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Effects of NO and solids on the oxidation of methane to formaldehyde

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The selective oxidation of methane has been studied both in the presence and absence of solids (inert or catalysts) with and without NO added, at 1 bar of total pressure. NO enhances the yield to formaldehyde, while the solids favor its decomposition. These results, together with abundant literature data, show a maximum for formaldehyde yield of about 4.0%.

Keywords: formaldehyde; gas-phase reactions; methane partial oxidation; oxide catalysts; nitric oxide

1. Introduction

The direct conversion of methane to higher valued products has attracted the attention of industry and academia both for its economic appeal and scientific interest. The most studied routes have been the oxidative coupling to higher hydrocarbons and the selective oxidation to formaldehyde. The former option seems to have reached a yield limit of 20–25% due to the intrinsic stability of reaction products [1]. Does a yield limit exist for the aldehyde product, too?

Methane can be oxidized to formaldehyde in the absence or presence of catalysts. In the former case, higher pressures increase yields to formaldehyde [2]. Baldwin et al. [3] reported good yields at 5 bar and at 600–675°C. Higher pressures, up to 20 bar lead to the production of methanol (400–650°C) [4,5]. McConkey and Wilkinson [6] studied the promoting effect of gaseous additives working at atmospheric pressure with a fluidized bed reactor. Numerous studies have been published using solid catalysts [7–27] but, with only two exceptions, the reported yield is below 3%.

This work was aimed at investigating the possible existence of a maximum in yield to formaldehyde by studying the oxidation of methane in the absence of catalyst, with the addition of NO and in the presence of both Mo/SiO_2 and V/SiO_2 catalysts, in all cases at atmospheric pressure.

2. Experimental

2.1. CATALYST PREPARATION

A commercial silica Cabot Aerosil (particle size 5–30 nm, BET area 200 m^2 g^{-1}) was impregnated with aqueous solutions of ammonium heptamolybdate or ammonium metavanadate in such quantities as to obtain 5% w/w of Mo and 1.6% w/w of V. Preparation has been described in detail elsewhere [28].

2.2. KINETIC MEASUREMENTS

Steady-state kinetic experiments were performed using a single-pass flow reactor made of fused silica with an inside diameter of 18.0 mm and a heated length of 38.6 mm. The total flow rate was 17 cm^3/min, with a ratio CH_4/O_2 of 9, unless otherwise indicated.

Four types of kinetic experiments were run: (a) $CH_4 + O_2$ with and without solid catalyst, (b) $CH_4 + O_2 + 2\%$ NO with and without solid catalyst. When the reaction was studied in the absence of solid catalyst the reaction zone was empty or filled with either quartz wool or quartz chips (40–70 mesh). Catalysts (0.2 g), when used, were mounted in the center of the fused silica tube and held in place by quartz wool plugs. Matheson specialty gases with the following purities were used: CH_4 (99.98%); O_2 (99.96%) and NO (99%).

Methane conversion and product distribution were measured between 480 and 670°C at $P = 1$ bar. The reactor effluent was analyzed by GC; CH_2O, CO and CO_2 being the major reaction products. When NO (2%) was used as homogeneous catalyst, only trace amounts of N_2 were present in the products, while nitrous oxide was not detected in the whole range of temperatures studied.

3. Results and discussion

3.1. NO CATALYZED REACTION

The non-catalyzed reaction of methane with oxygen starts around 600°C under the experimental conditions used in this work. The maximum formaldehyde yield is 0.35% at 650°C. When 2% NO is co-fed as homogeneous catalyst, the reaction begins at 450°C. Fig. 1a shows that the maximum conversion is reached at 560°C under the experimental conditions used in these experiments (reaction zone filled with glass wool). The selectivity to formaldehyde in this temperature interval varied between 48 and 32% with a maximum molar yield of 3% at 560°C, while the CO_2/CO ratio ranges between 0.17 and 0.29 (fig. 1b). NO is referred to as catalyst in this system since only trace amounts of N_2 and no N_2O are detected among the reaction products.

Fig. 2 shows the variation of methane conversion as well as CO, CO_2 and CH_2O selectivities with space velocity which was calculated dividing the reactor volume by the gas flow rate at 25°C and 1 bar pressure. From the shape of the

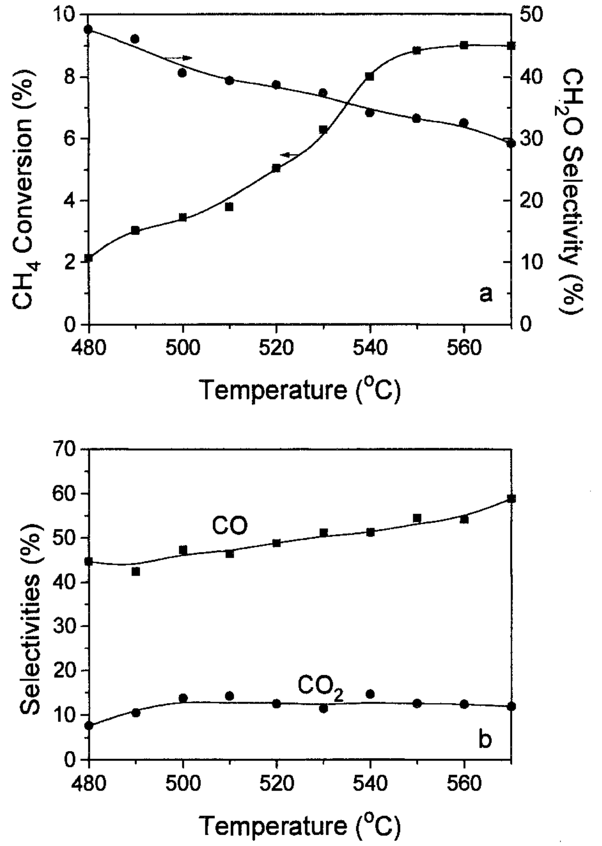

Fig. 1. NO catalyzed homogeneous reaction. Total flow rate 17 cm^3/min, gas composition: CH_4 88.2%, O_2 9.8%, NO 2%. Reaction zone filled with glass wool.

curves, it is concluded that both CH_2O and CO_2 are primary reaction products while CO is a secondary one. The same observation has been made in solid catalyzed reactions [10]. CO originates from CH_2O decomposition which is also catalyzed by NO [6].

The effect of CH_4/O_2 ratio on methane conversion and product formation at a constant space velocity has also been studied. The selectivity to formaldehyde reaches a limiting value of 45% at $CH_4/O_2 = 10$, while the conversion of methane decreases linearly with the reactant ratio.

Table 1 compares the data obtained when the reactor was empty or filled with either glass wool or quartz chips keeping the residence time constant. These results are in agreement with those reported by Baldwin et al. [3] for the homogeneous non-catalyzed oxidation of methane at 5 bar and with those of Hatano et al. [29] for the oxidative coupling reaction. The empty reactor has the highest methane conversion and formaldehyde yield, while a sharp decrease in both conversion and yield is observed for the reactor filled with quartz chips. Instead, when quartz wool is used, the results are intermediate between the other two.

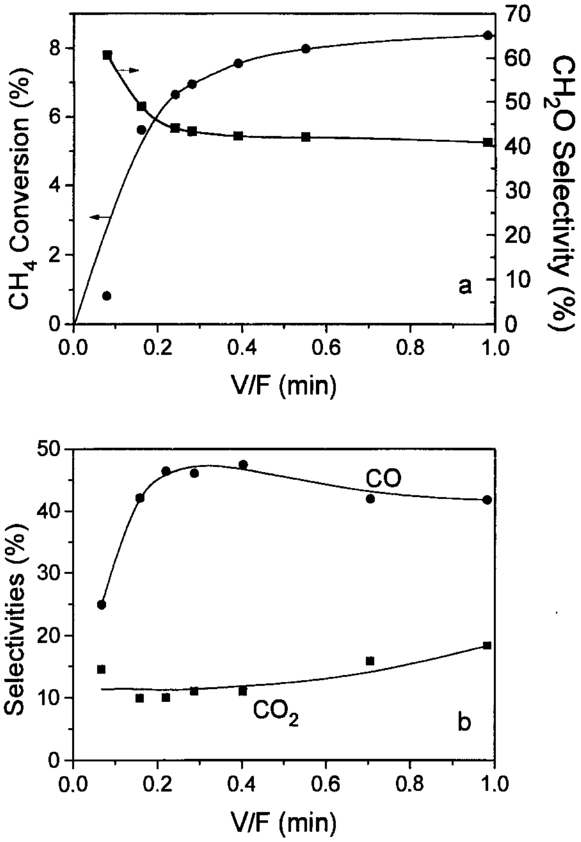

Fig. 2. Effect of residence time (at 25°C, 1 bar) upon conversion and product distribution obtained during the NO catalyzed oxidation of methane. $T = 560°C$, gas composition: CH_4 88.2%, O_2 9.8%, NO 2%. Reaction zone filled with glass wool.

The promoting effect of NO in the partial oxidation of methane was studied by McConkey and Wilkinson [6], in a fluid bed reactor using different, apparently inert, materials to improve heat transfer conditions. Based upon previous studies of Semenov [30] and Stern [31] which showed that $OH\cdot$ and $HO_2\cdot$ are the main chain-carrying radicals, McConkey and Wilkinson proposed the following reaction mechanism:

$$NO + CH_4 \rightarrow HNO\cdot + CH_3\cdot \tag{1}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{2}$$

$$NO_2 + CH_4 \rightarrow HNO_2 + CH_3\cdot \tag{3}$$

$$O_2 + HNO\cdot \rightarrow OH\cdot + NO_2 \tag{4}$$

$$O_2 + HNO\cdot \rightarrow HO_2\cdot + NO \tag{5}$$

Table 1
Effect of inner packing on NO catalyzed methane conversion and formaldehyde selectivity [a]

T^{b}(°C)	Packing	C^{c}(%)	S^{c}(%)	Y^{c}(%)
480	empty reactor	6.29	42.86	2.70
480	quartz wool	2.14	47.59	1.02
480	quartz chips	0.77	24.48	0.19
500	empty reactor	6.88	40.93	2.81
500	quartz wool	3.53	40.63	1.43
500	quartz chips	1.85	22.91	0.42
520	empty reactor	7.78	39.10	3.05
520	quartz wool	5.94	38.73	2.30
520	quartz chips	3.29	22.08	0.72
540	empty reactor	9.12	41.17	3.75
540	quartz wool	8.00	34.14	2.73
540	quartz chips	4.48	20.97	0.93
560	empty reactor	9.66	40.97	3.96
560	quartz wool	9.01	33.50	3.01
560	quartz chips	4.76	17.21	0.82

[a] Residence time 33 s (25°C, 1 bar), gas composition: CH_4 88.2%, O_2 9.8%, NO 2%.
[b] Gas-phase temperature. This was 15–20°C higher than the reactor wall temperature.
[c] *C*: conversion, *S*: selectivity to formaldehyde, *Y*: yield ($C \times S$).

$$OH\cdot + CH_4 \rightarrow H_2O + CH_3\cdot \tag{6}$$

$$HO_2\cdot + CH_4 \rightarrow H_2O_2 + CH_3\cdot \tag{7}$$

$$CH_3\cdot + O_2 \rightarrow CH_2O + OH\cdot \tag{8}$$

$$OH\cdot + CH_2O \rightarrow H_2O + HCO\cdot \tag{9}$$

$$HO_2\cdot + CH_2O \rightarrow H_2O_2 + HCO\cdot \tag{10}$$

$$CH_2O + O_2 \rightarrow HCO\cdot + HO_2\cdot , \tag{11}$$

where eqs. (1)–(5) represent initiation reactions due to the presence of NO; eqs. (6)–(8) correspond to chain propagation and formaldehyde formation; eqs. (9) and (10) lead to formaldehyde destruction through the same chain carriers $OH\cdot$ and $HO_2\cdot$ while the slower, less probable, reaction (11) might also contribute to yield decrease.

The $CH_3\cdot$ radicals may react to form other products such as ethane and CO besides formaldehyde. In this case, however, ethane is never detected and carbon monoxide (main non-selective product) most probably derives from formaldehyde decomposition [10,23]. Therefore, the assumptions advanced by McConkey and Wilkinson [6] seem reasonable.

More schematically, the main reactions leading to the formation and disappearance of formaldehyde may be written as follows:

$$R\cdot + CH_4 \rightarrow RH + CH_3\cdot \qquad (I)$$

$$CH_3\cdot + O_2 \rightarrow CH_2O + OH\cdot \qquad (II)$$

$$R\cdot + CH_2O \rightarrow RH + HCO\cdot \qquad (III)$$

The following kinetic equations may be derived:

$$\frac{d(CH_4)}{dt} = -k_I(CH_4)(R\cdot)\,, \qquad (12)$$

$$\frac{d(CH_2O)}{dt} = k_{II}(CH_3\cdot)(O_2) - k_{III}(R\cdot)(CH_2O)\,. \qquad (13)$$

From the steady-state approximation applied to the methyl radicals and the above kinetic expressions, eq. (14) is obtained:

$$\frac{d(CH_2O)}{d(CH_4)} = \frac{k_{III}(CH_2O)}{k_I(CH_4)} - 1\,. \qquad (14)$$

This equation was integrated by Mc Millan [32]:

$$\frac{(CH_2O)}{(CH_4)^o} = (CH_4)\frac{1 - [(CH_4)/(CH_4)^o]^{(k_{III}/k_I - 1)}}{(CH_4)^o(k_{III}/k_I - 1)}\,. \qquad (15)$$

Using the data reported in fig. 2a the calculated value of k_{III}/k_I is equal to 25.2 ± 1.4 at $T = 560°C$. From the data reported in fig. 1a and using the Arrhenius equation the difference in activation energies was calculated: $E_I - E_{III} = 9.4$ kcal mol^{-1}.

McConkey and Wilkinson [6] reported k_{III}/k_I ratios between 14 and 40, at 670°C using several non-active solids. Our extrapolated value at this temperature is 49. The high k_{III}/k_I ratios reflect the higher lability of the partial oxidized product and are consistent with the low yields reported in the literature.

Further comparison of our results with those of McConkey and Wilkinson [6] shows that we obtain higher conversion and selectivity to formaldehyde at lower temperatures. They also reported [6] that the presence of inactive solids increased both the conversion and the selectivity when compared to the empty reactor. This is at variance both with our results (table 1) and those of Baldwin et al. [3]. The reason for this discrepancy may be found in their own results and in the reactor type they used. It was a fluidized bed reactor made of stainless steel tubing, 1 inch in diameter and 15 inches long. When it was normally operated (with solids) the temperature measured at the center of the tube was not more than 15°C lower than that measured on the wall. However, when empty, they reported 620°C for the center and 800°C on the wall. This may explain the low values of selectivity reported in the absence of solids [6].

In view of the above, the presence of solids in McConkey and Wilkinson's experiments may be held responsible for the lower conversions reported in their work which in turn requires higher reaction temperatures therefore leading to lower selectivities. The results shown in table 1 and figs. 3–5 when different solids are used, further support this view. Besides, at higher pressures (5 bar) the quenching effect of solids is enhanced, as shown by Baldwin et al. [3] who reported about one or two orders of magnitude decrease in conversion when the reactor was filled with an inert packing material. Despite these differences in reactor type and operation conditions both their kinetic results [6] and ours are described by the same overall kinetic model.

3.2. THE EFFECT OF THE SOLID CATALYSTS UPON THE $CH_4 + O_2$ REACTION

Fig. 3 shows the conversions and selectivities to CH_2O obtained using Mo 5/ SiO_2 and V 1.6/ SiO_2. The data obtained in the same reactor in the absence of any catalyst are also shown for comparison.

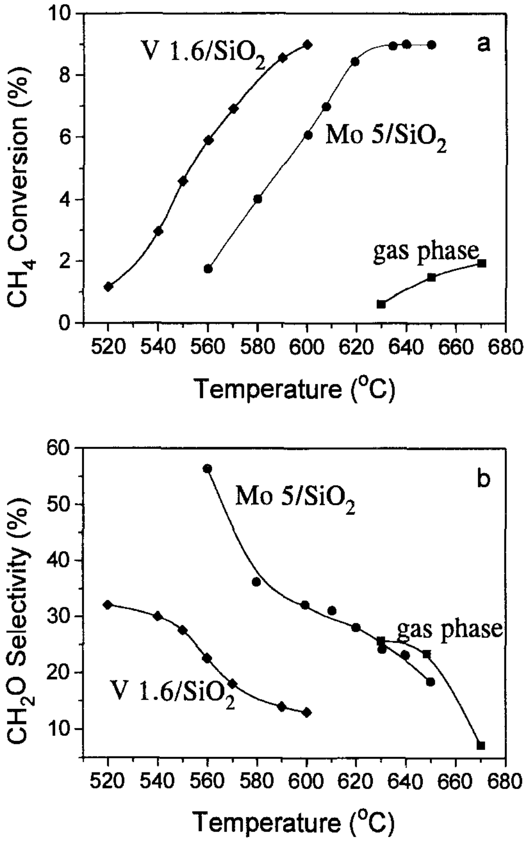

Fig. 3. Methane oxidation in the gas phase, on Mo 5/ SiO_2 and V 1.6/ SiO_2. $CH_4/O_2 = 9$, total flow rate 17 cm^3/min.

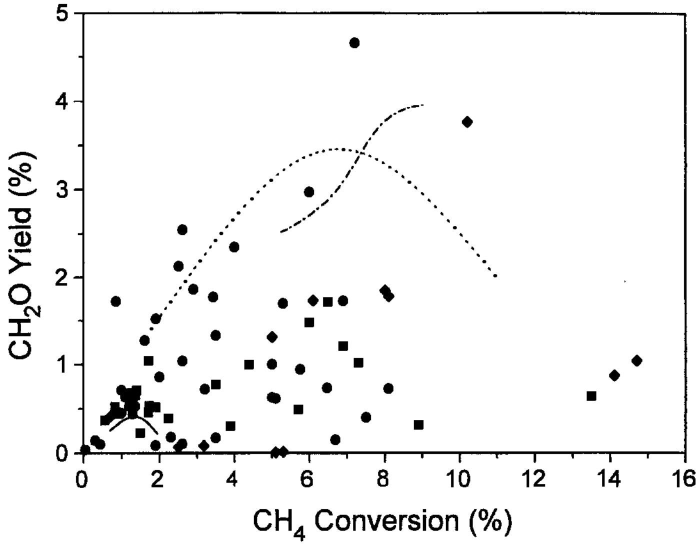

Fig. 4. The production of formaldehyde in the gas phase, 1 bar (——) and 5 bar [3] (· · ·), in the presence of NO (empty reactor) (– · –), and on solid catalysts published and own data included: (●) Mo-based catalysts [7–11,13–15,17,18,23,26]. (■) V-based catalysts [11,14–16,18,22,24]. (◆) Other catalysts: FeNbB–O, $FeNbO_4$, $B_2O_3/FeNbO_4$ [12]; SiO_2 [10,15,20]; Cr_2O_3/SiO_2 [18]; Cu–Fe–ZnO, ZnO [19]; MgBP–O/SiO_2, BeBP–O/SiO_2, CaBP–O/SiO_2 [21].

It is illustrative to compare the yields obtained in the non-catalytic system with those achieved in the presence of NO or a solid catalyst. Fig. 4 shows this comparison including numerous results reported in the literature. Note that there is only one report so far [13] which claims higher yields than those achieved in the presence of NO. They used silica supported Mo/Sn/P catalyst in their studies. Also note that an increase in pressure up to 5 bar increases the yield of the non-catalyzed reaction to 3.4% [3].

The data shown in fig. 4 may be symptomatic of a higher rate of CH_2O destruction on the catalyst surface than in the gas phase in the presence of NO. To test this hypothesis NO was added to the feed of the reactor containing the solid catalyst, either Mo 5/SiO_2 or V 1.6/SiO_2. The results shown in fig. 5 clearly indicate that the presence of either solid strongly diminishes the formaldehyde selectivity, thereby confirming the deleterious effect of the solid catalyst in the yield to the aldehyde due to its increased rate of destruction.

In brief, these studies together with the abundant data compiled from the literature show a maximum yield of about 3.5–4% in the production of formaldehyde by the reaction of CH_4 with O_2 at pressures up to about 5 bar or in the presence of NO or the solid catalysts so far studied (fig. 4). Through the use of non-conventional reactors, e.g. membrane, or more selective catalysts, it might be possible to overcome this limitation.

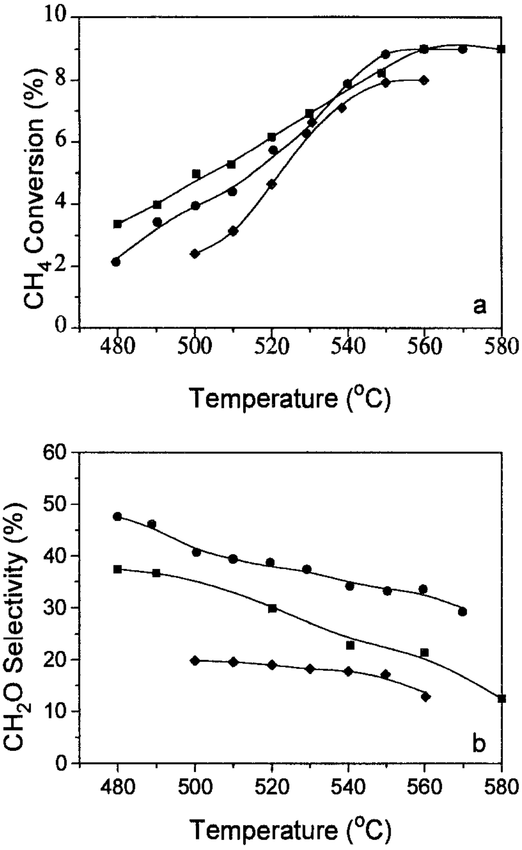

Fig. 5. Formaldehyde oxidation due to the presence of solids. Gas phase (reaction zone filled with glass wool) (●), Mo 5/SiO$_2$ (■) and V 1.6/SiO$_2$ (◆). Gas composition: CH$_4$ 88.2%, O$_2$ 9.8%, NO 2%. Total flow rate 17 cm^3/min^{-1}.

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