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Formaldehyde Formation in Coupled Oxidation of Methane and Methanol over V_2O_5 and MoO_3 Silica Supported Catalysts[*]

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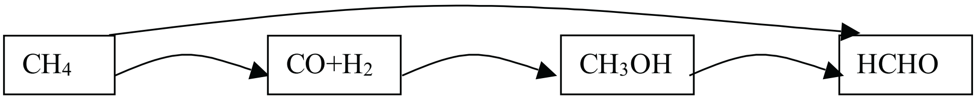
The effect of methanol on partial oxidation of methane has been studied on standard molybdena and vanadia catalysts supported on silica. Prior to catalytic tests the catalysts were characterized by BET, SEM/EDAX and TPR/O methods. Three types of catalytic tests were performed giving temperature and contact time dependence on the catalyst activity and selectivity: partial oxidations of methane, methanol and methane/methanol mixtures. The methanol showed an activating impact on the partial oxidation of methane over all used catalysts samples, but the strongest one over MoO_3/SiO_2. In the absence of CH_3OH the only catalyst, which exhibited HCHO selectivity, was a low loaded vanadia catalyst. It has been put forward that methanol may enhance formation of oxygen active species, prerequisites for activating methane molecules, through reducing vanadia cations and causing breakage of vanadium oxygen bonds.

Key words: methane selective oxidation, methanol selective oxidation, formaldehyde

Direct conversion of methane or natural gas into useful chemicals, such as liquid fuels or methane oxygenates, is a challenging area in contemporary catalysis. In particular, a part of the current investigation is aimed at partial oxidation of methane to formaldehyde (MPO). On an industrial scale, formaldehyde is produced from methanol in the series of processes, which start from natural gas or coal:



Thus, for economic reasons, it seems reasonable to find the way to bypass endothermic reforming of methane, developing one-step methane conversion route directly to formaldehyde.

During the past decade, efforts have been made to find the best catalyst and to optimize conditions for MPO [1–9]. The best catalysts found for this reaction are low loaded (2–5%) molybdena and vanadia catalyst supported on silica [3,4]. They are active in MPO in a relatively narrow temperature range from 500 to 700°C. In order to

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avoid consecutive oxidation of formaldehyde to carbon oxides, it is recommended to use short contact times and a methane excess [1–3,7,10,11]. However, even under thus optimized conditions the HCHO yield does not exceed 1–3% [1–3,12,13]. Moreover, the contribution of the gas-phase reaction in the overall reaction rate makes the results difficult to interpret in terms of the reaction mechanism [8,14]. For the above reasons, the most recent research is focused on the systems, which would be capable of activating methane at a lower temperature and of suppressing the total oxidation of products. Gaseous promoters modifying both the catalyst surface properties and reaction intermediates, seem promising to meet this challenge. The promoter we have chosen in our study was methanol, mainly because methanol was not considered before for MPO. The suggested mechanism of MPO is said to proceed through methyl radicals [6,7], whose formation is the rate determining step for this reaction [13,15,16]. Thus, methanol being oxidized on a catalyst surface through the formation of surface M–O–CH_3 intermediates [17,18,19] may take part in activating C–H bonds to form methyl radicals, providing active oxygen species on the catalyst surface. The aim of this work is to prove the effect of methanol on methane partial oxidation to formaldehyde on standard vanadia and molybdena catalysts in an attempt to unravel the underlying scientific issues behind this intriguing pattern behaviour.

EXPERIMENTAL

Catalysts preparation: Catalysts containing various loadings of MoO_3 (2%, 5%, 10 wt. %) and V_2O_5 (2%, 3.2%, 5 wt. %) were prepared by incipient wetness impregnation of silica (PQ Silica, Akzo, GmbH & Co, BET surface area, 185 $m^2 \cdot g^{-1}$) with solutions of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (POCh, Gliwice) and ammonium metavanadate (NH_4VO_3, SERVA, Heidelberg). Due to a low solubility of ammonium metavanadate in water, V_2O_5/SiO_2 catalysts containing 2–3% were prepared by gradual impregnation of SiO_2 with a 0.043 M solution of NH_4VO_3. In the synthesis of 5% V_2O_5/SiO_2, hot basic (10% ammonium, pH $\cong$ 12) solution of ammonium metavanadate was used to increase its solubility. After impregnation, all catalyst were dried in air at 150°C for 3 h, and then calcined in air at 600°C for 24 h. The grains fraction used for further tests was 0.2–0.385 mm.

Catalyst characterization. *BET surface measurements*: The BET surface area of calcined samples was measured by ASAP 2010 (Micromeritics). Before each BET measurement, calcined samples were dried for 6 hours at 300°C at a reduced pressure (2–4 μmHg).

SEM analyses: SEM images of the surface of the samples were taken in a scanning electron microscope (Philips XL20) possessing an X-ray probe for elemental analyses (EDAX).

Temperature programmed reduction and oxidation: Temperature programmed reduction (TPR) and oxidation (TPO) experiments were carried out in a typical apparatus, equipped with a tubular quartz microreactor and a TCD detector. The experiments were performed at a heating rate of 10°C/min in the temperature range usually from 20 to 800°C in gas mixtures containing: 5 vol. % H_2 in Ar or 5 vol. % O_2 in He. Prior to TPR/O experiments the samples (50 mg) were heated up to 600°C in He in order to dispose of water adsorbed on the surface of the catalyst.

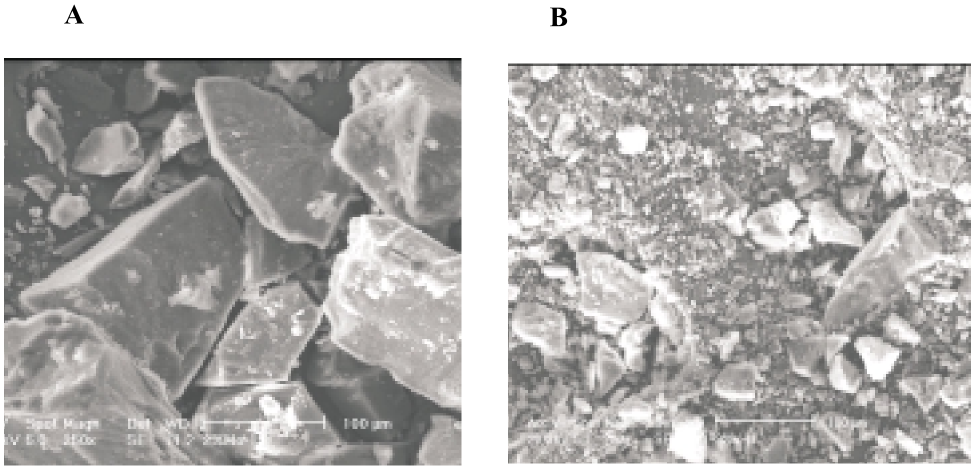
Catalytic tests: The catalytic tests were performed in a microreactor unit. The reactants were analyzed in GC/TCD system (Shimadzu, GC-14A) equipped with a micropacked column (Carboxen 1004, 2 m× 1/16”, Supelco). The gases used for the catalytic tests were: He (PRAXAIR) purified in a gas purifier (SUPELCO), CH_4 (MESSER) and O_2 (POLGAZ). The flow rates were regulated by mass flow controllers (BROOKS). In methanol oxidation experiments He or CH_4 was saturated with CH_3OH (POCH, Gliwice) in a saturator stabilized at 0°C. To avoid water or formaldehyde condensation, the gas pipes behind the reactor were heated, and formaldehyde was collected in a cold trap. Prior to catalytic reaction the catalyst samples (100 mg) were activated in O_2 at 550°C for 1 h. After attaining a desired reaction temperature a gas mixture ($CH_4/O_2 = 5$, $He/CH_3OH/O_2 = 100/4/21$ or $CH_4He/CH_3OH/O_2 = 100/4/21$) was introduced into the reactor. Temperature dependence on catalyst activity was measured at steady state: after three analyses at a given temperature the temperature was increased by 25 or by 50°C. The concentration of methanol was calculated from Antoine Equation: $\log_{10}(P_{CH_3OH}) = A - (B/(T+C))$ where, P_{CH_3OH} is the vapor pressure of methanol, T is temperature and A, B and C empirical parameters.

RESULTS AND DISCUSSION

Catalyst characterization: The results of BET measurements are presented in Table 1, along with the catalysts' symbols used in this paper. All the calcined catalysts posses a slightly lower surface area than the support material. It is noteworthy, that two catalysts with low loadings (V2SA2 and M2SA1) and the largest surface area further showed the highest activity in the selective oxidation of methane. As seen in SEM photographs, a molybdena sample is built of large crystals of the size about 100 μm, while a vanadia sample consists of much smaller well-dispersed crystallites (Fig. 1). As results from the elemental analysis by EDAX, neither the samples of the support nor the catalysts were contaminated with sodium. The TPR were performed on four catalysts samples: V2SA2, V5SA1, Mo2SA1, Mo5SA1, which prior to experiments were outgased or oxidized in TPO (see Figure 2 and Table 2). The factors influencing the reducibility of molybdena catalysts are the catalyst loading and the preparation conditions. The tendency is that the sample with a lower molybdena loading, Mo-2SA1, is reduced at a temperature by 100°C higher than the one with a higher loading, Mo5SA1 (Table 2). This observation is quite consistent with the TPR results provided by Arena *et al.* for MoO_3/SiO_2 (Akzo 400 m^2/g), and according to these authors can be accounted for by the strong metal support interactions [12] or by the formation of molybdenosilicates prevailing for low loaded samples [11,12]. Such an explanation, however, seems contradictory to the results of Raman *in situ* experiments obtained by Bañares *et al.*, who stated that at temperatures above 300°C silicomolybdic acid decomposes giving rise to the formation of molydena oxide crystallites [20], however, as these authors also notice, such assignments depend on both pretreatment conditions and engaged techniques. The most reasonable explanation for the occurrence of higher temperature of reduction of Mo2SA1 samples is a sodium impurity, probably coming from the precipitation used during preparation of Akzo silica support, which may form difficult to reduce sodium molybdates. The details concerning the characterization of silica (Akzo and Cabosil) supported vanadia and molybdena catalyst are included in our next paper [21]. Alkaline molybdates were observed in Raman spectra by Baňares *et al*. [17]. The two maxima present in TPR profiles can be assigned to the consecutive reduction of Mo^{+6} to Mo^{+4} and Mo^{+4} to Mo^{o} [12,7]. However, the temperature range 50–800°C used by us was too narrow to fully reduce the molybdenum, which is reflected in the reduction degree values (Table 2).

Table 1. Results of BET measurements of vanadia and molybdena catalysts.

Catalysts' symbol	MeO loading (% wt)	BET ($m^2\ g^{-1}$)	Mean pore diameter (Å)*	Total pore volume ($cm^3\ g^{-1}$)
SA	Pure silica (Akzo)	186	97	0.451
V2SA1	2% V_2O_5	150	151	0.564
V2SA2	2% V_2O_5	163	132	0.536
V3SA1	3.2% V_2O_5	135	124	0.436
V5SA1	5% V_2O_5	160	147	0.590
V5SA2	5% V_2O_5	128	133	0.449
Mo2SA1	2% MoO_3	162	123	0.522
Mo5SA1	5% MoO_3	152	112	0.424
Mo10SA1	10% MoO_3	130	141	0.456



Elemental EDAX analysis

2% V_2O_5/SiO_2	2% MoO_3/SiO_2
V, Si	Mo, Si
locally Na, S	locally Na

Figure 1. SEM photographs of vanadia (A) and molybdena (B) silica (Akzo) supported catalysts (250x) and results of EDAX analysis.

Loading does not significantly affect the reduction pattern of vanadia catalysts. The maximum was observed around 630°C, similarly to the results by Arena *et al.* [12]. Under the conditions used by us, V_2O_5 is said to be reduced to V_2O_3 [7,12,14].

It is worth pointing out that higher reduction degrees were observed for lower loaded catalysts (Table 2): Mo2SA and V2SA, which were also more active in catalytic tests. This may arise from higher dispersion of these samples as shown by BET results (Table 1). Indeed, the isolated molybdena and vanadia species, as "mono-oxo" MoO_6 and VO_4, were observed for silica supported molybdena [17] and vanadia [18,19] catalysts with a low metal oxide coverage.

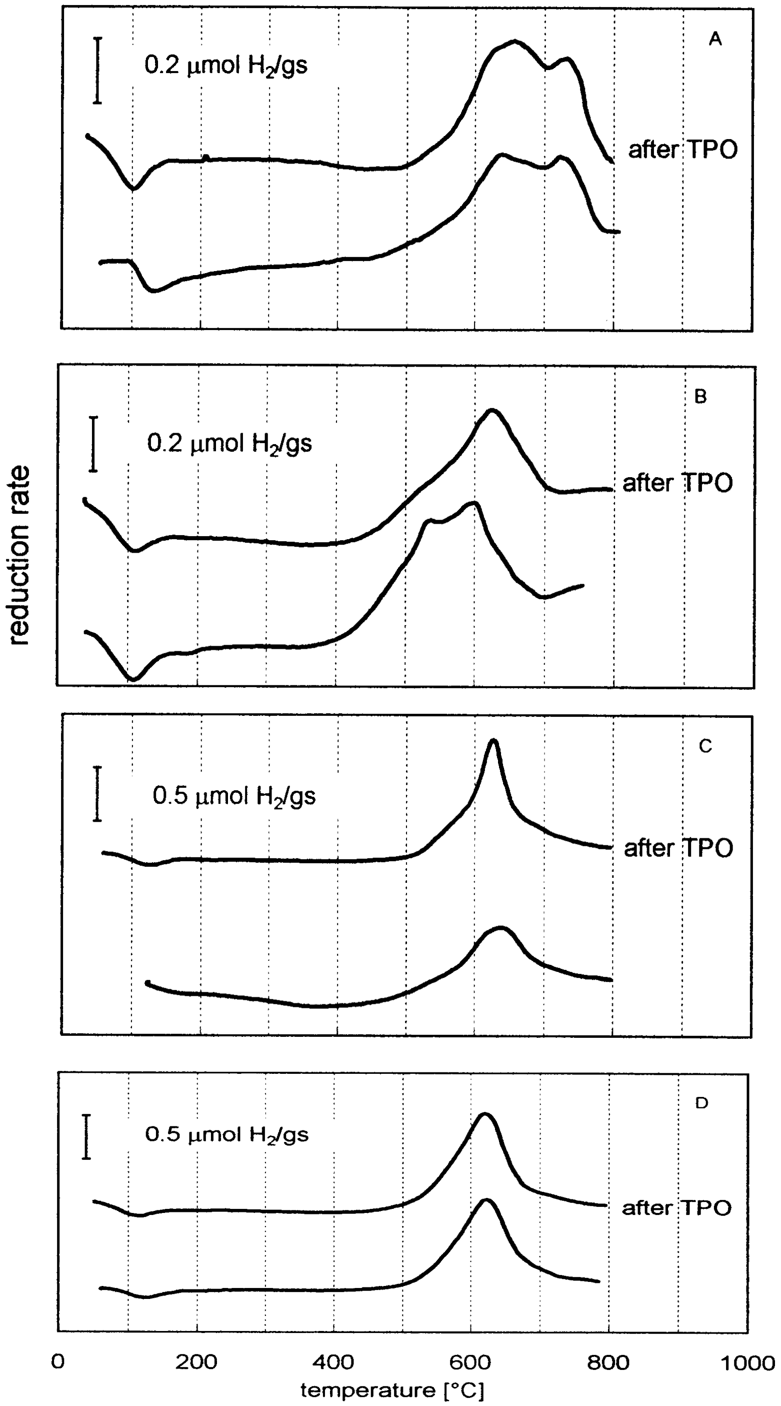


Figure 2. TPR results of molybdena and vanadia catalyst samples outgased or oxidized in TPO prior to the reduction; A – Mo2SA1 sample, B – Mo5SA1 sample, C – V2SA1 sample, D – V5SA2 sample.

Table 2. Quantitative results of TPR of vanadia and molybdena catalysts.

Catalyst	Treatment	T_{max} [°C]	$n(H_2)$ μmol	O/M
2% MoO_3/SiO_2	outgased	640 740	16.1	2.2
	TPO	660 740	20.4	2.9
5% MoO_3/SiO_2	outgased	530 600	14.6	0.9
	TPO	– 630	10.9	0.6
2% V_2O_5/SiO_2	outgased	630	17.3	1.6
	TPO	640	5.37	2.4
	TPO	630	26.9	2.5
	TPO	640	20.7	1.9
5% V_2O_5/SiO_2	outgased	630	25.7	0.9
	TPO	630	34.9	1.3
	TPO	630	24.0	0.9
	TPO	630	27.4	1.0

Catalytic tests: Three different reactions have been studied for the series of catalysts: (i) partial oxidation of methane; (ii) partial oxidation of methanol; (iii) partial oxidation of methanol/methane mixtures.

Methane partial oxidation: Temperature dependence on methane conversion (X), yield (Y) and selectivity (S) for the series of molybdena and vanadia catalysts is presented in Figure 3 A–C. The general observation is that molybdena catalysts were more active in complete methane oxidation rather than in selective oxidation (Fig. 3. A). The results of elemental analysis by EDAX suggest that the low activity of catalyst supported on silica may arise from the formation of sodium molybdate, which is a catalyst poisson. The reproducible activity and selectivity towards HCHO was therefore exhibited only by 2% vanadia catalyst (Fig. 3 B, C). For this catalyst the CH_4 conversion increased with temperature and reached about 10% at 650°C, whereas the HCHO selectivity decreased from about 18% at 610℃ to about 2% at 650℃ (Fig. 3. C). Moreover, CO seems to form in the consecutive reaction route from CH_4, through HCHO, since temperature shows an opposite impact on HCHO and CO selectivity. It also seems, that CO_2 is formed in an independent path, at least in a lower temperature range. This observation is contradictory to the results provided by Hall *et al.* [8], who stated that on molybdena catalysts CO_2 can be formed directly from methane in an independent route, while on vanadia catalysts it is a product of consecutive oxidation of CH_4 through HCHO and CO. However, another model assuming an independent reaction path also on V_2O_5/SiO_2 catalysts has been proposed by Bañares *et al*. [7].

In an attempt to ascertain the best reaction conditions, we studied the influence of contact time on the conversion and selectivity in MPO. Figure 4 shows the results obtained for the V2SA2 catalyst at 550°C. As it was expected, CH_4 conversion increases with prolonging the contact time. At a short contact time (21 s/g/ml), when there is still no CO, the HCHO selectivity shows a maximum, while CO_2 selectivity – a minimum.

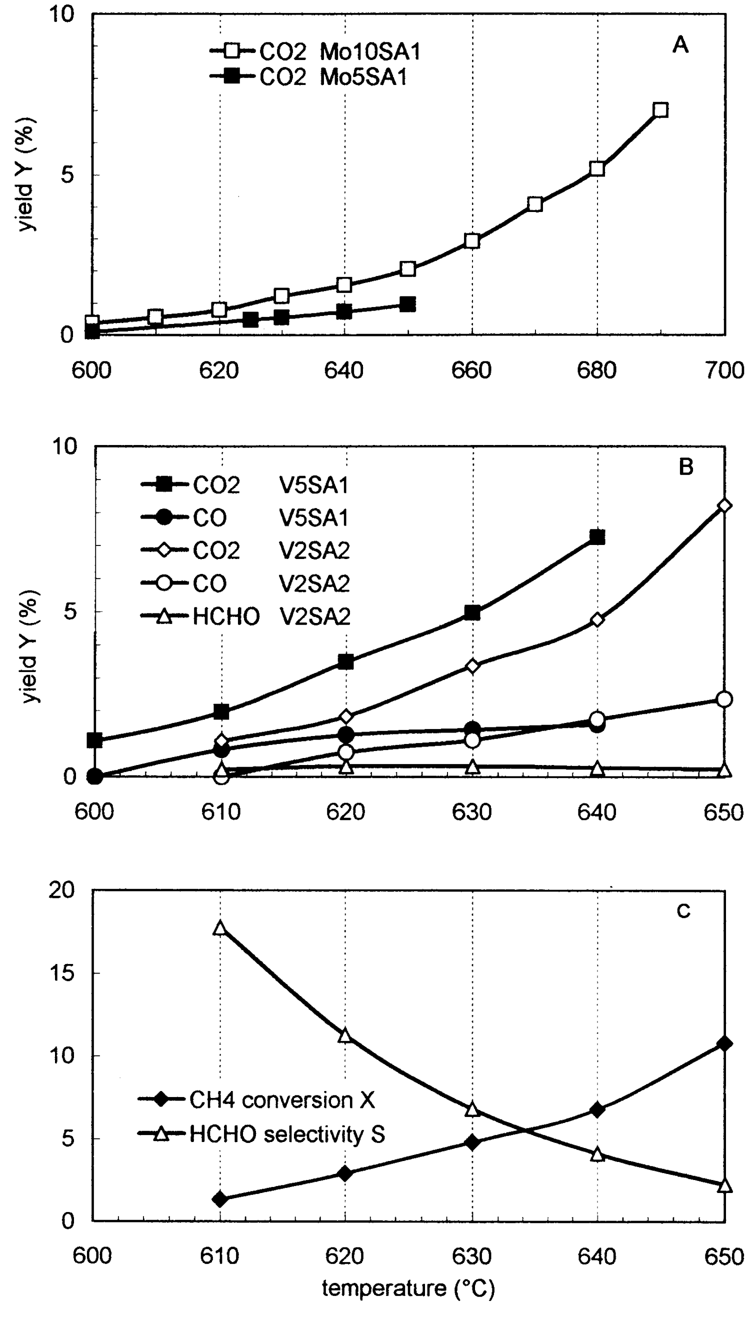


Figure 3. Temperature impact on catalytic performance in the partial oxidation of methane, $CH_4/O_2 = 5$; A – product yields (Y) for molybdena catalysts, B – product yields (Y) for vanadia catalysts, C – CH_4 conversion (X) and HCHO selectivity (S) of V2SA2 catalysts.

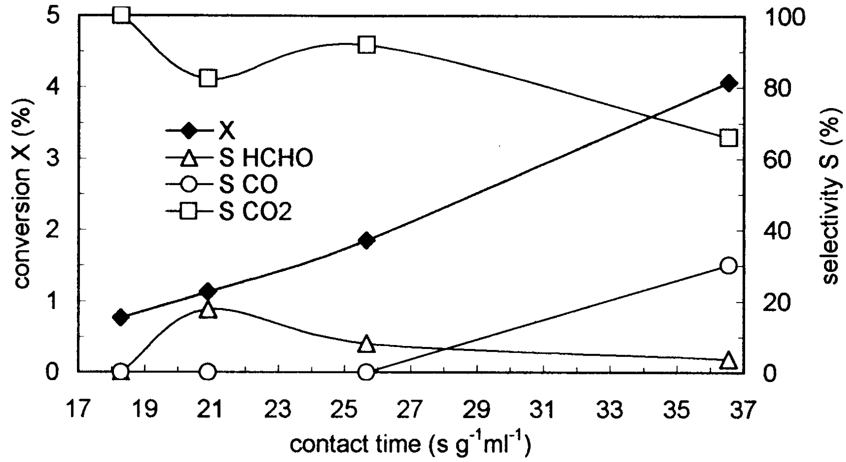


Figure 4. Contact time influence on catalytic performance in the partial oxidation of methane on V2SA2 catalysts at 550°C.

These facts indicate, that the reaction path to HCHO competes with the other one, which gives CO_2. The maximum of CO selectivity emerges at a longer contact time.

Methanol partial oxidation: Temperature dependence on the catalyst activity and selectivity in methanol oxidation is presented in Figure 5 A, B. Methanol oxidation proceeds at much lower temperatures, giving much higher CH_4 conversion and HCHO selectivity than methane oxidation. On the whole, the conversion increases sigmoidally with temperature from around 10% to 80% in the studied temperature range, while the selectivity shows a maximum (80–100%) at temperatures around 400–450°C for all catalysts samples. As seen in Figure 7 the highest yield of HCHO was achieved for the Mo5SA1 sample.

Effect of methanol on methane partial oxidation: The results of the methanol/methane coupled oxidation are envisaged in Fig. 6 A and B. To investigate this effect, after several hours of isothermal methanol oxidation, helium flowing through CH_3OH saturator was replaced by CH_4; the example of such an experiment performed on the Mo2SA1 sample is shown in Fig. 6 A. The appearance of CH_4 in the reaction mixture was accompanied by a rapid increase of HCHO yield (Fig. 7 and 6 A). The largest effects were observed for 2% molybdena catalyst samples. This amplification effect was alleviated – there was nearly a negligible product formation – as soon as the methanol feed was ceased. It was also observed, that on disappearing CH_3OH, methane concentration simultaneously increased (by 8 mol. %) (Fig. 6 B). Accordingly, the oxygen consumption rose during coupled oxidation (by 8 mol. %) and slumped by 30% after cutting off CH_3OH from the feed. This indicates that methane takes part in methanol/methane coupled oxidation towards formaldehyde.

Methanol influence on MPO has not been studied before and the role methanol plays in the coupled methane oxidation is not clear. The commonly approved MPO mechanism assumes activation of methane molecules by active oxygen species, ori-

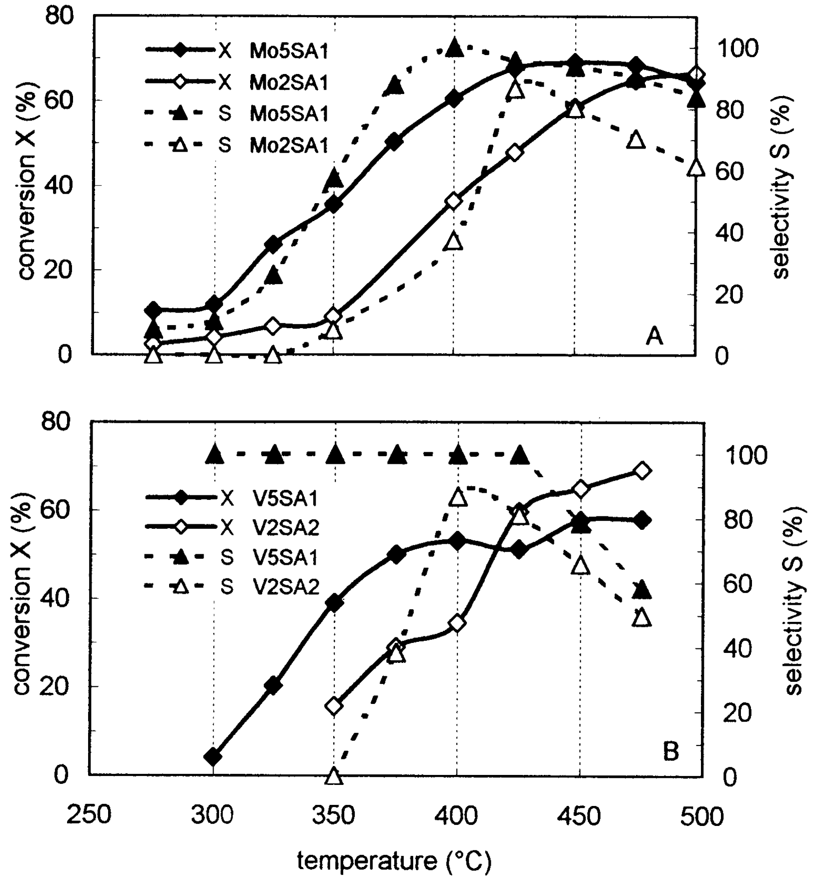


Figure 5. Temperature dependence of methanol conversion (X) and HCHO selectivity (S) in the selective oxidation of methanol, $He/CH_3OH/O_2 = 100/4/21l$; A – molybdena catalysts, B – vanadia catalysts.

ginating from lattice or gas-phase oxygen. Thus formed methyl radicals undergo further oxidation to formaldehyde [6,13]. On the other hand, methanol oxidation is known to proceed *via* metal methoxide groups formation [17,18], which for a vanadium catalyst are very stable as evidenced by Raman *in situ* measurements [17,18,19]. As can be inferred from the literature and our results, methanol adsorbing on *e.g.* vanadium centers may break V=O terminal or V–O planar bonds, which should lead to the formation of active oxygen species, which in turn give rise to the formation of methyl radicals. Alternatively, methanol, as a better reducing agent than CH_4, must also influence redox properties of the catalysts surface. Vanadia catalysts are said to be active in a slightly reduced form, V^{+4}, which facilitates formation of active oxygen necessary to oxidize methyl groups [3,22]. Indeed, the XPS results obtained for thin V_2O_5 films evidence the presence of a nonstoichiometric oxide [23,24].

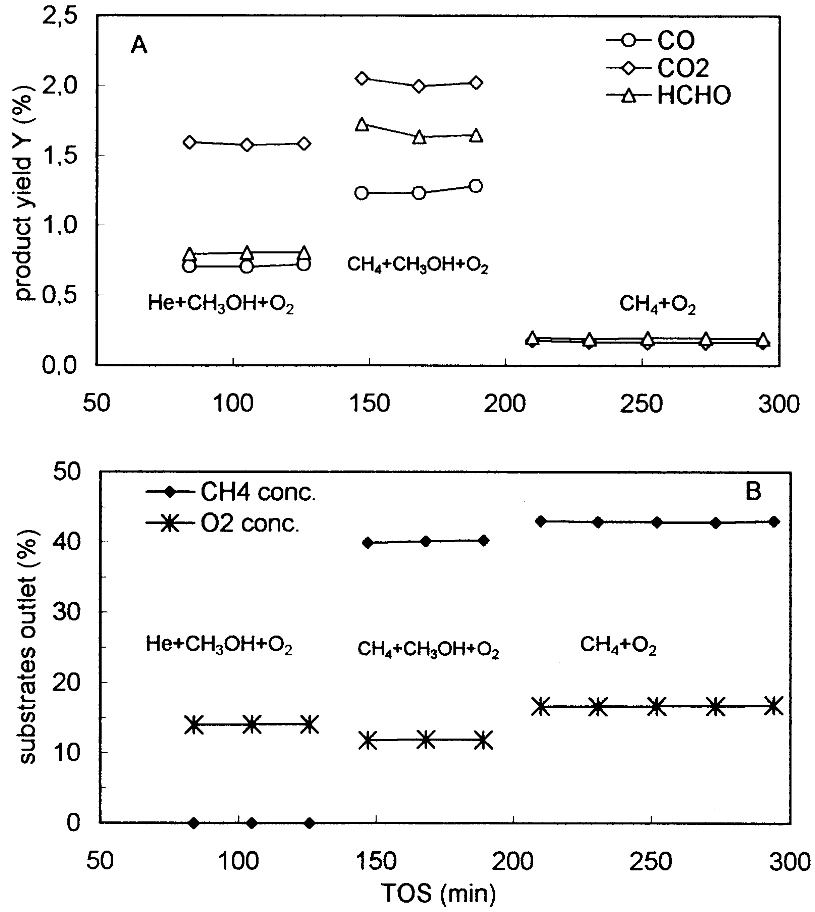


Figure 6. Methane and methanol mutual effect in the selective oxidation to formaldehyde at 600°C, $He/CH_3OH/O_2$ = 100/4/21, $CH_4He/CH_3OH/O_2$ = 100/4/21, CH_4/O_2 = 5; A – product yields, B – substrates content.

CONCLUSIONS

This paper, the first in a series concerning our study on gaseous promoters for MPO, addresses the problem of methanol and methane coupled oxidation to formaldehyde. An interesting observation is that the addition of a small amount of methanol enhances oxidation of methane and the formation of formaldehyde over the catalysts, which were non-selective towards formaldehyde in methane oxidation. The possible explanation of this phenomenon is that the formation of methoxide groups on vanadia or molybdena centers is accompanied by the active oxygen formation, which in turn facilitates activation of methane molecules to methyl radicals. The occurrence of active oxygen may be due to reduction of vanadia V^{+5} to V^{+4} and the breakage of V=O terminal or V–O planar bonds.

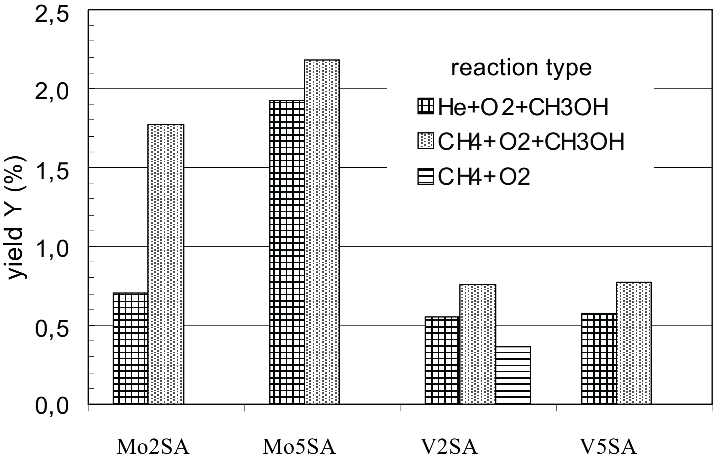


Figure 7. Summary of catalytic performance of vanadia and molybdena catalyst in three different catalytic tests at 600°C.

Acknowledgments

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