Selective oxidation of methane to methanol and formaldehyde over V_2O_5/SiO_2 catalysts. Role of NO in the gas phase

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The role of nitric oxide incorporation into the reaction feed for the partial oxidation of methane to C_2-hydrocarbons and C_2-oxygenates is evaluated. The addition of NO increases the conversion of methane under all the experimental conditions studied and has a strong effect on the product distribution. At low NO concentration the catalysts yield mainly C_2H_n hydrocarbons, but at higher NO concentrations, carbon oxides dominate. Amongst the C_1-oxygenates produced, methanol is the major compound observed and its proportion increases with increasing NO concentration. The highest C_1-oxygenates yield was 7% at atmospheric pressure.

Keywords: methane oxidative coupling, nitric oxide effect on methane oxidation, V_2O_5 catalyst for methane oxidation

1. Introduction

The partial oxidation of methane to methanol and formaldehyde and to C_2H_n hydrocarbons has been extensively studied, because of the relevance of monomers and C_1-oxygenates in the petrochemical industry. Apart of this technological importance, most of the efforts to produce them through a single catalytic step did not achieve yields beyond 4% [1,2]. It is known that the heterogeneous–homogeneous nature of methane activation has a great relevance on the total activity and product distribution [3,4], and the equilibrium between coupling and oxygenates production is determined by the nature of the catalyst components and its BET area. The contribution of the gas-phase reactions, which affords a remarkable effect on product distribution, is affected by the oxygen-to-methane ratio in the feed [6], the presence of void volume [7,8], and the use of radical initiators [9–11]. Thus, the conversion of methane has special requirements since the selectivity can be tuned by choosing the operation parameters. Hutchings et al. showed that the conversion of methane and the selectivity to C_2H_n hydrocarbons decrease during NO feed, whereas that of CO_2 increases [12]. A different trend is reported by Bañares et al. [13] upon addition of NO, where the conversion of methane and the selectivity of C_2H_n hydrocarbons increase. These differences arose mainly from the different experimental conditions used in these works: while the former feeds ca. 0.4% NO, the later study used a feed of ca. 0.03% NO. It is also interesting to note that on removal of the NO from the reactants the production of C_2H_n hydrocarbons passes through a maximum in time [12], which is higher than the values afforded under the NO-free feed. This could be associated to a decreasing transient concentration of NO upon its removal from the reaction feed, thus getting closer to the reaction conditions reported by Bañares et al. [13].

This work was undertaken with the aim to evaluate the role of NO concentration in the feed in the conversion of methane on a very low-area silica-supported vanadium oxide catalyst.

2. Experimental

The low BET area SiO_2 support was prepared from a commercial non-porous silica (Aerosil 200, BET area 174 m^2/g, particle size ca. 14 nm) by calcination at temperatures in the range of 1273–1423 K, up to 9 h. No significant crystallization of the silica is observed despite the high temperatures of the treatment. The low-surface-area silica support (ca. 1 m^2/g) was impregnated with an aqueous solution of ammonium metavanadate (Aldrich) and hydrogen peroxide in a rotary evaporator at 343 K. The vanadium oxide concentration was kept below the monolayer coverage of the support (0.03% V_2O_5) as confirmed by Raman spectroscopy. The impregnate was 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 diameter. The area of the catalysts was calculated by the BET method from the N_2 adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2000 apparatus.

The steady-state reaction studies were carried out at atmospheric pressure in a 10 mm i.d. quartz fixed bed microcatalytic reactor, designed to minimize the dead volume upstream and downstream from the bed of the catalyst. The minimum volume upstream decreases the activation of methane in the gas phase [7] so that all the activity originates from the catalyst alone; in addition, the minimum volume downstream prevents further decomposition of partial oxidation products [14]. Samples of 200 mg (CH_4 flow $=$ 100 mmol/h) were used in all of the experiments. Blank on SiO_2 substrate, inert packing SiC and empty reactor have been reported [7]. No significant differences could be observed between these and the empty reactor. The radical initiator NO (SEO-Air Liquide, 900 ppm in nitrogen) was cofed by means of mass flow controllers (Brooks). The NO concentration in the reaction feed ranged from 0.03 to 0.39 mol%. Reaction feed consisted of $CH_4 + O_2 + 900$ ppm NO in N_2. The concentration of oxygen and methane was the same for all the experiments irrespective of the concentration of the NO additive. Helium was used to compensate the variation of NO/N_2 feed. The pressure was measured upstream of the catalyst bed and did not increase beyond 0.15 atm above atmospheric pressure during the catalytic experiments (total pressure below ca. 1.1 atm). The homogeneous conversion of methane to methanol and formaldehyde is negligible under $CH_4{+}O_2$ at atmospheric pressure [1], but it is important in the presence of NO, the presence of the catalyst further improves the performance. All the experiments were repeated at least three times using fresh samples on clean new quartz microreactors to check the reproducibility of the data.

The reactor products were analyzed by on-line gas chromatography (HP 5890 II) fitted with a thermal conductivity detector, a Chromosorb 107 column and a 4A molecular sieve column, using helium as the carrier gas. A clean new quartz micro-reactor was used on each experiment to avoid the contributions of small amounts of catalyst impurities on the catalytic performance.

Experiments with different NO concentration in the feed and at different temperatures were carried out to evaluate the role of NO on the CH_4 conversion and product distributions. Methane has very little reactivity in the absence of radical initiators on very low BET area catalysts. The conversions of methane and oxygen versus reaction temperature at different concentrations of NO in the reactants are presented in figure 1. As expected, any increase in reaction temperature or NO concentration in the feed stream increases methane and oxygen conversion. The limiting oxygen conversion is reached above 890 K for the highest NO concentration in the reactants stream. During the catalytic experiments, formaldehyde and methanol (C_1-oxygenates), CO and CO_2 (CO_x products), and C_2H_6 and C_2H_4 (C_2H_n hydrocarbons) along with water were the only products observed.

The effect of concentration of NO in the feed on the yield of the three groups of carbon-containing products: C_1-oxygenates, C_2H_n hydrocarbons and non-selective oxidation products CO_x are presented in figure 2. The production of C_1-oxygenates increases with increasing NO concentration values, reaching a maximum yield to C_1-oxygenate as high as 7% for the 0.39% NO in reactants. On the other hand, any increase of NO concentration affords very important increase in the methanol production.

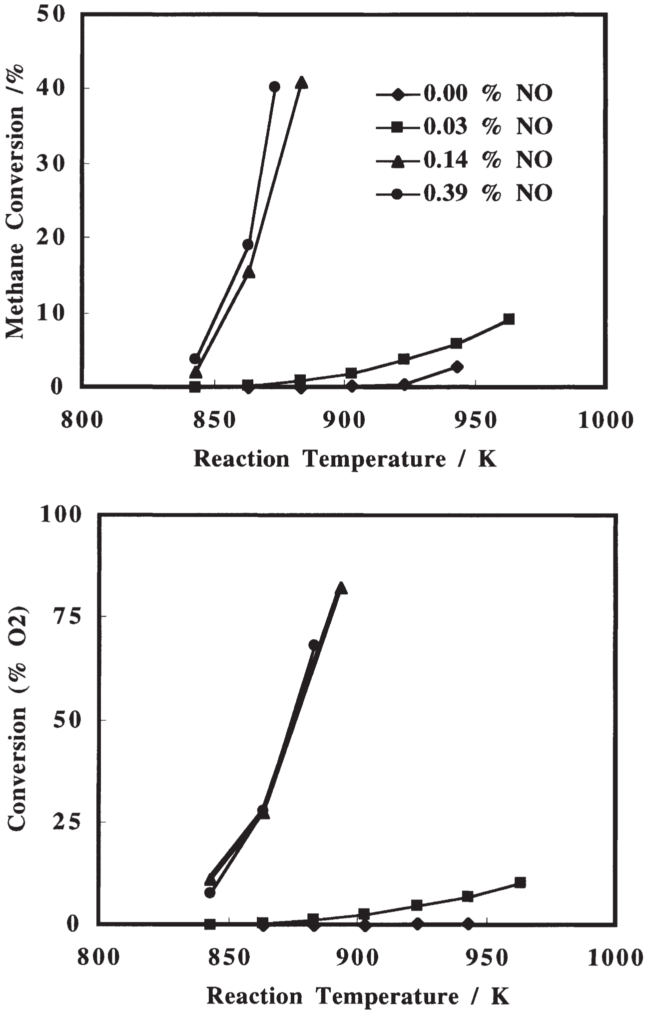

Figure 1. Methane conversion on low-surface-area silica-supported vanadia catalyst as a function of NO concentration in the reactants. Reaction conditions: $F = 89.6$ ml/min, $W = 200$ mg, in a 10 mm i.d. reactor.

This trend suggests that formaldehyde is most related to the heterogeneous process on the catalyst, while methanol can be produced through the gas-phase reactions. The extensive literature work on the direct oxidation of methane indicates that methanol is produced at very low selectivity under very mild conditions, the yield to methanol being very low. However, in this work, methanol is the principal formed oxygenate. The yield of C_2H_n hydrocarbons presents quite a different trend. Low concentrations of NO in the feed triggers the formation of C_2H_n hydrocarbons, although at high NO concentrations both hydrocarbons display a negligible yield. Similarly to C_1-oxygenates, the production of CO_x is always promoted by NO; this increase is essentially due to the formation of CO.

In order to provide a better understanding of the effect of NO additive in the reaction scheme, figure 3 displays the selectivity vs. conversion plots. The selectivity to C_1-oxygenates is remarkably promoted: in the absence of NO the selectivity to C_1-oxygenates (formaldehyde and methanol) decreases very fast. Little amounts of NO (0.03%) in reactants afford a significant increase of C_1-oxygenates selectiv-

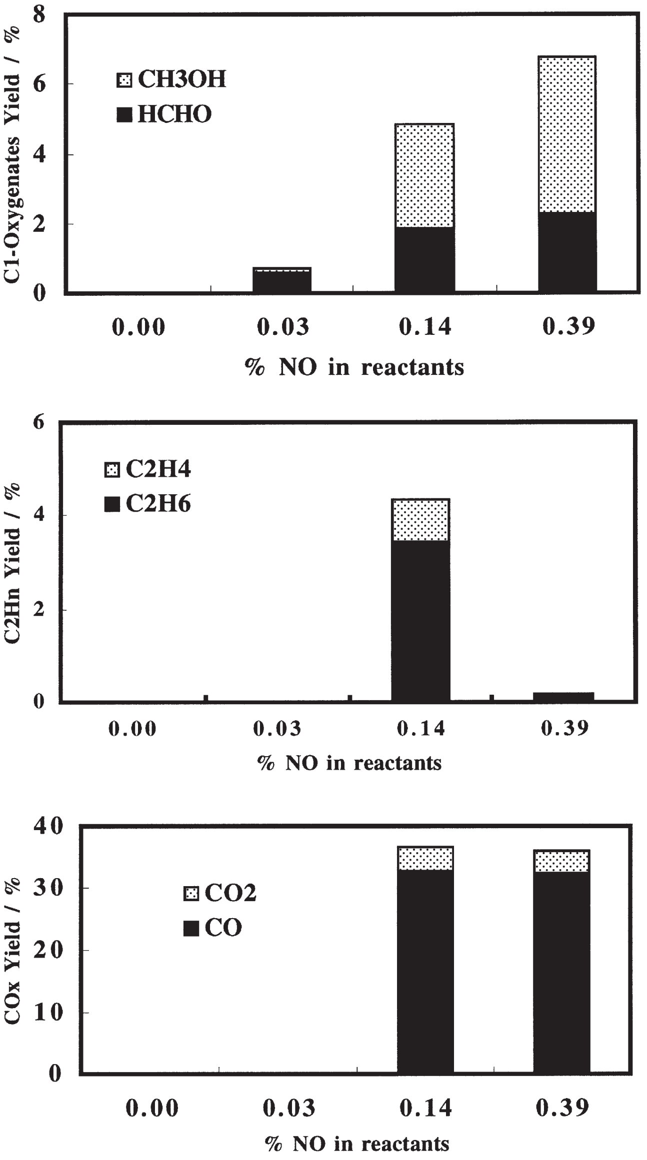

Figure 2. Yield to the different products at different NO concentration values. Reaction conditions: 883 K; $F = 89.6$ ml/min, $W = 200$ mg, in a 10 mm i.d. reactor.

ity, which is doubled under 0.14% NO and is best at 0.39% NO. The selectivity to C_1-oxygenates remains above 20% at ca. 30% methane conversion, which is far better than most of the results presented in the literature since most of the reported data show negligible selectivity to formaldehyde above ca. 15% methane conversion [1,2]. In addition, the selectivity to methanol produced at atmospheric pressure is reported to be very low or negligible, however, our reactor configuration affords its formation even above 50% CH_4 conversion. It is interesting to note that while the selectivity to formaldehyde decreases with conversion, that to methanol demonstrates a distinct maximum (figure 4). The selectivity to C_2H_n remains high in the absence of NO or under low NO concentration in reactants (0.03% NO), although somewhat higher NO concentration decreases the selectivity to C_2H_n to very low or negligible values. Conversely selectivity to CO_x is rather high in the absence of

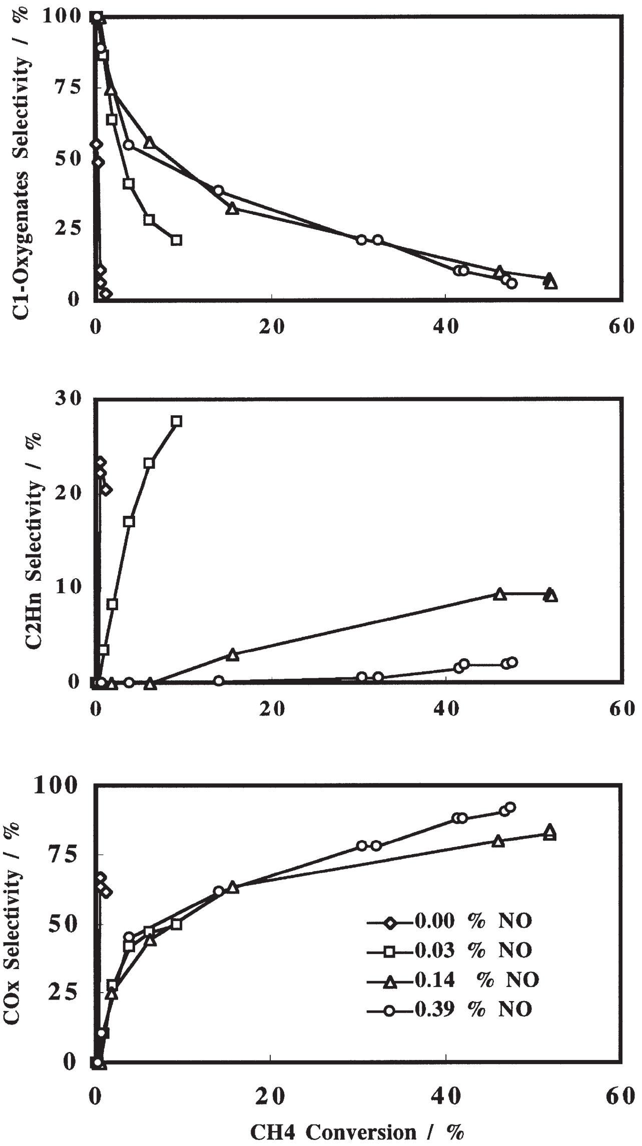

Figure 3. Selectivity to the different products vs. methane conversion at different NO concentration values in the reactants. Reaction conditions: $F = 89.6$ ml/min, $W = 200$ mg, in a 10 mm i.d. reactor.

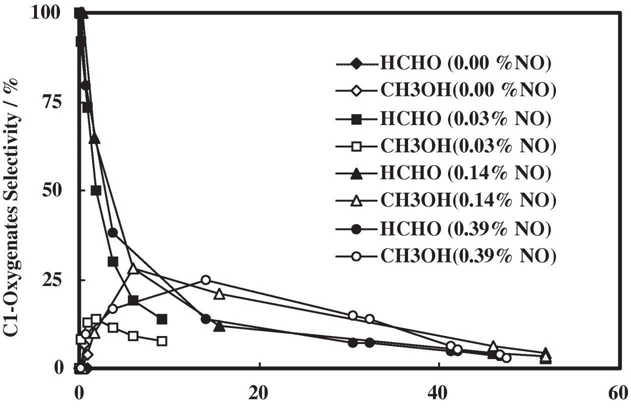

Figure 4. Selectivity to the methanol (open symbols) and formaldehyde (closed symbols) vs. methane conversion at different NO concentration values in the reactants. Reaction conditions: $F = 89.6$ ml/min, $W = 200$ mg, in a 10 mm i.d. reactor.

NO, due to the very high reaction temperature required to compensate the very little activity of this specific configuration. Moreover, activity not only is higher in the presence of nitric oxide but also the selectivity to CO_x increases drastically.

3. Discussion

As it has been documented in many works, the results presented here indicate that the generation of radicals triggers the activity and that different initiators of radicals afford different performances. Klier and co-workers used a double-bed catalyst: the upstream catalyst generated radicals, and the downstream catalyst (MoO_3/SiO_2) reached a very high conversion [11]. Another approach consists in dosing azomethane to generate methyl radicals in the gas phase which then favor the activation of methane, yielding methanol and formaldehyde [10]. NO incorporation in the feed stream behaves similarly since it increases the conversion and shifts the selectivity to oxygen-containing products [9,13]. However, it has been observed that the destruction of C_1-oxygenates occurs mainly on the catalyst surface [1,9]. The generation of radicals is one role of the catalysts for methane conversion [15], which is directly related to its surface area, but it is detrimental for its selectivity for the oxidative coupling and C_1-oxygenates [7]. To circumvent these two opposing effects, the approach followed in this study was to use very-low-area catalysts with radical generation in the gas phase (NO additive or $CH_4 + O_2$ mixing volume) as a mean to increase the conversion of methane but not to deeply oxidize the partial oxidation products [7,13], thus obtaining a remarkable increase of selectivity at an activity level comparable to the high-area catalysts. While the use of $CH_4 + O_2$ mixing volume essentially shifts the selectivity to methane coupling products [7], the effect of NO is much less evident [12,13].

The results presented above underline the large increase of methane conversion upon addition of NO. The very low activity in the absence of NO is due to the lack of any source or radicals since the catalyst has a very low BET area and no $CH_4 + O_2$ mixing volume is provided. The sharp effect on methane conversion when small amounts of NO are added to the feed stream must be due to the chain propagation of radical reactions. The conversion of oxygen increases in parallel, and oxygen-limiting conditions dominate above ca. 880 K in the presence of NO. Apart from the enhancement of activity upon addition of NO in the feed, some changes are also observed in product distributions. NO appears to shift the selectivity towards oxygen insertion [13]. C_1-oxygenates increase continuously with NO concentration value. Although the yield of formaldehyde shows little change with NO concentration value, the yield of methanol increases fast. Lunsford and co-workers observed that formaldehyde could originate from the degradation of methanol or that both could have a common intermediate [10]. It appears that methanol and formaldehyde must follow parallel routes since for a given reaction temperature the production of methanol increases faster than that of formaldehyde, thus the NO appears to promote the genesis of methanol, from an intermediate common to formaldehyde. The different selectivity–conversion profiles of methanol and formaldehyde further support this view. We had previously observed that C_1-oxygenates are promoted to a larger extent by NO than by the $CH_4 + O_2$ mixing volume upstream from the catalyst bed [13], we can now clearly establish the relevance of NO concentration in reaction for the production of C_1-oxygenates. The non-selective CO_x products are essentially constituted by CO (>90%) and deep oxidation CO_2 is always low. CO_x production increases significantly with NO concentration up to 0.14% in reactants, and then remains constant, whereas C_2H_n hydrocarbons pass through a maximum at 0.03% NO. Only at very low NO concentration does the coupling of methane become significant, as NO concentration increases the C_2H_n hydrocarbons decrease very fast. It seems that NO concentration affects the equilibrium that determines the shift between the coupling of methane and the production of oxygen-containing products. It has been proposed that the radicals would interact with sites of the catalyst which will determine whether methane coupling or C_1-oxygenates shall dominate [3,17]. Thus, in addition to the catalyst, the amount of NO in the reactants alters the equilibrium towards oxygen-containing product at high concentration, while some coupling is afforded under very low NO concentrations.

4. Conclusions

The low activity for methane activation displayed by low-area catalysts can be promoted by increasing gas-phase reactions since NO promotes the activation of methane and affords conversions comparable to high-surface-area catalysts at significantly better selectivity to partial oxidation products. We propose that the presence of NO must alter the equilibria in the gas-phase reactions and in the surface-catalyzed reactions, thus determining the selectivity trends. Accordingly, C_2H_n hydrocarbons form at low NO concentration, while C_1-oxygenates (methanol and formaldehyde) afford yields as high as 7% at high NO concentration in reactants.

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References

[1] T.R. Baldwin, R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 74 (1991) 137.

[2] C. Batiot and B.K. Hodnett, Appl. Catal. A 137 (1996) 179.

[3] J.H. Lunsford, Catal. Today 6 (1991) 1.

[4] J.C. Mackie, Catal. Rev. Sci. Eng. 33 (1991) 169.

[5] (a) K. Aika, N. Fujimoto, M. Kobayashi and E. Iwamatsu, J. Catal. 127 (1991) 1;
(b) E. Iwamatsu, T. Miruyama, N. Takasaki and K. Aika, J. Chem. Soc. Chem. Commun. (1987) 19.

[6] J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Nature 348 (1990) 428.

[7] F. Martín Jiménez, J.M. Blasco, L.J. Alemany, M.A. Bañares, M. Faraldos, M.A. Peña and J.L.G. Fierro, Catal. Lett. 33 (1995) 279.

[8] G.S. Lane and E.E. Wolf, J. Catal. 113 (1988) 144.

[9] S. Irusta, E.A. Lombardo and E.E. Miró, Catal. Lett. 29 (1994) 339.

[10] (a) S. Pak, M.P. Rosynek and J.H. Lunsford, J. Phys. Chem. 98 (1994) 11786;
(b) S. Pak, C.E. Smith, M.P. Rosynek and J.H. Lunsford, J. Catal. 165 (1997) 73.

[11] Q. Sun, J.I. Di Cosimo, R.G. Herman, K. Klier and M. Bhasin, Catal. Lett. 15 (1992) 371.

[12] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, Catal. Today 6 (1990) 399.

[13] M.A. Bañares, L.J. Alemany, J. Martín-Jiménez, J.M. Blasco, M. López Granados, M.A. Peña and J.L.G. Fierro, in: ACS Symp. Series, Vol. 638, eds. B.K. Warren and S.T. Oyama (Am. Chem. Soc., Washington, 1996) p. 78.

[14] M.A. Bañares and J.L.G. Fierro, in: ACS Symp. Series, Vol. 523, eds. S.T. Oyama and J.W. Hightower (Am. Chem. Soc., Washington, 1992) p. 354.

[15] (a) O.V. Krylov, Catal. Today 18 (1993) 209;
(b) V.I. Vedeneev, O.V. Krylov, V.S. Arutyunov, V.Ya. Basevich, M.Ya. Goldenberg and M.A. Teitelboim, Appl. Catal. A 127 (1995) 51.

[16] J.H. Cardoso, M.A. Bañares, J.M. Correa Bueno and J.L.G. Fierro, in preparation.

[17] M. Yu Sinev, S. Setiadi and K. Otsuka, Stud. Surf. Sci. Catal. 82 (1994) 357.