydrocarbons and formaldehyde selectivities over the carbon oxides even within the differential reactor regime at 780°C. This suggests that the formaldehyde did not originate from methyl radicals, but rather from methoxy complexes formed upon the direct chemisorption of methane at the silica surface at high temperature. Very high formaldehyde space time yields (e.g., 812 g/kg cat h at the gas hourly space velocity = 560000 ℓ(NTP)/kg cat h) could be obtained over the silica gel catalyst at 780°C with a methane/air mixture of 1.5/1. These yields greatly surpass those reported for silicas earlier, as well as those over many other catalysts. Low CO_2 yields were observed under these reaction conditions, and the selectivities to formaldehyde and C_2 hydrocarbons were 28.0 and 38.8%, respectively, at a methane conversion of 0.7%. A reaction mechanism was proposed for the methane activation over the silica surface based on the present studies, which can explain the product distribution patterns (specifically the parallel formation of formaldehyde and C_2 hydrocarbons).

Keywords: Methane; formaldehyde; silica; Cabosil; coupling catalyst

1. Introduction

Catalytic partial oxidation reactions of methane to C_1 oxygenates (particularly methanol and formaldehyde) have been intensively studied during the last decade by many research groups worldwide [1,2]. Most studies have focussed on increasing the overall formaldehyde yields and selectivities, while very few efforts have been placed on mechanistic understanding of the reactions. Silica has been widely used as a support for metal oxide catalysts for methane partial oxidation to oxygenates [3–8]. A number of papers have shown that silica itself has discernible activities for methane oxidation to formaldehyde [5,7,9–13]. Kasztelan and Moffat [7] have shown that up to 4.5% of the methane co-fed with O_2 can be converted at 593°C at relatively high contact times, but selectivity to formaldehyde was poor (8%) and no formaldehyde was detected with N_2O as oxidant. Kastanas et al. [9] reported detailed studies on methane partial oxidation over Vycor, quartz walls of reactor tubing, and silica compounds as well. In the temperature region employed (620–720°C), C_2 hydrocarbons were also observed as coproducts. Parmaliana et al. [12] recently reported that precipitated and sol–gel silicas have higher activities than MoO_3 catalysts supported on silica (Cabosil and gel), and it was noted that high temperature treatment (1000°C) of the silica catalyst was very beneficial for methane conversion. However, there have been very few attempts to explore the reaction mechanism by which methane is activated over the silica surface to form formaldehyde and methyl radicals.

Recent studies in this laboratory have shown that a double bed catalyst configuration can greatly increase the yield of formaldehyde from a CH_4/air = 1.5/1 reactant mixture [14], in particular over a double-layered catalyst bed of Sr/La_2O_3 followed by MoO_3/SiO_2. Formaldehyde was formed at a significantly higher space time yield (187 g CH_2O/kg cat h) than that from the individual catalyst beds, as well as from a bed of the two mechanically mixed components. This indicated that the methyl radicals generated upstream over the Sr/La_2O_3 catalyst bed were trapped by the MoO_3/SiO_2 catalyst surface to produce formaldehyde. The reaction sequence can be partially explained with the following general scheme for methane-to-formaldehyde over the MoO_3/SiO_2 catalyst proposed by Liu et al. [3]:

$$\mathrm{Mo^{VI}O^{2-}} + {}^{\cdot}\mathrm{CH_3} \rightarrow \mathrm{Mo^{V}OCH_3^-}, \tag{1}$$

$$\mathrm{Mo^{V}OCH_3^-} + \mathrm{Mo^{VI}O^{2-}} \rightarrow \mathrm{Mo^{IV}} + \mathrm{Mo^{V}OH^-} + \mathrm{CH_2O}. \tag{2}$$

A similar study has been carried out in the present work with double bed catalysts of Sr/La_2O_3 and pure silica catalyst supports, as well as single bed silica catalysts without promoting metal oxides such as MoO_3. Methane conversion and product selectivities were studied as a function of the reaction conditions, especially the reactant residence times. Further information on the reaction mechanism was obtained, and a reaction scheme is proposed for methane activation over the silica surface based on the experimental results.

2. Experimental

Fumed silica (Cabosil) and silica gel (Grace 636 gel) obtained from Aldrich with surface areas of 385 and 480 m^2/g, respectively, have been used in this

Table 1
Methane conversion, formaldehyde space time yields, and product selectivities over the SiO_2 (Cabosil and Grace 636 gel) catalysts and the dual bed catalysts of Sr/La_2O_3 followed by SiO_2 with CH_4–air (1.5 : 1) reactant at ambient pressure and 730°C and gas hourly space velocity = 70000 ℓ/kg cal h

	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]				
			CH_2O	C_2	C_3	CO_2	CO
SiO_2 (0.100 g)							
Cabosil	0.31	75.7	46.0	39.1	–	14.9	–
gel	1.36	267.0	38.8	11.4	–	8.0	41.4
Sr/La_2O_3 (0.025 g)/SiO_2 (0.100 g)							
Cabosil	20.5	29.5	0.3	61.2	4.0	20.0	14.5
gel	19.1	–	–	69.3	2.4	22.6	5.7

[a] Total methane conversion (mol%).
[b] Space time yield of formaldehyde (g/kg cat h).
[c] Selectivities are given in carbon atom%.

research. The 1 wt% Sr/La_2O_3 catalyst with a surface area of 6.5 m^2/g was used as distributed by AMOCO Oil Co. under their Natural Gas University Research Program. Catalytic testing was carried out in the temperature range of 630–780°C in a fixed-bed continuous-flow 9 mm o.d. (7 mm i.d.) quartz reactor using 0.100–0.125 g of catalyst. A standard reactant mixture of CH_4/air (1.5/1) was used under ambient pressure. The principal products analyzed by on-line sampling using gas chromatography were CO_2, C_2 ($C_2H_6 + C_2H_4$), C_3 ($C_3H_8 + C_3H_6$), CO and H_2O. Formaldehyde was condensed from the exit stream with two water scrubbers and quantitatively determined by iodometric titration [15], which has been well-established as a reliable method for determining small amounts of formaldehyde in aqueous solutions. In the present research, the carbon mass balance was always better than 90% and usually better than 95%.

3. Results and discussion

The methane conversions over the silica catalysts at 730°C, and comparison studies of the double bed catalysts of Sr/La_2O_3 followed downstream by silica catalysts, are listed in table 1. Because of the high space velocities employed, blank tests with the empty reactor have shown that contributions from reactor wall and gas phase reactions were negligible. Table 1 shows that the silica supports alone indeed have significant activities for methane partial oxidation to formaldehyde, and the formaldehyde space time yield (267 g/kg cat h) obtained here with the silica gel is among the highest yields reported to-date [16]. The silica gel is several times more active than the fumed silica under the same reaction conditions. It was pointed out earlier by Parmaliana et al. [12] that the controlling effect by the silica support on the activity of the silica-supported oxide catalysts should be studied more thoroughly. This is evident in the case of the MoO_3/SiO_2 system, which has methane conversion levels comparable to those of the silica supports alone [5]. Apparently, the support contributes significantly to the overall methane conversion. However, the product distributions obtained from the MoO_3/SiO_2 catalyst and that from the silica support are quite different [3–5,9]. The main selectivity difference lies in the considerable amounts of C_2 hydrocarbons formed over the silica catalyst. On the other hand, over the MoO_3/SiO_2 catalyst it has been well established that the major products are formaldehyde and carbon oxides when oxygen was used as oxidant, with negligible C_2 hydrocarbon product [5]. The reason for this is that the surface MoO_3 species are capable of trapping the methyl radicals (eq. (1)) and convert them into formaldehyde before they recombine to form C_2 hydrocarbons in the gas phase. A very high sticking coefficient for the methyl radical over the MoO_3/SiO_2 catalyst surface has been reported by Tong and Lunsford [17].

In the previous study of methane activation over the double-layered catalysts of Sr/La_2O_3 followed by MoO_3/SiO_2, a significant promotional effect of the Sr/La_2O_3 catalyst on formaldehyde generation was observed [14]. The Sr/La_2O_3, which is one of the most active and selective methane oxidative coupling catalysts [18,19], has been shown to be an excellent methyl radical producer [20,21]. The Sr/La_2O_3 catalyst produces C_2 and C_3 hydrocarbons and carbon oxides but not formaldehyde [18,19]. With a small amount of the Sr/La_2O_3 (0.025 g) upstream of the MoO_3/SiO_2 (0.100 g) catalyst, the formaldehyde production rate was increased about fourfold over that of the MoO_3/SiO_2 catalyst alone under the same reaction conditions [14]. However, the data in table 1 clearly show that the Sr/La_2O_3 combined with silica in a double bed configuration did not promote the formaldehyde production. This indicates that the silica surface cannot effectively trap the methyl radicals generated by the Sr/La_2O_3 catalyst and convert the radicals to formaldehyde like the MoO_3/SiO_2 catalyst. The facts that (i) silica itself does produce formaldehyde as one of the major products at low methane conversions and (ii) the Sr/La_2O_3 catalyst produces methyl radicals without formaldehyde formation suggest that the formaldehyde generated over the silica surface does not originate from methyl radicals.

The effective activation energies determined in the present study corroborate the difference in reaction mechanisms for C_2 hydrocarbons and formaldehyde. The overall activation energies for methane conversion were 34 and 47 kcal/mol over Cabosil and silica gel catalysts, respectively (table 2), while the apparent activation energies for formaldehyde formation were 26 kcal/mol over Cabosil and 41 kcal/mol over the silica gel. If formaldehyde were formed in the gas phase by the reaction of methyl radicals and oxygen, the overall activation energies for formaldehyde formation would be at least equal to that of methane conversion. However, the apparent activation energies for formaldehyde forma-

Table 2
Catalyst surface areas (before and after the catalytic test) and the apparent activation energies for methane conversion and C_2 and formaldehyde formation over silica catalysts

Catalyst	Surface area (m^2/g) before/after	Apparent activation energy (kcal/mol) (± 5)			Temperature range (°C)
		CH_4	C_2H_6	CH_2O	
Cabosil	385/365	34	57	26	630–780
silica gel	480/260	47	68	41	630–780

tion are appreciably less than that observed for methane conversion. This suggests that the formaldehyde is formed by a surface reaction over the silica catalysts. The apparent activation energies should include terms for surface reactions, which could give the lower value observed. On the other hand, the C_2 hydrocarbon formation proceeds in many cases via gas phase methyl radical coupling [20,21]. The apparent activation energies for C_2 products are 57 kcal/mol over the Cabosil and 68 kcal/mol over the silica gel catalyst. These values are much higher than the activation energies for methane conversion, which implies that the methyl radical desorption processes are difficult ones.

To attain a better understanding of the silica system for methane oxidation, the methane conversion and the product selectivities were studied over a wide range of the flow rate at fixed temperature (780°C) over the silica gel (table 3). Fig. 1 shows the methane conversion and formaldehyde space time yield as a function of the contact time. It is apparent that several points at short contact

Table 3
Methane conversion, formaldehyde space time yields, and product selectivities over the pure SiO_2 gel catalyst with CH_4–air (1.5 : 1) reactant at 780°C and ambient pressure and different gas hourly space velocities (GHSV)

GHSV (ℓ/kg cat h)	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]				
			CH_2O	$C_2^=$ [d]	C_2	CO_2	CO
35000	5.96	147.5	9.8	6.2	13.3	11.5	59.2
52500	4.95	234.3	13.5	5.0	13.0	8.9	59.6
70000	3.96	307.0	15.0	4.6	14.4	7.3	58.7
105000	3.09	352.3	14.9	3.9	15.9	5.5	59.8
140000	2.65	344.7	13.2	4.3	17.5	5.5	59.5
210000	1.59	487.0	19.1	7.9	22.6	3.7	48.8
280000	1.20	549.2	21.2	7.9	25.2	3.7	41.5
420000	1.00	726.2	23.3	7.4	27.9	2.8	38.6
560000	0.68	812.8	28.0	7.2	31.6	3.2	30.0

[a] Total methane conversion (mol%).

[b] Space time yield of formaldehyde (g/kg cat h).

[c] Selectivities are given in carbon atom%.

[d] $C_2^= = C_2H_4$.

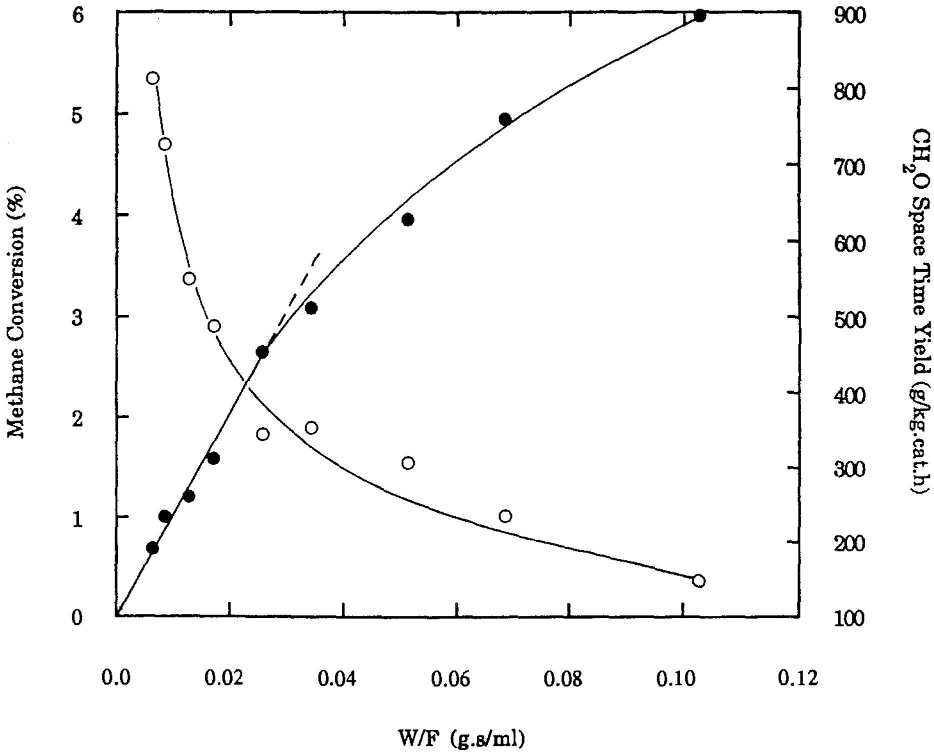

Fig. 1. Methane conversion (●) and formaldehyde space time yield (○) as a function of the contact time for methane activation over Grace 636 silica gel at ambient pressure and 780°C with CH_4/air = 1.5/1. W is the weight of catalyst and F is the flow rate of the CH_4/air mixture in ml(STP) per second. Thus, W/F is proportional to the contact time.

times were obtained in the differential reactor regime [22], where there is no diffusion limitation and the methane conversion increases linearly with the contact time. In fig. 2, product selectivities are plotted against the methane conversion for the same set of data. It appears that the C_2H_6 and formaldehyde products that exhibit parallel behavior are primary products, while the carbon oxides are secondary products. Similar product distribution patterns have also been observed by Kastanas et al. [9] with an empty quartz reactor.

So far, there have been very few explanations offered concerning the mechanism of methane activation over silicas. Low and coworkers [23,24] studied the so-called "reactive silica" for many years. They have shown that active silica that is capable of chemisorption of methane could be formed by methoxylating high surface area silica, pyrolyzing the methoxy layer, and then removing surface silanes and silanols formed during the pyrolysis via high temperature degassing. The resultant active site was assigned to be a special biradical center [24]. Extensive near-infrared, infrared, and Raman studies [25–29] suggested that the edge-shared tetrahedral surface siloxane defects could be formed with high

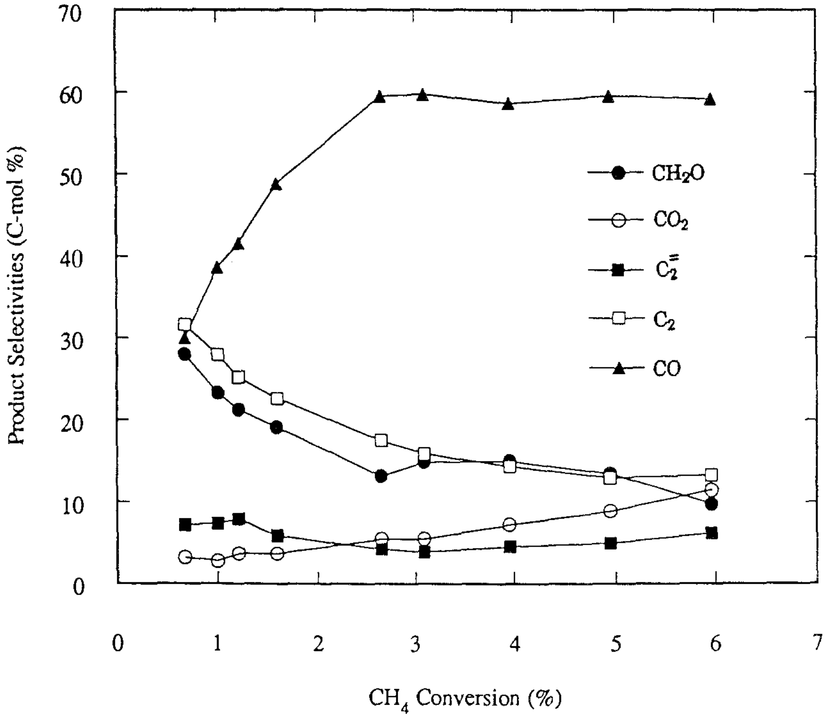

Fig. 2. Product selectivity as a function of the methane conversion for the same set of data as in fig. 1.

surface area silica upon dehydroxylation at high temperature (as shown on the left side of fig. 3). Several authors [30–32] have noted that the development of the Raman-active siloxane defect bands coincides with the disappearance of the Raman bands due to the surface silanol (Si–OH) groups. The strained surface defects in dehydroxylated silica exhibited enhanced reactivity compared to unstrained silica [33,34]. Polar molecules, such as H_2O, NH_3, CH_3OH, etc., readily reacted with dehydroxylated silica via dissociative chemisorption on the defect sites. Sheppard and Yates [35] studied the interaction of various molecules with Vycor glass by IR spectroscopy, and physisorbed methane was observed at low temperature. Unfortunately, there are no detailed reports on methane interaction with the high surface area silicas at elevated temperatures (> 600°C).

It is proposed herein that methane can dissociatively chemisorb on the siloxane defect sites of the dehydroxylated silica surface at high temperatures. Two kinds of intermediate complexes could be formed upon chemisorption, as illustrated in fig. 3. The complex (I), consisting of a surface methoxide group, could release a CH_2O molecule when decomposed at high temperature, with the residue being reoxidized back to the siloxane defect by oxygen. On the other hand, complex (II) would decompose, with greater difficulty than complex (I), to generate a methyl radical that is released into the gas phase where it will likely

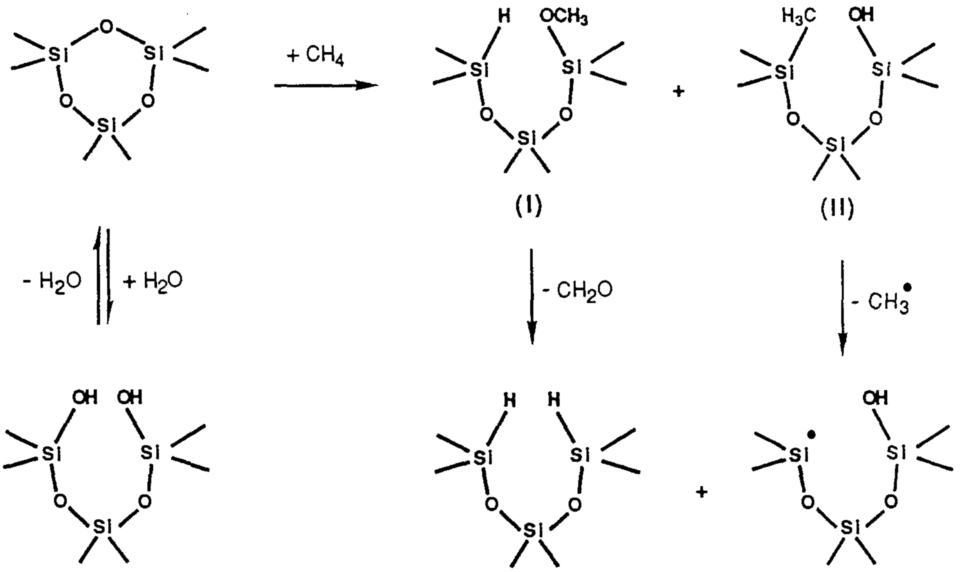

Fig. 3. Dehydroxylation of the silica surface and the reaction pathway for methane activation at the siloxane defect site over silica catalysts to yield gas phase formaldehyde and methyl radicals.

couple with another methyl radical to produce ethane. It is suggested herein that the methyl radicals are not readsorbed and are not utilized by the silica surface to produce formaldehyde. This reaction scheme shows that formaldehyde and C_2 hydrocarbons are parallel products when methane is activated over the silica surface at elevated temperatures, consistent with the observations presented in fig. 2. The differences in the apparent activation energies for CH_2O and C_2 formations are suggested to be largely determined by the relative decomposition rates of the intermediate complexes (I) and (II).

Parmaliana et al. [12] previously noticed that silica gel has higher activity for methane oxidation than fumed silica, in agreement with the present results. Silica gel is known to have a higher sodium level than Cabosil due to the different preparation methods employed. However, only a slight effect on activities was found for the acid washed silica gels, with much lower sodium contents, compared to those of the unwashed ones [5,12]. Infrared studies have shown that silica gel has three times higher surface concentration of hydroxyl groups than fumed silica at room temperature, but the hydroxyl concentrations reached the same level for the two types of silicas under vacuum heat treatment at 700°C [36]. It might be possible that high temperature dehydroxylation generates more readily accessible siloxane defect sites on the silica gel surface than the Cabosil surface, and this could be responsible for the higher methane conversion observed at high temperatures over the silica gel. Parmaliana et al. [12] observed that when methane partial oxidation was carried out at relatively low temperature (520°C), the precipitated silica, having an even higher surface

Table 4
Methane conversion, formaldehyde space time yields, and product selectivities over the pure SiO_2 gel catalyst with CH_4-air (1.5 : 1) reactant at ambient pressure and different reaction temperature and gas hourly space velocities (GHSV)

Temp. (°C)	GHSV (ℓ/kg cat h)	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]			
				CH_2O	C_2	CO_2	CO
630	8000	0.91	25.8	49.0	4.6	6.8	39.7
680	17500	1.53	77.7	40.2	6.4	5.0	48.3
730	70000	1.36	267.0	38.8	11.4	8.4	41.4
780	280000	1.20	549.2	21.2	33.1	3.7	41.5

[a] Total methane conversion (mol%).

[b] Space time yield of formaldehyde (g/kg cat h).

[c] Selectivities are given in carbon atom%.

hydroxyl concentration than the silica gel [36], had significantly higher activity after heat treatment at 1000°C.

In the present research, it was noticed that the product distribution for methane oxidation over silica catalysts depended on the reaction temperature, in addition to the level of methane conversion that has been demonstrated to affect the product selectivity. Data shown in table 4 were obtained after designing the reaction conditions (CH_4/air mixture flow rates and temperatures) so that the methane conversions were at a comparable level. It is evident that the overall selectivity to CO and CO_2 did not vary considerably with the reaction temperature at relatively constant methane conversions. On the other hand, low reaction temperatures clearly favored the formation of formaldehyde over the C_2 hydrocarbons, and vice versa at high temperatures. This is attributed to the significantly lower apparent activation energy for CH_2O generation compared to that for C_2 formation.

4. Conclusions

Silicas that are utilized as supports for oxide catalysts being investigated for methane activation and conversion to C_2 products (ethane and ethene), or especially to selective oxidation products such as formaldehyde, exhibit catalytic activity without the presence of surface-held promoters. It was shown that the silicas have high selectivities toward partial oxidation products, and the space time yields of formaldehyde are very high under optimum conditions, low temperatures and low conversions. It was also shown that readsorption of methyl radicals on the silica surface was highly unlikely to occur, in contrast to MoO_3/SiO_2 catalysts, and once desorption of the methyl radicals occurs, coupling in the gas phase is the dominant reaction.

This investigation indicates that there are two different, possibly parallel, mechanistic pathways for the conversion of surface activated methane into formaldehyde and C_2 products over silica. The first involves conversion of surface methoxy species into formaldehyde and the second involves desorption of surface-held methyl groups as gas phase methyl radicals. These two pathways have different apparent activation energies that are reflected in the temperature dependence observed in the product selectivity trends.

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