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Kinetics of the oxidative dehydrogenation (ODH) of methanol to formaldehyde by supported vanadium-based nanocatalysts

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Abstract

The aim of the present contribution was to develop a detailed kinetic analysis of the oxidative dehydrogenation (ODH) reaction of methanol to formaldehyde on a nano-structured supported vanadium oxide catalyst, selected in a preliminary screening. The chosen vanadium catalyst, supported on TiO_2/SiO_2, has been prepared by grafting vanadyl alkoxide, dissolved in dioxane, and characterized by BET, XRD, Raman, XPS and SEM. An exhaustive set of experimental runs has been conducted in an isothermal packed bed tubular reactor by investigating several operative conditions, such as: temperature, contact time, methanol/oxygen feed molar ratio and water feed concentration. Depending on the operative conditions adopted, the main products observed were formaldehyde and dimethoxymethane while lower amounts of methyl formate and CO_2 were also found. At low contact time, the main reaction product was dimethoxymethane which was then converted into formaldehyde through the reverse equilibrium reaction with water. As a confirmation of this observation, a peculiar behaviour was detected consisting in an increase of selectivity to formaldehyde by increasing methanol conversion. The obtained experimental data of methanol conversion and selectivity towards products were modelled by means of an integral reactor model and the related kinetic parameters were determined by non-linear regression analysis. The adopted reaction rate expressions were of the Mars van Krevelen–Langmuir Hinshelwood type and a good agreement was found between the model theoretical prediction and the experimental data. A reaction mechanism and a detailed reaction scheme (*rake-type*) were proposed for methanol ODH on a nano-structured catalyst that were able to interpret correctly the collected experimental observations.

Keywords: ODH methanol; Formaldehyde; Vanadium-based nanocatalysts

1. Introduction

Formaldehyde is one of the most versatile chemicals and is employed by the chemical and other industries to produce a large number of indispensable products used in daily life [1]. The largest amounts of formaldehyde are mainly used to give a wide range of condensates, i.e. urea-phenolic and melamine resins, and, to a small extent, their derivates. The properties of these compounds have been adapted by industry to a very large number of applications, such as the manufacture of chipboards (compressed wood) and plywoods. Other well-established applications are in the production of papers, paints, adhesives, cosmetics, explosives, fertilizers and textiles.

The selective catalytic oxidation of methanol represents the most relevant route on which the industrial formaldehyde production is based [1]. In particular, the industrial processes currently used can be divided in: (a) silver catalyst process, based on partial oxidation and dehydrogenation with air in the presence of silver crystals, steam and excess methanol at atmospheric pressure and 680–720 °C; (b) Formox process, in which a metal oxide (Fe-Mo) is used for the conversion of methanol to formaldehyde, by oxidation with excess air, essentially at atmospheric pressure and 250–400 °C. In both processes, a conversion of about 99 and 92% of selectivity to formaldehyde are obtained. However, the very low reaction temperature used in the Formox process, which permits to achieve high selectivity to formaldehyde, and the very simple method of steam regeneration, which reduces the operating costs, make this process easily controlled and more attractive from the industrial point of view. For this reason, the most common actual plants (more than 70%) employ Formox methanol oxidation to produce formaldehyde. However, iron-molybdate catalysts become less active in the presence of an excess of methanol and therefore require a relatively high

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Nomenclature

b_j	adsorption parameter of the component jth (atm^{-1})
C	methanol fractional conversion
F_j	molar feed flow rate of component jth (mol/min)
k_i	reaction rate constant of the reaction ith (mol/min g_{cat} atm)
k_{ox}	catalytic site re-oxidation constant (mol/min g_{cat} $atm^{0.5}$)
K_{eq}	equilibrium constant for reaction 5.2
n_c	number of carbon atoms in the ith reaction product
N_r	number of reactions
P_j	partial pressure of the component jth (atm)
r_i	reaction rate of the reaction ith (mol/min g_{cat})
$\upsilon_{j,i}$	stoichiometric coefficient of the component jth in the reaction ith
W	catalyst weight loaded in the reactor (g)
Y_i	fractional yield to product ith

oxygen partial pressure to remain active [2]. Multi-component unsupported Ni–Fe–Bi–Ti–P–O catalysts [3] or catalyst containing Cu, Zn, Ni, etc. have also been proposed [4]. However, the stability and catalytic performances of these catalysts make them less favorable for an industrial application. Thus, motivated by the perspective to look for catalysts with better physico-chemical properties, the ODH of methanol to formaldehyde has been widely studied in the literature [5–7]. Good catalytic performances in terms of both activity and selectivity have also been documented for supported metal oxide catalysts, which consist of two-dimensional surface metal oxide overlayers on high-surface support oxides (e.g. Al_2O_3, TiO_2, SiO_2, etc.) [8]. Among all the catalysts explored, supported vanadium oxides have received much attention in recent years [9–11]. Their application is strongly affected by the specific interaction between vanadium oxide and the support. Several authors have compared the properties of vanadia supported on different carriers (e.g. SiO_2, Al_2O_3, TiO_2, ZrO_2, MgO) and have concluded that, depending on the specific support, vanadia based catalysts may show different catalytic activity and selectivity. Apart from the role of the support, the importance of the preparation method on the final catalyst behaviour and uniformity of the vanadia species has been largely discussed in literature. At this purpose, the catalyst preparation by using the grafting technique has gained interest in the recent years as a route for obtaining well-dispersed catalysts. It has been pointed out that grafting techniques lead to more dispersed catalysts that are stable when an opportune support is used. In our previous works [12–16] we have used, for example, vanadyl alkoxide, dissolved in different aprotic solvents, to undertake the grafting operations and we have tested their catalytic performances in different reactions, such as: SCR of nitrogen oxides by ammonia and ODH of propane, *n*-butane, isobutane and ethanol. We have found that the different catalytic properties of vanadia catalysts can be related to the surface structure of vanadium species and, generally, a good surface vanadium dispersion is one of the key-factors to obtain very active and selective catalysts. In particular, the results obtained in the ODH of ethanol to acetaldehyde, investigated in a previous works [15,17], showed that supported vanadium catalysts may be able to promote this process under mild conditions of both temperature and pressure, allowing to achieve high activities and selectivities, to prevent coke formation and to improve the catalyst lifetime.

More recently, we focused our attention on the study of the catalytic performances of vanadium-based catalysts in the ODH of methanol to formaldehyde [18]. At this purpose, a detailed catalytic screening over vanadium catalysts, supported on both silica and titania/silica by grafting, was performed. The influence of reaction temperature (140–260 °C), at a fixed contact time ($W/F = 25.3\ g_{cat}\ h/mol_{MeOH}$), and vanadium loading, as well as preparation method and type of support, on the activity and selectivity was thoroughly investigated. For a useful comparison, some catalysts were also prepared by impregnation. The results obtained showed that the catalysts, prepared by grafting vanadyl alkoxide on TiO_2/SiO_2 support, are more active than the impregnated ones with similar vanadium loadings. Moreover, by comparing the catalytic performances of the catalysts synthesized by grafting ($V_2O_5/TiO_2/SiO_2$), we observed that the activity increases by increasing the vanadium content, while the selectivity to formaldehyde only depends on the conversion level and seems to be independent of the coverage degree of the starting silica support by titania. Thus, we concluded that the vanadium loading and the surface dispersion are the key-factors which determine the activity. For what concerns the product-distribution, depending on the operative conditions adopted, the main products observed were formaldehyde and dimethoxymethane, as well as lower amounts of methyl formate and CO_2. The presence of CO, verified by using a different chromatographic column (Carboxen 1006 PLOT), in the reactor outlet has never been observed. An expected increase of methanol conversion resulted by increasing vanadium loading, from 1% up to 5% of V_2O_5 by weight. On the contrary, an unusual trend consisting in an increase of selectivity to formaldehyde as a function of methanol conversion, was observed. This trend may be explained by considering that the first reaction product was dimethoxymethane which is then converted to formaldehyde by the reverse equilibrium reaction with water. This observation has been supported by the experimental screening results, according to which, at low-temperature and conversion, the main product was dimethoxymethane, while, by increasing the temperature, an increase in formaldehyde formation was detected. At temperature higher than 220 °C, when methanol conversion is nearly complete, formaldehyde oxidation occurs and an increase in CO_2 production was observed. This scenario, provided by the screening, seems to confirm the structure-sensitivity of methanol oxidation, largely discussed in literature, according to which different products can be obtained by varying the catalyst nature and reaction conditions [19]. Thus, a good knowledge of the reaction mechanism is necessary to elaborate

Table 1
Operative conditions used for the preparation of the catalysts and some related properties

Precursor/solvent/support	Acronym	$Ti(O\text{-}^iPr)_4$ (g)	Support (g)	Volume of Solvent (cm^3)	% wt of MO_x	S_{BET} (m^2/g)	Pore volume (cm^3/g)
$Ti(O\text{-}Pr^i)_4$/dioxane/SiO_2	TSm	10.79	24	400	7.29[a]	278	1.70
$VO(O\text{-}Pr^i)_3$/dioxane/TiO_2-SiO_2	$4.69V_{graf}$/TSm	0.65	3	50	4.69[b]	200	1.02

[a] Percentage by weight of supported TiO_2.
[b] Percentage by weight of supported V_2O_5.

a correct interpretation of variations of the catalytic behaviour. In spite of the large number of papers devoted to investigate the influence of the surface properties and the interaction between the active phase and the support on the catalyst behavior, very few works reported a detailed kinetics model able to describe the products distribution. According to the literature, the selective oxidation of methanol to formaldehyde over metal oxide based catalysts follows a Mars and van Krevelen [20] type redox mechanism, in which the oxidation proceeds by a reduction of an oxidized surface site, which is subsequently re-oxidized with gas-phase molecular oxygen [21]. Several authors have studied the kinetics of the methanol partial oxidation to formaldehyde over a Fe-Mo catalyst and only a limited number of papers were addressed towards vanadium oxide catalysts. However, most of the previous works was limited to the formation of formaldehyde only and not much attention was paid to the formation of side products, such as carbon dioxide, dimethylether (DME) and dimethoxymethane (DMM). Moreover, all the kinetic data reported in the literature were measured at low methanol concentrations (maximum 6%) [22].

Thus, the lack of detailed kinetic data capable of describing all the products observed in the ODH of methanol, over supported vanadium-based catalysts, led us to investigate this reaction also from a kinetic point of view. In this work, we wish to propose a complete kinetic analysis on a supported vanadium-based catalyst ($4.69V_{graf}$/TSm), resulted from the catalytic screening as the best one in terms of both activity and selectivity. The effect of several operative variables such as: temperature, contact time, methanol/oxygen feed molar ratio and water feed concentration was investigated.

2. Experimental

2.1. Support and catalyst preparation

The support of silica coated with TiO_2, indicated with the acronym TSm, was prepared in a single-step grafting procedure, using titanium tetra-isopropoxide (Fluka) dissolved in anhydrous dioxane and a commercial silica (Grace S-432), calcined at 500 °C for 8 h. The quantity of titanium tetra-isopropoxide dissolved in dioxane corresponds to the monolayer coverage, assuming a conventional stoichiometry of one hydroxyl per alkoxide molecule [16]. After calcination, the silica was put in contact with the titanium alkoxide solution for 5h at room temperature under constant stirring. The solid obtained was then filtered, washed with dioxane, dried at 120 °C overnight, heated at 200 °C for 2 h and then calcined at 500 °C for 2 h. More details about the preparation method and the properties of this support are reported elsewhere [18]. The vanadium-based catalyst, indicated with the acronym $4.69V_{graf}$/TSm, was prepared by putting the described support in contact with a solution of vanadyl tri-isopropoxide ($VO[O\text{-}Pr^i]_3$, Aldrich 99.999%, $d = 0.963$ g/ml), dissolved in anhydrous dioxane. The grafting reaction was performed for 5 h in a well-stirred jacketed glass reactor, under inert helium atmosphere. The solid obtained was filtered, washed with dioxane, oven-dried at 120 °C overnight, heated at 200 °C and then calcined at 500 °C. The operative conditions used for preparing the support TSm and the vanadium catalyst $4.69V_{graf}$/TSm, respectively, are reported in Table 1 together with the resulted physico-chemical properties of the solids obtained.

2.2. Catalyst and support characterization techniques

The titanium loading was determined using a colorimetric method [23], after dissolution of titanium in a concentrated sulfuric acid solution, dilution, and then treatment with H_2O_2. The vanadium load in the prepared catalyst was determined by atomic absorption, after dissolution in concentrated sulfuric acid.

Textural analyses were carried out by using a Thermoquest Sorptomatic 1990 Instrument (Fisons Instrument) and by determining the nitrogen adsorption/desorption isotherms at 77 K. The samples were thermally pre-treated under vacuum overnight up to 200 °C (heating rate = 1 °C/min). Specific surface area (S_{BET}) and pores size distribution were determined by using the BET and Dollimore–Heal methods [24,25]. Details about other characterization analyses (XRD, XPS and NH_3-TPD), performed on both the support TSm ad the catalyst $4.69V_{graf}$/TSm, as well as the related results are reported elsewhere [18]. This catalyst has been selected for the kinetic study, because, corresponds to a vanadium load near to the monolayer and it has shown the highest TON with respect to other catalysts containing different amounts of vanadium oxide on the surface [18]. The activities shown for increasing amounts of vanadium on the surface increases almost linearly until to reach a maximum value in correspondence of 4.8–5.4% of V_2O_5 [18]. The support not containing vanadium has shown negligible activity in the reaction.

2.3. Methods, techniques and operating conditions used in the catalytic runs

Kinetic runs were performed in a stainless steel tubular reactor with an internal diameter of 1 cm, kept isothermal with a fluidized bed of sand. Liquid methanol was fed, by a syringe pump, into a vaporizer chamber kept at 250 °C and was then sent, after the addition of a stream of oxygen and helium, into a stainless steel coil kept at the same temperature of the reactor. The composition of the gases at the outlet of the reactor was gas-cromathographically analyzed by withdrawing a sample with an on-line sampling valve kept at 170 °C. The GC used was an HP 5890 instrument, with a Restek RT-Q-Plot 30 m × 0.32 mm column. Helium was used as the carrier gas. The conditions used for the analyses were as follows: temperature held at 50 °C for 2 min, increased at a rate of 5 °C/min to 100 °C and then at a rate of 20 °C/min to 180 °C for 5 min, and finally kept at this temperature for 5 min. A TCD detector kept at 250 °C was used. Samples of powdered catalyst, generally 0.3 g, were placed inside the reactor on a bed of glass wool. Two thermocouples located immediately upon and under the catalytic bed allowed the validity of the isothermal conditions to be controlled within ±1 °C. The operative conditions adopted are listed in Table 2.

Three different sets of kinetics runs were conducted. The first set of runs was performed in the temperature range 140–200 °C by changing the methanol residence time from 10 to 65 g_{cat} h/mol_{MeOH} but keeping the molar ratio between methanol and oxygen constant (1:1). The second set of runs was carried out at $T = 160$ °C by significantly varying both the methanol residence time (from 10 to 65 g_{cat} h/mol_{MeOH}) and the feed molar ratio between methanol and oxygen. The third set of kinetics experiments was conducted with the aim to investigate the effect of the presence of water in the feed on the catalytic performances. These last runs were carried out by using the following reaction conditions: 0.3 g of catalyst, methanol residence time ranging from 10 to 65 g_{cat} h/mol_{MeOH} while keeping at 180 °C the reaction temperature. Water was added in the feed with an apparatus similar to that of methanol (syringe pump).

Results are reported in terms of the methanol conversion and product yields. The methanol conversion is defined as

$$C = \frac{\text{Number of moles of methanol reacted}}{\text{Number of moles of methanol fed}}$$

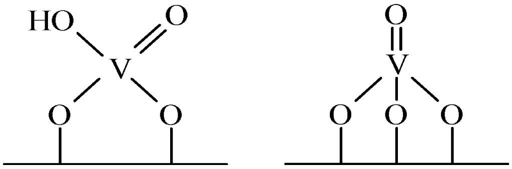
while the yields of the *i*th product is defined as

$$Y_i = n_c \frac{\text{Number of moles of product } i \text{ formed}}{\text{Number of moles of methanol fed}}$$

where n_c is the number of carbon atoms contained in the considered *i*th molecule.

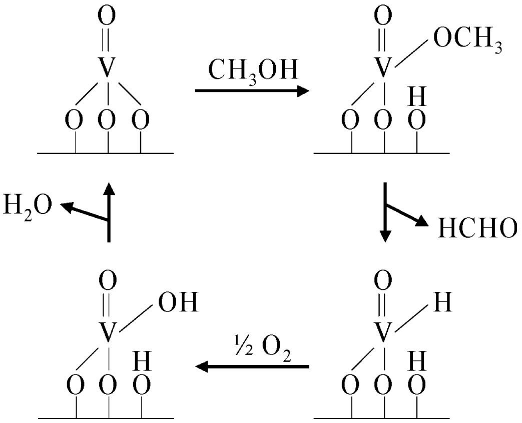
3. Results and discussion

The detailed mechanism of alcohols partial oxidation to aldehydes is still under investigation. It is well known that the oxygen responsible of the oxidation is present in the lattice structure. This is supported by the experimental evidence that oxygenated compounds are formed onto catalyst surface also in the absence of gaseous oxygen, as in the case of acrolein synthesis from propylene on mixed Mo/Bi oxides [26]; in other reactions, as the *n*-butane oxidation to maleic anhydride, the gaseous oxygen seems to be responsible for the oxidation process [27]. However, all these reactions occur at a relatively higher temperature if compared with the one used in the present study. Very probably dehydrogenation is, in our case, the first reaction step which involves hydride formation while the gaseous oxygen is responsible for catalytic site re-oxidation. Another uncertainty regards the structure of the active site that, in the case of vanadium-based catalysts, depends also on the vanadium load [28], on the hydration condition of the environment and on the used support. Despite the relatively high reaction temperature, the water produced could give place to the presence of a vanadium catalytic site in an hydrated form, characterized by a structure that is intermediate between the following ones:



(1)

Weckhuysen and Keller [21] have proposed a reaction mechanism for the partial oxidation of methanol to formaldehyde, on vanadium-based catalysts, that involves a single vanadium surface site for which the vanadium oxidation state is nearly constant (V) and a limited reduction was observed. According to this mechanism, the conversion of methanol to formaldehyde occurs in four steps that can be schematically represented as follows:



(2)

As can be seen from (2), the methoxydic intermediate V–O–CH_3, observed in literature through spectroscopy experiments [29], is the precursor to which the formaldehyde formation (assumed as the rate determining step) can be attributed while the molecular oxygen is responsible for the catalytic site re-oxidation which is then restored by water elimination.

It is interesting to observe that the proposed mechanism (2) accounts only for the main reaction to formaldehyde, while in our investigation significant amounts of other products have been observed, depending on the operative conditions adopted.

Table 2
List of runs and related operative conditions

Run ID	W/F (g_{cat} h/mol_{MeOH})	Methanol feed flow rate (liquid) (ml/h)	O_2 feed flow rate (gas) (ml/min)	Water feed flow rate (liquid) (ml/h)	Temperature (°C)
R1-R5	12.91	1.00	10.07	–	140–200
R6-R10	16.13	0.8	8.06	–	140–200
R11-R15	32.37	0.4	4.06	–	140–200
R16-R20	61.46	0.21	2.09	–	140–200
R21	12.91	1.00	5.03	–	160
R22	16.13	0.8	4.04	–	160
R23	32.37	0.4	2.03	–	160
R24	61.46	0.21	1.05	–	160
R25	12.91	1.00	15.1	–	160
R26	16.13	0.8	12.11	–	160
R27	32.37	0.4	6.09	–	160
R28	61.46	0.21	3.14	–	160
R29	12.91	1.00	10.07	0.08	180
R30	16.13	0.8	8.06	0.065	180
R31	32.37	0.4	4.06	0.04	180
R32	61.46	0.21	2.09	0.02	180

Other conditions: catalyst load $W = 0.32$ g; helium flow rate = 30 ml/min.

Table 3
Experimental data

Run ID	W/F[a]	Temperature (°C)	Feed molar ratio CH_3OH/O_2	Methanol conversion	Products yields[b]			
					F	MF	DMM	CO_2
R1	12.91	140	1	0.19034	0.01006	0.00750	0.15517	0.01760
R6	16.13	140	1	0.20076	0.01193	0.01071	0.15932	0.01879
R11	32.27	140	1	0.23034	0.04762	0.01428	0.13506	0.03339
R16	61.46	140	1	0.25428	0.14727	0.01535	0.03495	0.05671
R2	12.91	160	1	0.22961	0.01674	0.01506	0.18860	0.00921
R7	16.13	160	1	0.27392	0.03294	0.02120	0.20586	0.01391
R12	32.27	160	1	0.31864	0.09665	0.02294	0.16824	0.03079
R17	61.46	160	1	0.38799	0.22947	0.11163	–	0.04688
R3	12.91	180	1	0.26222	0.10816	0.02604	0.11275	0.01742
R8	16.13	180	1	0.33117	0.16248	0.03415	0.11728	0.01726
R13	32.27	180	1	0.35806	0.22538	0.07302	0.02467	0.03499
R18	61.46	180	1	0.57301	0.43106	0.08626	–	0.05569
R4	12.91	190	1	0.38276	0.21186	0.04694	0.11200	0.01196
R9	16.13	190	1	0.41255	0.22471	0.04972	0.12469	0.01343
R14	32.27	190	1	0.49893	0.38390	0.07377	0.01696	0.02429
R19	61.46	190	1	0.82799	0.62684	0.09231	0.00990	0.09894
R5	12.91	200	1	0.37585	0.24133	0.04420	0.07531	0.01501
R10	16.13	200	1	0.48011	0.34829	0.06027	0.04140	0.03016
R15	32.27	200	1	0.68976	0.56172	0.07448	0.00821	0.04535
R20	61.46	200	1	0.91946	0.72141	0.09027	–	0.10778
R21	12.91	160	0.66	0.28527	0.05027	0.01221	0.19741	0.02538
R22	16.13	160	0.66	0.30141	0.06976	0.01529	0.18603	0.03603
R23	32.27	160	0.66	0.32651	0.09424	0.01896	0.17373	0.03958
R24	61.46	160	0.66	0.45710	0.29185	0.03756	0.03135	0.09634
R25	12.91	160	2	0.19429	0.01721	0.00619	0.15924	0.01165
R26	16.13	160	2	0.26533	0.03288	0.01179	0.20050	0.02015
R27	32.27	160	2	0.30027	0.07750	0.01578	0.15293	0.05405
R28	61.46	160	2	0.31312	0.13749	0.00689	0.02220	0.14651
R29	12.91	180	1	0.31477	0.12573	0.02543	0.13139	0.03222
R30	16.13	180	1	0.31684	0.12695	0.02514	0.13566	0.02909
R31	32.27	180	1	0.40715	0.25941	0.04082	0.06218	0.04474
R32	61.46	180	1	0.67661	0.50895	0.06176	0.00828	0.09761

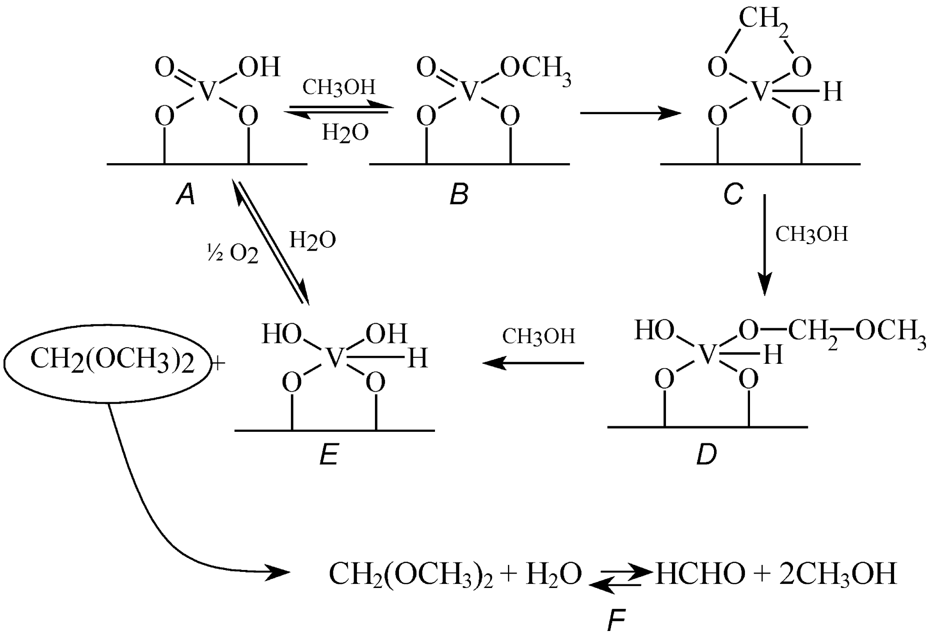
[a] (g_{cat} h/mol_{MeOH}).

[b] F: formaldehyde, MF: methyl formate, DMM: dimethoxymethane.

In particular, at low contact time, the main reaction product was dimethoxymethane while, increasing the contact time, an increased concentration of formaldehyde was observed (see for example the run at 160 °C reported in Fig. 2). This behavior is the classical one in kinetics for the consecutive reactions and suggests that the formation of dimethoxymethane and formaldehyde occurs in series, that is, dimethoxymethane is converted into formaldehyde by the reverse equilibrium reaction with water. As a further confirmation of this observation, an increase in selectivity to formaldehyde was generally observed in correspondence to an increase of methanol conversion (see Table 3). The described behavior is different from the one observed in the ODH of ethanol, performed in similar conditions with the same type of catalyst [17], suggesting a different operating reaction mechanism in the two cases.

However, the preminent formation of dimethoxy methane at low methanol conversions has already been observed also by other authors, in particular by Tatibouët and Germain [30], as reported in the review of Forzatti et al. [31].

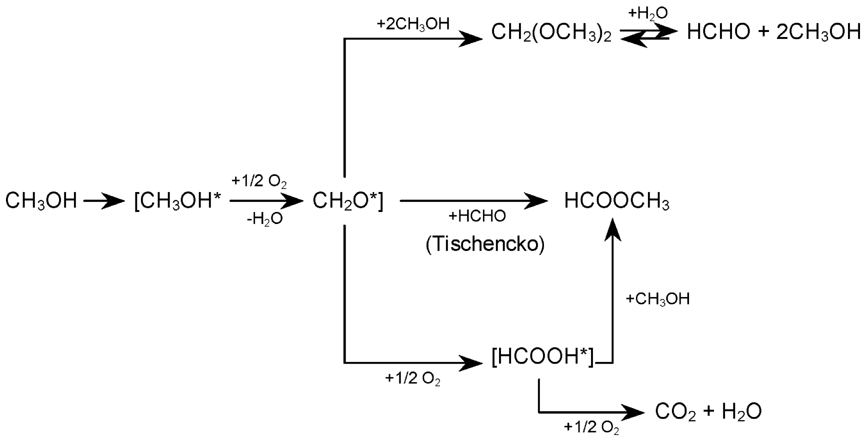
On the basis of the observations reported, we hypothesized a mechanism for the catalytic cycle of the ODH of methanol that starts from a vanadium site in hydrated form, (A), and that can be schematized as follows:



(3)

The first elementary step in this mechanism, that is, the formation of the methoxydic intermediate (B) by methanol dissociative adsorption, is in agreement with the suggestions of different authors [21,31,32], in particular by Wachs et al. that devoted different papers to this reaction performed in the presence of vanadium oxide supported on different supports [33–36]. In the subsequent step this intermediate is rearranged into a dioxymethylenic surface species, spectroscopically observed by Busca [38], with the vanadium atom which presents a vanadium-hydride bond. The dioxymethylenic group can further react with methanol adsorbed from gaseous phase and lead to the formation of dimethoxymethane in two successive steps. Formaldehyde is then formed for the occurrence of the hydrolysis equilibrium (F) when the methanol conversion is high and water is present at a sufficiently high concentration in the system. According to Wang and Wachs [36] and Tatibouët the formation of dimethoxymethane is favored by the presence on the surface of both redox and acid sites and by the low-temperature. Silica coated by grafting titanium alkoxide contains a great amount of Lewis acid sites of medium strength as recently shown by Bonelli et al. [37] and this could explain the obtained results. The catalytic site in the initial form (A) is finally restored from the reduced site (E) by the intervention of gaseous oxygen and by water elimination, closing the cycle. A mechanism substantially similar to (3) could be proposed also if we consider that there the initial vanadium site is in the dehydrated form.

According to the proposed mechanism, the presence of water is not detrimental for the formaldehyde production, because, it favorably promote the equilibrium reaction (F), as it has been confirmed by introducing small amounts of water (see Table 2) in the reactor feed obtaining a slight increase in formaldehyde yield (compare runs R3-8-13-18 with R29-30-31-32 of Table 3). A further experimental observation is that CO_2 formation appears significant only at high methanol conversion and this suggests that methanol is not directly involved in the total oxidation. No presence of CO traces has been detected in our experimental conditions. On the basis of the experimentally observed compounds and of their evolution with contact time, the following *rake-type* [30] reaction scheme can be proposed:



(4)

At higher temperatures, very probably, CO_x could also be formed from formaldehyde and a contribution of this route to the reaction scheme (4) would be considered although we think that oxidation reactions would follow the progressive steps methanol-aldheyde-acid-CO_x, for this reason we considered adsorbed formic acid the main source of CO_2.

According to the scheme (4), the adsorbed forms of methanol, formaldehyde and formic acid give place, through desorptive reactions, to all the observed products. In particular, methyl formate and dimethoxymethane are formed by reaction between an adsorbed oxidized species and unreacted methanol from gas-phase. In this way, the formation of both the products mentioned is predominant at low conversion when methanol partial pressure is still relatively high. On the contrary, when methanol is almost completely converted, the expected predominant products are formaldehyde, methyl formate (from Tischencko pathway between surface adsorbed methanol and gaseous formaldehyde) and carbon dioxide.

A comprehensive interpretation of the reaction scheme (4) in terms of elementary steps would involve too many parameters of difficult experimental evaluation. Thus, we adopted a simplified overall reaction scheme that takes into account all the products observed, represented as follows:

$$\begin{array}{ll} (5.1) & 3CH_3OH + 1/2O_2 \xrightarrow{k_1} CH_2(OCH_3)_2 + H_2O \\ (5.2) & CH_2(OCH_3)_2 + H_2O \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} 2CH_3OH + HCHO \\ (5.3) & CH_3OH + 3/2O_2 \xrightarrow{k_3} CO_2 + 2H_2O \\ (5.4) & CH_3OH + HCHO + 1/2O_2 \xrightarrow{k_4} HCOOCH_3 + H_2O \end{array} \qquad (5)$$

It must be pointed out that, even if the tendencies of formaldehyde to form CO_x is higher than that of methanol, in the reaction scheme (5) the route for CO_2 formation starts from methanol. This approximation has been introduced by considering that in the detailed reaction scheme (4) the actual CO_2 formation is due to formic acid in an adsorbed form which, in turn, comes from a formaldehyde surface specie that, ultimately, derives from methanol. This complex route has been lumped into the reaction (5.3). Furthermore, in our development, the CO_x has been identified with CO_2 because the presence of CO has not been detected.

On the basis of this approximation, only five kinetic parameters are necessary to completely describe an isothermal run. By adopting the standard form of material balance equation, related to a tubular packed bed reactor (plug flow, absence of diffusion resistances), for each component j present in the gas-phase:

$$-\frac{dF_J}{dW} = \sum_{i=1}^{N_r} \upsilon_{J,i}(-r_i) \qquad (6)$$

where F_j is the molar flow rate of the component j, W is the total amount of catalyst loaded in the reactor, $\upsilon_{j,i}$ is the stoichiometric coefficient of the component j in the reaction i and r_i is the ith reaction rate. In order to integrate the ordinary differential equations system (6) we have to introduce the expression for the reaction rates r_i. By assuming for the redox reactions occurring on the surface a Mars and van Krevelen mechanism [20], corrected, as suggested by Carrà and Forzatti [39], for the depressive effect that could be exerted by water and methanol, both adsorbing on the redox catalytic sites, we can write:

$$A + \text{Site-OX} \rightarrow \text{Product} + \text{Site-RED}$$

$$\text{Site-RED} + 1/2O_2 \rightarrow \text{Site-OX}$$

By assuming steady state conditions and considering that $\theta_{ox} + \theta_{red} + \theta_{occ} = 1$ the following general expression can be obtained:

$$r_i = \frac{k_i P_i}{1 + (k_i P)/(k_{ox} P_{O_2}^{0.5})} \times (1 - \theta_{occ})$$

By applying the general expression to each redox reaction, by assuming the surface oxidation as rate determining step and a depressive effect due to the adsorption of water and methanol on the redox sites we obtain:

$$r_1 = \frac{k_1 P_M}{1 + (k_1 P_M)/(k_{ox} P_{O_2}^{0.5})} \times \frac{1}{1 + b_M P_M + b_W P_W} \qquad (7)$$

$$r_3 = \frac{k_3 P_\mathrm{M}}{1 + (k_3 P_\mathrm{M})/(k_\mathrm{ox} P_{\mathrm{O}_2}^{0.5})} \times \frac{1}{1 + b_\mathrm{M} P_\mathrm{M} + b_\mathrm{W} P_\mathrm{W}} \qquad (8)$$

$$r_4 = \frac{k_4 P_\mathrm{M} P_\mathrm{F}}{1 + (k_4 P_\mathrm{M})/(k_\mathrm{ox} P_{\mathrm{O}_2}^{0.5})} \times \frac{1}{1 + b_\mathrm{M} P_\mathrm{M} + b_\mathrm{W} P_\mathrm{W}} \qquad (9)$$

The equilibrium reaction of DMM hydrolysis has been considered as a first approach occurring with a kinetic law of the type:

$$r_2 = k_2 P_\mathrm{A} P_\mathrm{W} - \frac{k_2}{K_\mathrm{eq}} P_\mathrm{M}^2 P_\mathrm{F} \qquad (10)$$

derived from the assumption of a two steps equilibrium involving also hemiacetal as intermediate.In the relations (7–10), *P* are the partial pressures, *k* are the kinetic parameters and *b* are the adsorption parameters. As mentioned, r_1, r_3 and r_4 are a combination of the Mars–van Krevelen and Langmuir Hinshelwood models (MVK-LH), but assuming that the re-oxidation of the catalytic sites occurs, in the three cases, with the same rate (one only parameter) and that only methanol and water compete for the adsorption on the redox catalytic sites. Obviously, other kinetic models could fit well the experimental runs but the adopted one is compatible with the postulated reaction scheme and mechanism.

The kinetic parameters in the expressions (7–10) have been determined by non-linear regression for the fitting of all the experimental data and have been correlated with temperature by means of the Arrhenius equation.

In Fig. 1, the results of conversion and yield to formaldehyde are reported as a function of contact time for all the temperature range investigated, in comparison with model prediction. In Fig. 2 is reported, as example, the agreement between the experimental products distribution, obtained for the set of runs R2-7-12-17, and the kinetic model. As an overall model agreement with respect to the experimental data, in Fig. 3 the parity plots are reported for both methanol conversion and formaldehyde yield. As can be seen, the adopted model, even if simplified, resulted in a satisfactory performance in the description of the experimental observations collected. The agreement between the experimental data and the adopted simplified model represents an element supporting the validity of the proposed reaction scheme. This is a necessary condition, even if not sufficient, and other models could have similar performances in describing the experimental observations. The values of the kinetic and adsorption parameters, employed in the model, are reported in Table 4 while in Fig. 4 the main kinetic parameters are plotted against the reciprocal of the absolute temperature in the Arrhenius plot. From this plot, an evaluation of activation energies for formaldehyde and

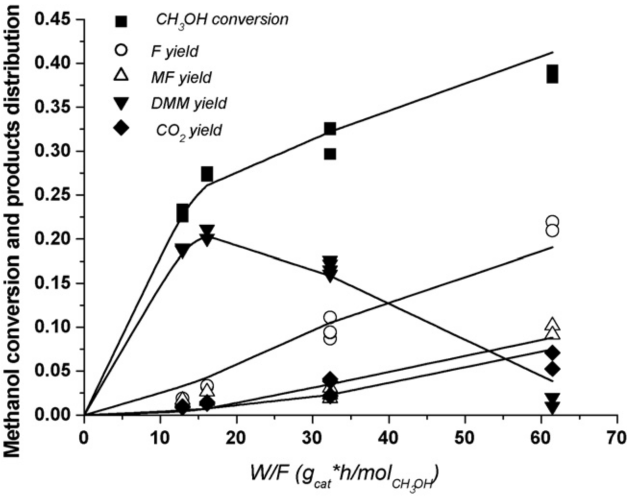


Fig. 2. Agreement between model behavior and experimental data of methanol conversion and products distribution as a function of methanol contact time W/F. Run R2-R7-R12-R17 at 160 °C. Legend: F – formaldehyde, MF – methyl formate, DMM – dimethoxymethane.

Table 4
Kinetic parameters

Constant	ln(*A*) or ln(b_0)	E_A or Δ*H* (kcal/mol)
k_1	23.9 ± 2.6	20.4 ± 2.3
k_2	20.6 ± 1.1	11.1 ± 1.0
k_3	15.6 ± 4.8	14.8 ± 4.2
k_4	39.0 ± 3.2	27.8 ± 2.8
k_ox	24.3 ± 3.8	19.0 ± 3.4
b_M	−28.8 ± 4.9	−28.9 ± 4.3
b_W	−23.2 ± 8.9	−25.3 ± 7.9

$k_\mathrm{i} = A\exp(-E_\mathrm{A}/RT)$ i = 1, 2, 3, 4, OX. $b_j = b_0\exp(-\Delta H/RT)$ j = M, W. $K_\mathrm{eq} = \exp(17.5 - 7548/T)$ experimental. $K_\mathrm{eq} = \exp(13.7 - 6090/T)$ from thermodynamic calculations.

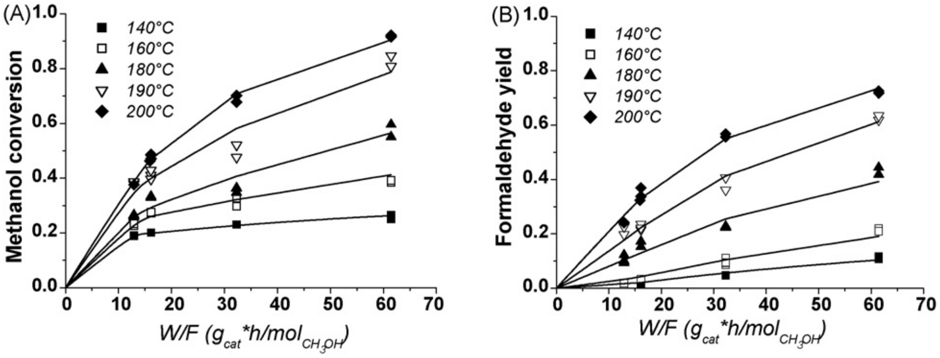


Fig. 1. Kinetic results at various reaction temperatures: comparison between kinetic model (continuous lines) and experimental data for (A) methanol conversion as a function of methanol contact time W/F and (B) formaldehyde yield as a function of methanol contact time W/F.

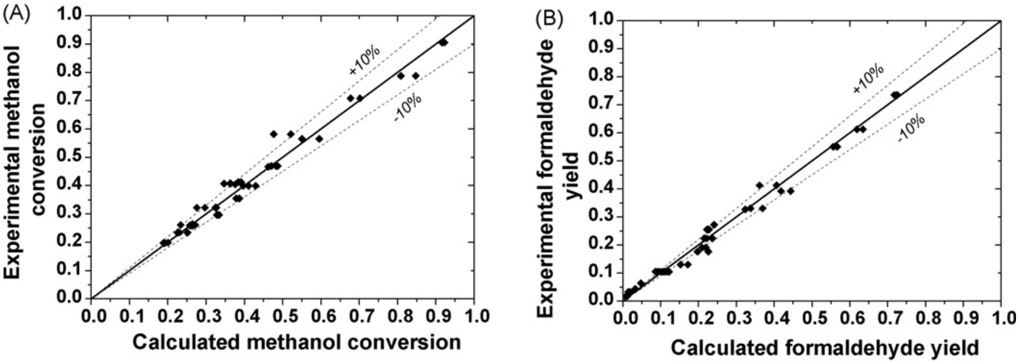


Fig. 3. Parity plots for (A) methanol conversion and (B) formaldehyde yield related to all the data collected. The absolute deviations of ±10% between model and experimental data (dotted lines), are also reported.

dimethoxymethane formation was possible and values of 20.4 and 11.1 kcal/mole, respectively, were obtained. These values are in agreement with those reported in the literature [30] in the range 10–20 kcal/mole for methanol ODH on supported and unsupported oxide catalysts. The equilibrium constant in Eq. (8), whose value is reported in Table 4, is in rather good agreement with the value obtained from thermodynamic calculations.

The values of the adsorption parameters for both methanol and water seem to indicate that adsorption effect is rather strong, although no discrimination between methanol and water was possible because both these components showed a similar behavior and no one can be neglected with respect to the other.

As mentioned above, the effect of the presence of water in the feed has no negative influence on catalytic activity, despite it seems to adsorb on the catalyst surface in competition with methanol. This behavior supports the proposed mechanism and reactions scheme in which water, at least in the explored concentration range, promotes the equilibrium reaction (5.2).

The effect of methanol/oxygen feed molar ratio was also investigated and a general increase of conversion and yield were observed by decreasing this ratio, in particular at high contact time. In other words, the oxygen partial pressure seems to have a positive effect on methanol conversion, probably due to the increased efficiency in the catalytic site re-oxidation. This phenomenon has also been observed by other authors [30], according to which iron-molybdate catalysts seem to become less active in the presence of an excess of methanol.

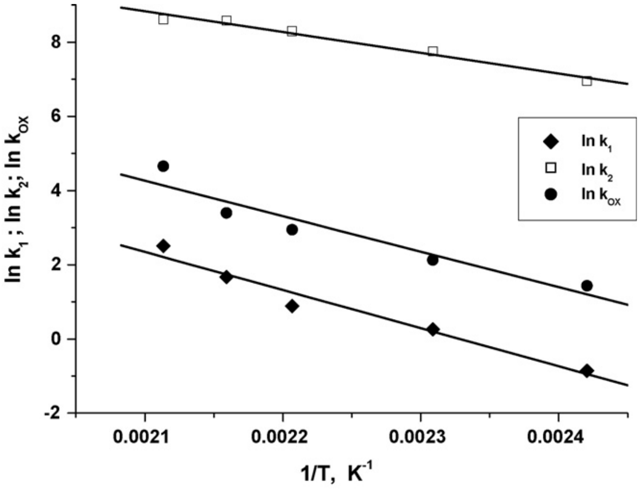


Fig. 4. Arrhenius plot for the kinetic constants k_1 (dimethoxymethane formation), k_2 (formaldehyde formation) and k_{ox} (catalytic site re-oxidation).

At last, it is interesting to point out that the adopted kinetic model well reproduce also some apparently strange results appearing in Table 3 such as the very small increase of methanol conversion (from 19 to 25%) for a large change in the contact time (from 12.91 to 61.4) corresponding to a very strong change in the selectivities passing from a large preminence of DMM to the one of formaldehyde. This behaviour can be explained considering a very low rate of DMM hydrolysis at low-temperature.

4. Conclusions

The kinetics of the ODH of methanol to formaldehyde on vanadium-based grafting catalysts has been extensively investigated. The effect of various operative conditions (temperature, contact time, feed composition) has been studied and a detailed kinetic model has been developed to interpret the collected integral data of a tubular packed bed reactor. A simplified kinetic model was formulated on the basis of a reaction mechanism that led us to a rake-type reaction scheme in which all the observed products derive from adsorbed species of methanol, formaldehyde and formic acid. The agreement between the model and the experimental data, in the range of operating conditions adopted, can be considered satisfactory and worth to be deepened in the perspective of an industrial development.

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