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Promoting methane partial oxidation: homogenous additives impact on formaldehyde yield on vanadia catalyst

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Abstract

Are there any chances to increase oxygenates yield in partial oxidation of methane (MPO) to economically efficient level? The effect of various homogenous promoters of MPO was studied in terms of their role in the MPO mechanism on vanadia silica supported catalyst. Accordingly they were classified into three groups: equilibrium shifting (H_2O), reducing (H_2) and intermediate supplying (MeOH, EtOH, CH_2Cl_2). The most profound promoting effect was exhibited by H_2, which decreased MPO temperature by 50–520 °C, at which unpromoted MPO gave no products. Among organic promoters the most efficient with respect to the added amount appeared ethylene, which enhanced both formaldehyde yield and methane conversion and also methanol. In the presence of these promoters the achieved HCHO yield was comparable to the highest values reported in the literature (1200 g HCHO per kg catalyst per h). The contribution of organic additives to the formaldehyde yield was experimentally excluded.

Keywords: Methane partial oxidation; Formaldehyde; Gaseous promoters; Vanadia catalyst; Kinetic model

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1. Introduction

While a direct conversion of methane into useful chemicals, such as liquid fuels or methane oxygenates has long been a subject of a heated scientific debate, the results of investigations seem still far from meeting industrial requirements mainly due to very low yields of reactions leading to higher hydrocarbons or oxygenates as compared to these in syngas processes. A question thus arises, whether further modifications of laboratory catalytic systems can give a real quantitative improvement in yields without either re-establishing the reaction understanding or leaving it behind.

Despite a great difference between chemical reactivity and thermal stability of methane and the products of its transformation in selective oxidation of methane (MPO), low selectivity towards oxygenates results mainly from the kinetic control. Therefore, typically the selectivity is enhanced either by an appropriate adjustment of the reaction conditions (temperature, contact time, oxygen content) or of catalysts properties mainly at a preparation stage [1]. However, it seems that the reaction kinetics could also be manipulated during catalytic reaction by addition of a low amount of a homogenous reagent capable of modifying catalyst redox state and/or reaction intermediates.

In an attempt to prove the above, in this study we have placed under our surveillance a number of homogenous promoters of selective oxidation of methane. They have been selected according to their abilities to: (i) shift the reaction equilibrium towards less oxygenated products, (ii) interact with the catalyst surface (reducing/oxidizing ones) and (iii) guide the reaction along a definite path by providing a reaction intermediate.

In order to avoid a mismatch of information coming from catalytic experiments with the use of a modified reaction mixture, certain reaction variables have been set (catalyst, reaction conditions). From among other vanadia and molybdena catalysts, varying in loading and a support type, studied by us previously [2–4], for this study we have selected a vanadia catalyst supported on fumed silica: 2% V_2O_5/SiO_2 (Cab-O-Sil). This catalyst has proved the most active and stable in MPO, for which we optimised the conditions so that the light off temperature was not

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approached and the reaction achieved the highest yield to formaldehyde; the results being presented in [2,3]. Another reason for this catalyst selection is a copious experimental data gathered for it in the literature [1,5–9], which is hoped to help us to understand the promoters roles in the reaction network.

2. Experimental

2.1. Catalyst

The physicochemical characteristics of the vanadium/fumed silica catalyst used in this study (2% V_2O_5/SiO_2 (Cab-O-Sil) was reported elsewhere [3]. In short, the catalyst was synthesised from ammonium metavanadate by the incipient wetness method and then calcined at 600 °C for 12 h. For catalytic experiments a grain fraction 0.18–0.38 mm was chosen. This catalyst showed little reducibility and low capacity for oxygen chemisorption as evidenced by TPR and TPD experiments, which was correlated with vanadia high dispersion and strong metal support interactions [3].

2.2. Kinetic experiments

All kinetic tests with and without additives were performed in a plug flow microreactor unit operating at atmospheric pressure. A small glass tube reactor, 4.25 mm i.d., was placed inside a thermostat and filled with the catalyst bed (each time 50 mg). The reaction temperature was controlled by two K-type thermocouples placed in the reactor directly above and under the catalyst bed. The temperature gradient did not exceed 4 °C.

The reactants were analysed in GC/TCD system (Shimadzu, GC-14A) equipped with a micropacked column (Carboxen 1004, 2 m × 1/16 in., Supelco). The gases used for the catalytic tests were: He (Praxair, 5.0) purified in a gas purifier (Supelco), CH_4 (Messer, 3.5) and O_2 (Polgaz, pure). The flow rates of gases were adjusted by electronic mass flow controllers (Brooks).

For the kinetic study the reaction was performed at atmospheric pressure with varying: contact time, reaction mixture composition and temperature in the range 570–590 °C. The methane conversion was maintained at a constant level below 5% by tuning total flow rate of reagents between 35 and 50 ml/min. The reactant concentration dependence was obtained at a constant total flow rate: one reactant concentration was varied while the other was fixed, and the total flow rate balanced with an appropriate amount of He. The concentrations expressed as molar percents varied in the range:

- CH_4 dependence: x_{CH_4} 40–90 mol%, x_{O_2} fixed at 10 mol% and x_{He} 50–0 mol% for a balance.
- O_2 dependence: x_{O_2} 8–18 mol%, x_{CH_4} fixed at 72 mol% and x_{He} 20–10 mol% for a balance.

Thus, the CH_4:O_2 molar ratio varied between 4 and 9. The same procedure was repeated at different temperatures.

Since the conversion was maintained below 5% a differential plug-flow reactor approximation was used to calculate the reaction rate from the Eq. (1) given below:

$$r_i(\mu\text{mol/g s}) = N\frac{F_{CH_4}XS_i}{V_{mol}m_{kat}} \qquad (1)$$

where F_{CH_4} is the volumetric flow rate of methane [cm^3/min], V_{mol} the molar volume of an ideal gas [dm^3/mol], m_{kat} the catalyst mass, X the fractional methane conversion, S_i the selectivity of a given product (HCHO, CO or CO_2) and N the factor recalculating units. The values of conversion and selectivities were calculated from the chromatographic analyses of a post reaction gas mixture.

2.3. Homogenous additives tests

The reaction conditions were standardized in order to achieve optimal catalyst performance: reaction mixture content $x_{CH_4} : x_{O_2} = 5$, a total flow rate 50 ml/min balanced with He, and the temperature from the range 550 to 600 °C. The exception was the experiments with use of hydrogen carried out in a broader temperature range: 520–600 °C. The reaction tests were performed in two modes: without an additive (unpromoted reaction) and with an additive in the feedstream (promoted reaction). The promoted reaction was initiated after a stationary state of the reaction had been achieved, by replacing He with an additive in a gaseous state or with a vapour additive saturating He.

Three kinds of additives were used: inorganic and organic vapours (H_2O, CH_3OH, C_2H_5OH, CH_2Cl_2, $CHCl_3$); dilute gases (C_2H_4, N_2O 5 vol.% in He) and pure gases (H_2, CO_2, N_2O). The vapours were fed into the reactants stream from a saturator stabilised at various temperatures to achieve a desired vapour concentration. The concentrations were calculated from the Antoine equation and they were maintained at the low level to be able to investigate the promoting effects.

Three types of catalytic tests were done: isothermal tests, additive concentration dependence under isothermal conditions and temperature dependence at constant additive concentration.

The concentration of promoters used for isothermal tests and temperature tests calculated from the Antoine equation are listed in Table 1 and expressed as molar percent of an additive (x_p, mol%). Low concentrations of the additives practically precluded a reasonable chromatographic analysis. The question thus aroused how to determine the conversion of pure methane in the presence of carbon-containing additives, which also contributed to the products of oxidation. To estimate this, the concentrations of the reagents taking part in the promoted and unpromoted MPO calculated from GC analyses were compared with the additives concentration. These are given in Table 1 and expressed as molar percents. The Δx_{CH_4} is a difference

Table 1
Comparison of methane conversion and formaldehyde amount increase with respect to added promoter amount during standard MPO

Additives	x_p	x_{oCH_4}	Δx_{CH_4}	x_{oHCHO}	Δx_{HCHO}
MeOH	0.53	82	−4.5	0.21	0.13
EtOH	0.22	83	−4.4	0.21	0.16
$CHCl_3$	1.10	88	−1.5	0.39	−0.31
CH_2Cl_2	2.00	82	−2.2	0.33	0.06
C_2H_4	0.14	83	−10	0.25	0.09
N_2O	0.64	81	−2.0	0.33	0.06
H_2O	0.08	81	−2.5	0.13	0.04
H_2	3.00	82	−2.5	0.33	−0.45

All values are expressed as molar percents.

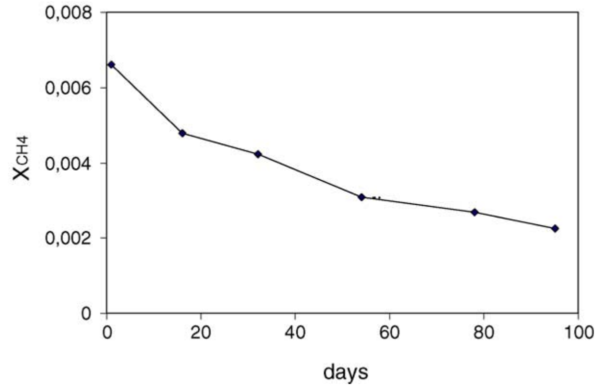

Fig. 1. Vanadia catalyst deactivation during MPO proceeding with time. The value X express an average methane conversion of the unpromoted MPO measured for several hours during one experimental day each time on the same sample.

between average methane concentration on the reactor outlet during promoted (x_{oCH_4}) and unpromoted MPO; the (x_{HCHO} is a difference between average formaldehyde concentration during promoted (x_{oHCHO}) and unpromoted MPO.

3. Results

3.1. Kinetic experiments

The purpose of this part of our study was three-fold: to determine the kinetic equation which would describe our catalytic system, to find optimal reaction conditions for the tests with additives, and finally to check the catalyst deactivation with time to be able to separate the effect of additives from that of the catalyst activity.

The results of the kinetic study are summarised in Table 2. The contact time dependence of the reaction rate has been published elsewhere [2], the general conclusion being that prolonging contact time favours oxidation to CO rather than to HCHO, while it does not influence CO_2 formation.

The following rate law was fitted to the curves representing the rate of the formation of products (HCHO, CO, CO_2) obtained at various temperatures:

$$r_i = k_i x_{CH_4}^{a_i} x_{O_2}^{b_i} \quad (2)$$

The parameter optimization brought the values of rate constants and reaction orders of both the reactants (Table 2). The HCHO formation is practically a first-order reaction with respect to CH_4 and zero-order to O_2, which indicates that CH_4 molecule activation (or dissociative adsorption) is a rate determining step of MPO towards HCHO. As regards CO formation, the reaction orders are on average 1.5 with respect to CH_4 and −0.3 to O_2. The reaction orders both to HCHO and to CO show a slight increase with temperature, unlike the order of CH_4 for the CO_2 formation, which decreases with temperature. The activation energies derived from the rate constants amount to 330 and 430 kJ/mol for HCHO and CO, respectively. The CO_2 yield was too low for reliable activation energy estimation.

The deactivation of the catalyst proceeds slowly with time and the activity is practically constant during 10 h catalytic tests. However, the catalyst deactivation is noticeable on larger time scale covering several months (Fig. 1): the points on the deactivation curve represent an average methane conversion (X_{CH_4}) from one experiment lasting several hours. Owing to the deactivation, a series of results obtained on the same catalyst will be referred to the catalyst current activity.

3.2. Homogenous additives tests

The results of isothermal tests performed under the standard reaction conditions in the presence of various promoters are summarised in Figs. 2 and 3 and in Table 1. These results were collected for the lowest applied concentrations of additives given in Table 1. The price we had to pay for the low additive concentration was a low accuracy of chromatographic analyses of additives.

To evaluate a possible contribution of organic additives to the formaldehyde yield we performed oxidation of the additives mocking the conditions of the standard reaction in

Table 2
Kinetic parameters from Eq. (2) optimised by fitting it to kinetic curves obtained for MPO on vanadia catalyst at various temperatures

T (°C)	HCHO ($r_{HCHO} = k_1 x_{CH_4}^{a_1} x_{O_2}^{b_1}$)			CO ($r_{CO} = k_2 x_{CH_4}^{a_2} x_{O_2}^{b_2}$)			CO_2 ($r_{CO_2} = k_3 x_{CH_4}^{a_3} x_{O_2}^{b_3}$)		
	k_1 (μmol/g s)	a_1	b_1	k_2 (μmol/g s)	a_2	b_2	k_3 (μmol/g s)	a_3	b_3
570	4.0	1.06	−0.16	1.21	1.43	−0.42	–	–	–
580	8.2	1.13	−0.01	3.5	1.45	−0.26	0.38	1.78	−0.24
590	11.9	1.21	0.01	5.0	1.53	−0.24	0.64	0.64	−0.01

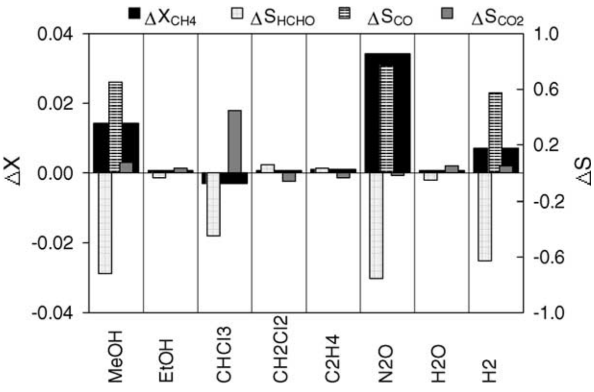

Fig. 2. The differences in methane conversion ((X) and selectivities of MPO products ((S) between promoted and unpromoted reaction performed at 570 °C, CH_4:O_2 = 5.

the temperature range 520–600 °C; in the standard reaction mixture, methane was replaced with He preserving the same total flow of reagents and oxygen concentration. The only detectable carbon containing product from the organic additives oxidation was CO_2. We also proved that methanol selective oxidation to formaldehyde performed on the same vanadium catalyst proceeded at much lower temperature than that used by us in this study [2]. Additionally, all organic additives increased methane conversion, what is indicated by negative values of Δx_{CH_4}. These values referring to the extra amount of methane converted in the presence of additives were much greater than the initial concentration of the additives (methanol, ethanol and ethylene); for ethylene the increase in methane conversion 72 times exceeds initial ethylene concentration, and for methanol – almost 10 times. The increased methane conversion only partly reflected in formaldehyde production (Δx_{HCHO} is much less than the absolute value of Δx_{CH_4}) because the additives enhanced also CO or CO_2 formation. For the above reasons, we postulate that, an additive have a promoting effect provided that it is added in small amount and it causes an increase of both formaldehyde yield and methane conversion.

The differences in the methane conversion and in the selectivities during the unpromoted and promoted MPOs are shown in Fig. 2. A decrease in conversion was observed only for $CHCl_3$, while CO_2 showed no impact on MPO, whatsoever. The most profound effects on methane conversion had methanol and N_2O. The addition of N_2O led to CO whose appearance compensated for the loss of formaldehyde selectivity. To be able to compare the influence of various additives irrespective of the catalyst deactivation, relative yields of formaldehyde were calculated. The relative yield was defined as a yield of formaldehyde during promoted MPO (Y) related to the average initial yield of the unpromoted MPO (Y_0) measured each time prior to supplying an additive into the reaction mixture (Fig. 3a). In such a representation, the promotion effect was found to be the highest for methanol and dichloromethane, both intensifying HCHO yield nearly two-fold. In the next classification regarding additive amount (relative yield related to the additive amount, x_p), the most efficient promoter (Fig. 3b) appeared ethylene, which also favoured methane conversion the most, followed by ethanol and methanol.

The inorganic additives were tested in terms of their concentration impact on MPO to HCHO (Fig. 4). In this group no significant promotion effect was observed: hydrogen hindered HCHO yield with increasing concentration at 570 °C, while H_2O vapour was able to increase the HCHO yield maximum 1.2 times similarly to N_2O. The N_2O effect was noted only at the low concentrations because its overall trend was negative. Looking closer at the N_2O behaviour (Fig. 5), it can be inferred that except an initial formaldehyde rise, N_2O favoured CO and to a lesser degree

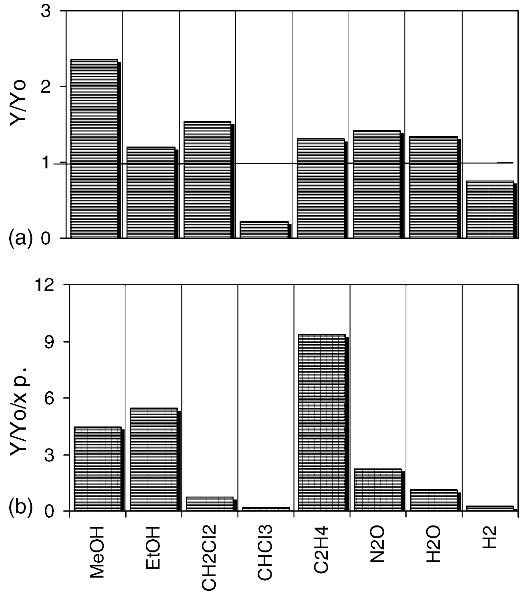

Fig. 3. (a) Relative formaldehyde yield expressed as a ratio of HCHO yield for promoted MPO (Y) and initial HCHO yield for the unpromoted MPO (Y_0) performed at 570 °C, CH_4:O_2 = 5; (b) effectiveness of additives expressed as relative formaldehyde yield vs. additive concentration (x_p).

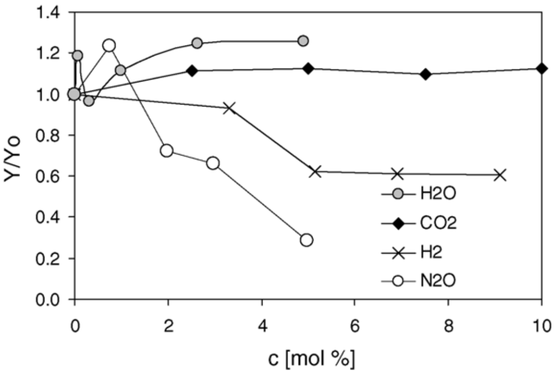

Fig. 4. Inorganic additives concentration dependence of HCHO relative yield obtained at 570 °C.

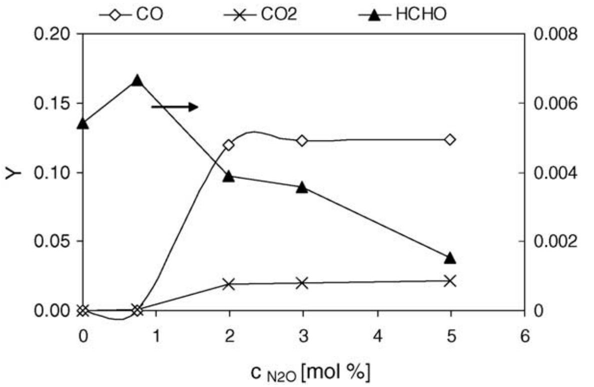

Fig. 5. Nitrous oxide concentration dependence of yields of all products. Reaction temperature: 570 °C. Note a different scale for HCHO yield.

CO_2 formation whose increase was not compensated by HCHO decrease.

An interesting behaviour was noted for hydrogen exhibiting a beneficial influence on the catalyst performance in MPO at lower temperature than 570 °C accepted by us as a standard (Fig. 6). The addition of H_2 at 520 °C, where we did not observe any products of the unpromoted MPO, gave rise to HCHO with a yield comparable to that observed at 570 °C for the unpromoted MPO. At the lower temperature (520 °C, Fig. 6a), an increase in H_2 concentration in the range 3–15 mol% brought about an increase in HCHO yield upto a saturation value achieved at about 10 mol% H_2, and a more intense increase of CO_2 yield, but evidently, the path leading to CO was almost totally suppressed. At the standard temperature (570 °C), hydrogen enhanced CO formation rather than HCHO and CO_2. Such behaviour indicates that hydrogen affects catalyst redox state to a higher degree than the composition of reaction intermediates.

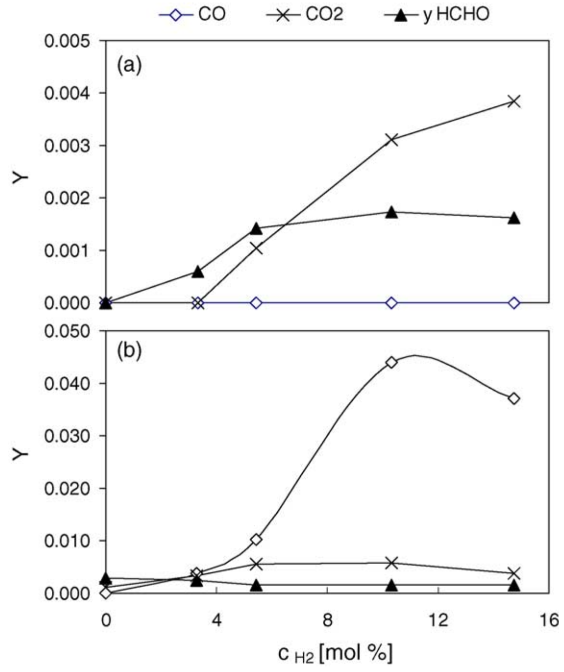

Fig. 6. Hydrogen concentration dependence of yields to all products obtained at: (a) 520 °C and (b) 570 °C.

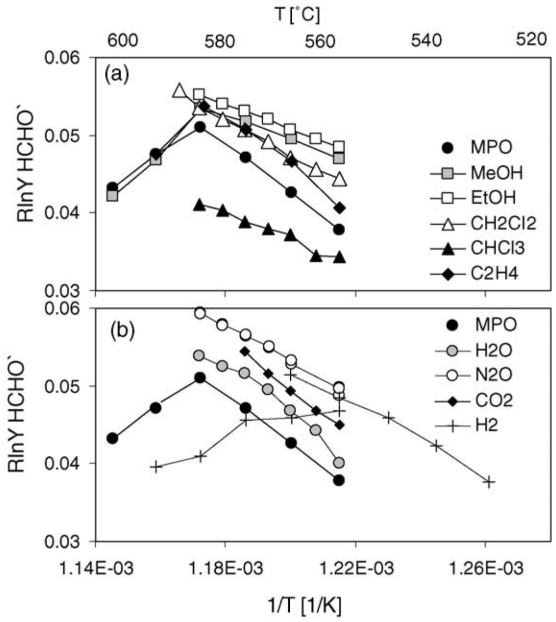

Fig. 7. Arrhenius plots of the unpromoted and promoted MPO for HCHO formation: (a) MPO and organic additives; (b) MPO and inorganic additives.

The additives reflected similar trends to those presented above in the values of activation energies estimated from the temperature tests (Fig. 7); for the sake of clarity organic and inorganic additives are shown separately. Each point in the Arrhenius plot represents an average of several values of HCHO yield (not normalised *Y*) measured at a given temperature. The temperature of 580 °C, above which HCHO rate of the unpromoted MPO decreases, probably due to both consecutive oxidation to CO and to the change in the reaction control from kinetic to diffusional regime, seems boundary for estimation of activation energy. Most of the additives exhibited a similar pattern except H_2, which showed a reverse temperature dependence of HCHO rate when the reaction was initiated at 550 °C; and increasing temperature dependence when the reaction was initiated at 520 °C.

Various additives impact on the activation energy of MPO was different—they show nearly no effect or decreased its value to a higher or lower extents (Table 3). The classification of additives according to the values of activation energy matches our classification according to their supposed roles in the MPO mechanism. The value of activation energy found for the unpromoted MPO (320 ± 16 kJ/mol) will be a reference point to compare the additives effects. This value is an average of 20 different measurements performed within 2-year period, which evidence the reproducibility of the experiments and, what is more, it agrees with the value of activation energy found from the kinetic equation (Table 2). Thus, according to Table 3, no change in activation energy was noted for H_2O,

Table 3
Values of activation energies for the unpromoted and promoted MPO

	Ea (kJ/mol)
MPO	320 ± 15
MeOH	150
EtOH	160
CH_2Cl_2	220
$CHCl_3$	170
C_2H_4	300
CO_2	325
N_2O	230
H_2O	340
H_2	260

and for CO_2 used as promoters. When reducing or oxidizing agents such as H_2 or N_2O were added, the activation energy decrease was less than 100 kJ/mol. Accordingly, for C_2H_4 – a weaker reducing agent – this decrease was only 20 kJ/mol. A good agreement between the values of activation energies obtained for dilute and pure N_2O additionally validates the employed experimental procedure. The lowest activation energy, around 160 kJ/mol, was observed for methanol and ethanol as well as for $CHCl_3$ (HCHO inhibitor).

4. Discussion

The additives impact on the catalyst activity will be discussed with regard to the mechanism of selective oxidation of methane. The kinetic equation (2) describing our reacting system is in keeping with the literature data [10]. Unfortunately, since the literature does not provide systematic results on the homogenous promoters for MPO, our results can only be partly related to the data presented by others. Another serious obstacle to compare the results is that the majority of reported additives were supplied in much greater amounts than those used by us.

4.1. Equilibrium shifting promoters

The MPO reaction on vanadia catalyst is of a consecutive-parallel type where CO_2 is formed in an independent path. The CO_2 formation proved little prone to the changes both with contact time [2,3] and with reactants concentrations, as shown in this study.

$$CH_4 \xrightarrow{O_2} HCHO + H_2O \xrightarrow{O_2} CO + H_2O,$$

$$CH_4 \xrightarrow{O_2} CO_2 + H_2O$$

Such a reaction mechanism has also been postulated for MPO on vanadia and molybdena catalysts [8,11], although Arena and Parmaliana suggest consecutive type reaction for all the products discussed [10,12].

Accordingly to the above, H_2O vapour enhanced HCHO formation by changing surface equilibrium concentrations and shifting it to less oxygenated products and did not change the value of MPO activation energy, thus indicating that no change in the MPO mechanism took place. The observed overall effect of water vapour on HCHO yield is positive, though insignificant, most probably because H_2O surface coverage, or more precisely the occupation of active centres by H_2O, is low at such high temperatures due to a high desorption rate. This is in accordance with observations made by Liu et al. [13], who indicated that water molecules could compete for the same active centres with methane molecules on molybdena supported catalyst. This finding and the assumption of the MPO rate determining step proceeding through methane dissociative adsorption (or equally its activation) can account for the minimum on the concentration curve presented in Fig. 4. Water as an additive to a reaction mixture ($CH_4 + N_2O$) has also been studied earlier [9,14], but the relatively high amounts used there suggest mixed mechanism of methane oxidation including its steam reforming [15]. Our findings comply with those by Liu et al. who observed that water vapour is able to facilitate formaldehyde formation during MPO by N_2O (on molybdena silica supported catalyst) at a relatively low partial pressure under 30 Torr (<4 mol%), while at higher pressure it showed no effect [13], although the value of activation energy found for this reaction in the presence of H_2O (160 kJ/mol) is much lower than that found by us. This may suggest a different mechanism of methane oxidation with nitrous oxide on molybdena catalyst.

Notably, our observations concerning the participation of CO_2 in MPO are that CO_2 produces no effect on the reaction, which is effectively in keeping with the parallel reaction model assumed above. However, these results do not comply with the results by Demoulin et al. who found a promoting influence of CO_2 in ODP performed on Mo-containing mixed oxides catalysts [16].

4.2. Redox promoters

It is generally accepted that the prerequisite for activation of methane molecule is the generation of active oxygen on the catalyst surface. According to some researchers [17,18] such oxygen species can be formed as a result of a charge transfer in the surface lattice of vanadium oxide: $V^{5+} + O^{2-} = V^{4+} + O^{1-}$, induced both by light or elevated temperature. The pair $V^{4+}$and O^- is claimed to be an active centre of MPO. The presence of traces of V^{4+}in calcined vanadia catalyst at ambient and elevated temperature has been confirmed by numerous of results described in [19] and quite recently in [20]. Following this train of thought, the reaction mechanism seems more of Mars van Kravelen rather than of Langmiur–Hinshelwood type, because HCHO formation rate is zero order of oxygen concentration, which implies that there is lattice oxygen involved in formaldehyde oxidation. The methane activation may thus proceed through electron transport from an active centre to a methane molecule with CH bonding cleavage, and further to molecular oxygen adsorbed on catalyst surface, which closes the catalytic cycle and restores active centres. It can therefore be summarized that the active centres for MPO can be obtained by in situ manipulating the redox properties of the catalyst surface, or more specifically, the electron distribution in V–O bond. Indeed, as shown in this study, reducing agents (H_2) or (-electrons donors (C_2H_4) are able to facilitate HCHO formation, unlike strong oxidizing agents (N_2O – atomic oxygen supplier). The beneficial effect of hydrogen attributed to lowering MPO temperature and the value of activation energy can thus be accounted for by the reduction of V^{5+} to V^{4+}. Otsuka and Wang, having studied MPO to methanol and formaldehyde in the presence of hydrogen (in higher amounts than those used by us) derived similar conclusions for iron and molybdenum containing catalysts [21,22]. There, however, must be an optimal reduction degree of the catalyst surface, since at higher temperature hydrogen evidently reduces vanadium (V) oxide to a higher extent eliminating active centres of HCHO formation. It also seems that V^{4+} centres seem selective for HCHO because their further reduction enhances CO formation.

The overall effect of nitrous oxide on MPO is negative for the concentrations higher than 1 mol%. However, in the lowest used amount (0.7 mol%), N_2O was also found to be able to slightly facilitate MPO towards HCHO, which is in accordance with the results by Demoulin et al. obtained for other mixed oxide catalysts in ODP reaction [15]. Again it seems to be a competing process, where atomic oxygen donated by N_2O at first reacts with methane molecules but then oxidizes V^{4+} centres. The cited authors derived similar conclusion for the Mo-containing catalyst. Such a role of N_2O in the catalyst/reactants redox system was also proposed by Kondratenko and Baerns who using various spectroscopic techniques studied the ODP on vanadia catalyst [23]. For this reason for the lowest applied N_2O concentration we observed lowering of the activation energy of MPO towards HCHO. The beneficial effect of other nitrogen oxides (NO_x, $x = 1, 2$) on HCHO yield in MPO was reported by Takemoto et al. [24], Teng et al. [25] and Bañares et al. [26]. They attributed this effect to activation of CH_4 by NO_x to form $CH_3^{\bullet}$ radicals. Quite an opposite opinion was that of Bañares who explain the effect by the shift in the reaction equilibrium.

As inferred from a small change in activation energy, ethylene shows hardly any influence on the reaction mechanism. This might indicate that ethylene reversibly modifies an effective charge present on vanadium cations. This conclusion can also be supported by the fact that it was chromatographically detected in the post reaction mixture in almost unchanged amount. Its efficiency is therefore the most pronounced among other promoters.

4.3. Intermediate promoters

Methoxo intermediates are claimed common for both methane and methanol partial oxidation to formaldehyde [13]. They are also very stable as evidenced by Raman in situ and IR measurements [13,27]. In consequence, methane derivatives such as methanol, chloromethanes and ethanol, added in low amounts to the reaction mixture, can be a direct source of such intermediates. Thus by changing their population on the catalyst surface the reaction path towards formaldehyde can be favoured. As possessing reducing properties, methane derivatives mentioned above may also take part in the formation of V^{4+} hence providing both active oxygen on the catalyst surface and centres selective for HCHO. Additionally, as can be inferred from our and other authors results, methanol adsorbing on vanadium centers may break V═O terminal or V–O planar bonds, which should also lead to the formation of active oxygen species. In this study we demonstrated that methanol and ethanol are good MPO promoters – their positive effect as promoters being reflected by the methane consumption increase (Table 1). These additives have not been studied intensively before, however, some information on their effect on MPO towards methanol on mixed titania and copper silica supported catalyst can be found in [28].

The influence of chloromethanes (CH_xCl_y) on MPO varies with Cl percentage in the molecule, as summarized by Hall et al.; the highest methane conversion and the highest activity being observed for CH_2Cl_2 [1]. A disadvantageous performance of $CHCl_3$ may be explained by the formation of chlorine active species, which favour methane coupling rather than oxygen substitution, as observed for $CHCl_3$ and CCl_4 [29,30].

5. Conclusions

The promoting effect of additives, described by both an increase in formaldehyde yield and in methane conversion, was studied in terms of their role in the methane partial oxidation mechanism. Accordingly, the studied promoters can be divided into three groups.

(1) Equilibrium promoters: H_2O – competing with methane for the same active centres and shifting the equilibrium to less oxygenated products.
(2) Redox promoters: H_2 – providing V^{4+} active centres at temperature <570 °C; N_2O – eliminating V^{4+} centres; C_2H_4 pseudo-redox promoter reversibly decreasing the effective charge on vanadium cations by doping π-electrons.
(3) Intermediate promoters: methane derivatives 1 or 2 substituted providing methoxo-groups facilitating a path to formaldehyde, also reducing V^{5+}.

The most profound promoting effect was exhibited by H_2, which decreased MPO temperature by 50 °C at which unpromoted MPO gave no products. The highest observed yields, expressed as a space time yield, are around 1 kg HCHO per kg catalyst per h for the best promoters (ethylene, methanol) and they are comparable to the best achieved values reported in the literature [1,20], but not significantly higher than those. Thus a practical conclusion of our work is that methane partial oxidation has still remained an academic dominion.

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