Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 100 (2005) 441–445

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective oxidation of methanol to formaldehyde over V–Mg–O catalysts

G.V. Isaguliants [*], I.P. Belomestnykh

N.D. Zelinsky Institute of Organic Chemistry (Russian Academy of Sciences), 47, Leninsky Prosp., Moscow 117913, Russia

---

Abstract

The results of a complex investigation of V–Mg–O catalysts for oxidative dehydrogenation (ODH) of methanol are presented. The efficiency of vanadium–magnesium oxide catalysts in production of formaldehyde has been evaluated. Strong dependence of the formaldehyde yield and selectivity upon vanadium oxide loading and the conditions of heat treatment of the catalyst were observed. The parameters of the preparation mode for the efficient catalyst were identified. In optimised reaction conditions the V–Mg–O catalysts at the temperature approximate 450 °C ensured the formation of formaldehyde with the yield of 94% at the selectivity of 97%.

No visible changes in the performance of the catalyst (methanol conversion, formaldehyde yield and selectivity) were detected during the 60 h of operation in prolonged runs. Characterization of the catalyst by XRD, IR, and UV methods suggests the formation of species of the pyrovanadate type ($Mg_2V_2O_7$) with irregular structure on the surface of a V–Mg–O catalyst. These species make the catalyst efficient for methanol ODH.

Keywords: Oxidative dehydrogenation; V–Mg–O catalysts; Methanol; Formaldehyde

---

1. Introduction

Highly reactive carbonyl compounds (aldehydes and ketones) are widely used in organic synthesis and chemical industry. Some of them are applied as intermediates in the production of drugs, dyes, photographic materials, amide fibres and other fine chemicals. The main methods for their production are dehydrogenation and oxidative dehydrogenation of alcohols. Catalysts for these processes are, therefore, of great interest [1,2].

Oxidative dehydrogenation (ODH) of methanol to formaldehyde is a very important process for the modern chemical industry. Although several catalysts for the process had been already developed, considerable efforts are made to improve them or elaborate novel catalysts. Using silver catalysts, it is possible to reach a selectivity of 90% towards formaldehyde at the almost complete conversion of methanol at the temperatures around 600 °C [3]. The catalysts based on $Fe_2(MoO_4)_3$–MoO_3 has found industrial application for ODH of methanol to formaldehyde at considerably lower temperature in flow-circulation system [4,5]. However, its thermal and mechanical stability necessitates further improvement [5]. Recently, catalysts for methanol ODH based on Sn and Mo oxides were developed [6]. Even at 210 °C, the catalysts showed a conversion of 64%, although selectivity to formaldehyde was moderate (21%).

In our recent investigations the V–Mg–O system proved to be active and selective in ODH of alkylaromatic hydrocarbons [7] and certain alcohols [1,2] but we have not found data on ODH of methanol to formaldehyde over this catalyst system.

In the present work, we present a study describing performance of V–Mg–O catalysts in ODH of methanol to formaldehyde. The composition, thermal treatment conditions of the catalyst, and the conditions of ODH reaction have been varied in wide ranges to obtain data for optimisation of the catalyst preparation and the process variables. Characterization of V–Mg–O catalysts by DTA, XRD, IR, and UV methods has been used for identification of the structure of the optimal catalyst that

---

[*] Corresponding author.
E-mail address: gvi@ioc.ac.ru (G.V. Isaguliants).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.10.029

provides high activity and selective in the production of formaldehyde.

2. Experimental

2.1. Catalyst preparation

The MgO powder was suspended in an aqueous solution of ammonium vanadate at 40–60 °C under stirring. The obtained material was evaporated at 60 °C by using a rotary evaporator, and dried in air at 120 °C. The further treatment was performed in air flow by the stepwise temperature increase keeping the sample for 1 h at 260, 360, 400, 500 °C, and for 3–4 h at the terminal thermal treatment temperature. The latter varied from 550 to 850 °C. The powder formed was pressed into tablets and crushed into pieces of a required size before using.

2.2. Catalyst characterization

BET surface areas were determined by N_2 physisorption at the temperature of liquid nitrogen.

X-ray diffraction was investigated using a Guinier-Hagg focusing camera Fr-552 and automatic powder X-ray diffractometer “STADI-P” with imaging plate (Cu Kα radiation, 2θ range was from 7 to 60).

DTA-DTG analysis was performed in the air flow at the temperature range of 20–1000 °C using MDTA 85 SETARAM apparatus. The heating rate was of 5 °C/min.

IR spectra were recorded by a “Specord 75IR” instrument using the mineral oil disc technique and calibrated amounts of the samples (5 wt.%) in the region 4000–200 cm^{-1}. The spectra were recorded in air using a 2 cm^{-1} resolution.

2.3. Catalyst testing

The performance of catalysts in the ODH of methanol to formaldehyde was carried out in a fixed-bed quartz flow reactor under atmospheric pressure. The catalyst samples of 0.5–1.0 mm in diameter were diluted with quartz of a grain size equal to 1–1.5 mm in the volume ratio of 1:2. Parameters of the reaction were varied in a broad range. The reaction was performed for methanol–air mixture in a temperature interval of 250–450 °C. The reactor temperature was measured and controlled by a PID controller with a coaxial thermocouple. The reactants and reaction products were analysed by gas chromatography: a column filled with Porapak Q (80–100 mesh) was used for the analysis of methanol, formaldehyde, other oxygenates, CO_2, and, O_2, and a column filled with molecular sieve 5A, for the analysis of CO, CH_4, O_2, and CO_2.

3. Results and discussion

The primary testing of V–Mg–O catalysts has revealed that the ODH of methanol proceeds selectively in a temperature range between 250 and 450 °C, and the major reaction product being formaldehyde. No reaction products other than HCHO, CO_2, H_2O were detected.

We had found previously for the ODH of hydrocarbons that the activity and selectivity of V–Mg–O catalysts depend significantly on the vanadium loading and the conditions of thermal treatment of the sample [7]. A series of catalysts has been prepared to investigate the influence of both factors on the ODH of methanol, and to identify the optimal catalyst content and thermal treating temperature. The vanadium loading varied from 5 to 25%, the temperature of thermal treatment, from 550 to 850 °C. The results are presented in Table 1.

With increasing the V_2O_5 content in samples treated at 550 °C the conversion of methanol passes a maximum at 12%. The selectivity to formaldehyde shows a slight decrease. As a result, the dependence of the formaldehyde yield has a clear peak at the vanadium pentoxide loading of 12%. The conditions of the catalyst thermal treatment have a dramatic effect on their performance in the ODH of methanol. Increase of the temperature of thermal treatment from 550 to 850 °C induces a drastic decrease of both methanol conversion and selectivity to formaldehyde. As a result, in the mentioned interval of thermal treatment temperature the yield of formaldehyde decreases 3.5-fold. Thus, an extreme dependence was observed of the catalyst activity for the ODH of methanol and the selectivity to formaldehyde on vanadium pentoxide loading and on the conditions of thermal treatment. The catalysts, that exhibit a maximum formaldehyde yield and selectivity, were obtained in optimal conditions, i.e. at the V_2O_5

Table 1
Effect of V_2O_5 loading and heat treatment temperature of the catalyst on ODH of methanol (370 °C, LHSV of 1.5 h^{-1}, CH_3OH/O_2 = 1/1)

Catalyst sample	V_2O_5 content (%)	Heat treatment (°C)	BET area (m^2/g)	CH_3OH conversion	Formaldehyde (%)	
					Yield	Selectivity
5–550	5.0	550	98	29.8	26.0	87.0
12–550	12.0	550	105	74.2	72.0	97.0
25–550	25.0	550	70	40.0	28.0	70.0
12–550	12.0	550	105	74.2	72.0	97.0
12–750	12.0	750	60	37.4	30.0	79.0
12–850	12.0	850	50	29.4	20.0	68.0

content of 12 wt.% and the thermal treatment temperature of 550 °C.

DTA-DTG analysis has been used to monitor the changes occurring in the course of the thermal treatment of the catalyst. Investigation was carried out in the temperature range of 20–1000 °C. Endoeffects at 225, 255, 360 °C were observed when a catalyst dried at 120 °C was gradually heated up to 400 °C. These effects followed by a weight loss reflected the elimination of water and ammonia. The absence of exoeffects allows one to conclude that in the mentioned temperature range heating of MgO impregnated by NH_4VO_3 generate no additional substances.

Further increase of the temperature induced exoeffects at 408, 655, and 775 °C that were not followed by a weight loss. These are believed to reflect interactions between the active component and the support. The exoeffect at 408 °C is more pronounced for the samples with a V_2O_5 loading of 12%. In contrast, the exoeffects at 655 and 775 °C are pronounced for the samples with vanadium loading of 25%. The interaction was apparently completed before the temperature reached 800 °C, resulting in the formation of different magnesium vanadates. To interpret the nature of the vanadates the samples were subjected to the XRD, IRS and UVS investigation.

The X-ray diffraction pattern for catalysts containing 12% V_2O_5 and calcined at 550 °C is given in Fig. 1. Besides the dominating diffraction lines of MgO ($2\theta = 45, 65$) the spectrum revealed the diffraction lines of $2\theta = 18.9, 28.2$, attributed to α-$Mg_2V_2O_7$ (ASTM file 31-816), and weak lines of $2\theta = 20.69, 26.2, 26.31, 31.06, 53$, and 66 attributed to α-$Mg_3V_2O_8$ (ASTM file 37-351). For the catalyst with the V_2O_5 content of 25% treated at 850 °C (Fig. 2), lines attributed to α-$Mg_2V_2O_7$ ($2\theta = 18.9, 28.2$) became very weak (traces), whereas lines of $2\theta = 20.69, 26.2, 26.31, 31.06, 53$, and 66 (attributed to α-$Mg_3V_2O_8$) became more pronounced. In this connection, it is interesting to note that according to [10] the formation of $Mg_2V_2O_7$ can occur at about 410 °C, whereas the formation of $Mg_3V_2O_8$ necessitate heating to 600–800 °C.

To obtain additional information and to verify the XRD data several samples were subjected for investigation by IR-, UV-spectroscopy. Spectroscopy results were considered together with the ^{51}V NMR data obtained previously.

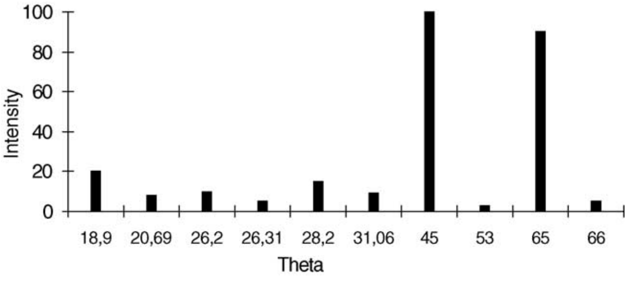

Fig. 1. X-ray diagram of V–Mg–O catalyst (V_2O_5 content of 12%, thermal treatment at 550 °C).

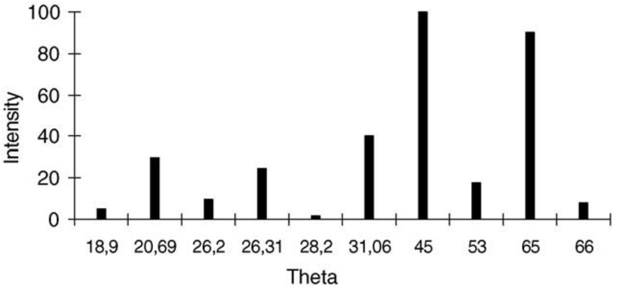

Fig. 2. X-ray diagram of V–Mg–O catalyst (V_2O_5 content of 25%, thermal treatment at 850 °C).

The IR spectrum of a fresh V–MgO catalyst dried at 120 °C with a V_2O_5 content of 12% shows the bands at 820, 860 and 960 cm^{-1}. After the thermal treatment of the sample at 550 °C, the band at 960 becomes more intense, and there appeared novel bands at 330, 360, 440, 570, and a broad band appeared in the range of 400–540 cm^{-1}. The band at 960 cm^{-1} is attributed to the V=O bond in the disturbed octahedron characteristic for $Mg_2V_2O_7$. The band at 860 cm^{-1} is attributed to the V–O–V bond in the orthovanadate ($Mg_3V_2O_8$) with VO_4^{3-} ions in the tetrahedral environment. The bands at 680 and 540 cm^{-1} can be attributed either to V–O–V bond, or to the V^{5+} ions in the octahedral environment [8,10]. The broad band at 400–540 cm^{-1} can be attributed to MgO.

The IR spectrum of V–Mg–O catalyst with the V_2O_5 content of 25% shows a broad band in the range 860 cm^{-1}, 1020–1050 cm^{-1} .The band at 860 cm^{-1} is attributed to the V–O–V bond in the orthovanadate ($Mg_3V_2O_8$) with the VO_4^{3-} ions in tetrahedral environment. The IR spectroscopic data are in good agreement with those obtained by X-ray diffraction.

The UV spectrum of V–Mg–O catalyst with a V_2O_5 content of 12% and treated at 550 °C revealed that this catalyst contained V^{5+} ions in the octahedral and tetrahedral coordination: V_{Oh}^{5+} (320 nm intense), V_{Oh}^{4+} (600 nm intense), V_{Sq}^{4+} (340–360 nm), V_{Td}^{4+} (800–880 nm, weak). Apparently, they belong to associated vanadium species of the magnesium pyrovanadate, containing the vanadium ions in octahedral coordination. The increase of the content of V_2O_5 to 25% and the thermal treatment at 850 °C results in the formation of magnesium orthovanadate $Mg_3V_2O_8$ containing the vanadium ions in the tetrahedral coordination: V_{Td}^{4+} (800–880 nm, intense) V_{Td}^{5+} (280 nm weak).

We have prepared similar V–Mg–O catalysts, in our investigation of ODH of butene [13]. These catalysts were studied with the use of ^{51}V NMR. The existence of a large number of vanadium coordination states on the catalyst surface was established. Their relative concentrations are determined by the surface concentration of vanadium. The isolated tetrahedral and octahedral vanadium species appear at low vanadium content (5% V_2O_5). Apparently, these species are responsible for complete oxidation [13]. At the V_2O_5 loading of 12%, associated vanadium forms

Table 2
Effect of temperature on the OD of methanol (LHSV of 1.5 h^{-1}, $CH_3OH/O_2 = 1/1$)

Temperature (°C)	Methanol conversion (%)	Formaldehyde selectivity (%)	Formaldehyde yield (%)
250	20.0	99.8	19.9
300	30.0	99.1	29.7
320	45.0	98.2	44.2
350	52.6	97.8	51.4
370	74.0	97.1	72.3
420	94.0	97.0	91.2
450	95.0	97.0	94.0

predominate. In these associated species, vanadium may exist in both octahedral and tetrahedral environment. We suggest the associated species favour the ODR of ethylbenzene to styrene [7]. At higher vanadium loading (25% V_2O_5) the phase of magnesium ortho-vanadate $Mg_3V_2O_8$ predominates that apparently does not favour the selective ODH of ethylbenzene [7,13].

The results of XRD, UV, and IR spectroscopy, and of ^{51}V NMR demonstrate that catalyst with a V_2O_5 content of 12% and treated at 550 °C favour the predominant formation of magnesium vanadates with irregular structure, apparently of the pyrovanadate type ($Mg_2V_2O_7$) with vanadium ions V^{5+} and V^{4+} in the octahedral and tetrahedral coordination. They exhibit high activity in the process of the oxidative dehydrogenation of methanol. Recently, similar conclusion was drawn for the ODH of ethanol over V–Mg–O catalyst [15].

In contrast, V_2O_5 content of 25% and the thermal treatment temperature of 800 °C lead to the predominant formation of regular structures of the orthovanadate type ($Mg_3V_2O_8$) [7,13] with V^{4+} ions in the coordination of distorted tetrahedron that are not efficient for the ODH of methanol. Such catalysts are preferable for the ODH of alkanes [8–16].

It turns out that the ODH of methanol and of ethylbenzene [7] requires identical active phase species that ensure high efficiency of the catalyst. These species are suggested to be magnesium vanadates apparently of the pyrovanadate type with an irregular structure, and V-ions in the octahedral coordination. They are predominantly formed when catalysts with 12% V_2O_5 are treated at 550 °C.

The performance of catalysts has been investigated by varying the reaction temperature, space velocity, and methanol/oxygen ratio in the feed to optimise he reaction conditions. The influence of the reaction temperature (250–450 °C), space velocity (0.8–2.5 h^{-1}), and methanol/oxygen ratio (0.5–2.0) on the ODH was investigated. It turned out that the temperature of 420–450 °C, CH_3OH/O_2 molar ratio of 1 in the feed, and LHSV of 1.5 h^{-1} should be considered as optimal ones. It is remarkable, that increasing the reaction temperature from 250 to 450 °C leads to an increase of methanol conversion from 20 to 99–97% (Table 2) while followed by an almost negligible decrease of selectivity to formaldehyde (from 99.6 to 97%).

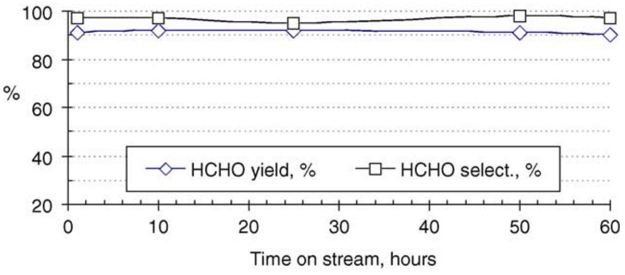

Fig. 3. ODH of methanol over V–Mg–O catalyst (420 °C, LHSV of 1.5 h^{-1}, CH_3OH/O_2 mole ratio of 1/1).

Testing the V–Mg–O catalyst in the prolonged runs has shown (Fig. 3) that it can be used for a long time. After 60 h on stream, the catalyst kept the initial methanol conversion and selectivity towards formaldehyde. The average formaldehyde yield was of 91% at the average selectivity of 97%.

Evaluating the effectiveness of V–Mg–O catalysts for the ODH of methanol one can conclude that the reaction proceeds with high yields and selectivity which are competable with those of industrial catalysts [3].

4. Conclusions

The efficiency of the oxidative dehydrogenation of methanol to formaldehyde over V–Mg oxide catalysts has been characterized.

A dramatic dependence of the catalyst activity and selectivity was observed in the ODH of methanol on vanadium pentoxide content and on the conditions of the thermal treatment.

The V_2O_5 content of 12 wt.% and the thermal treatment temperature of 550 °C were found to be optimal for the ODH of methanol. According to the obtained XRD and UV, IR data these conditions favour the formation of V–Mg–O species of the pyrovanadate type ($Mg_2V_2O_7$) with the irregular structure containing V^{5+} and V^{4+} ions in the octahedral and tetrahedral coordination.

The optimum reaction conditions have been found for production formaldehyde with high yields (95%) and selectivity (99–97%).

Testing the V–Mg–O catalyst revealed that it can be used in prolonged runs. During 60 h of operation the average formaldehyde yield was of 91% at the average selectivity of

97%. No visible decline of methanol conversion was as detected

References

[1] G.V. Isaguliants, I.P. Belomestnykch, Stud. Surf. Sci. Catal. 108 (1996) 415.

[2] G.V. Isaguliants, I.P. Belomestnykch, Catalysis of Organic Reactions, Marcel Dekker Inc., 1998 591.

[3] L. Leferts, J.G. van Ommen, J.R.H. Ross, Appl. Catal. 23 (1986) 385–402.

[4] D. Klyissurski, V. Rives, Y. Pesheva, I. Mitov, N. Abadzhjieva, Catal. Lett. 16 (1993) 265.

[5] D. Klyissurski, Y. Pesheva, N.N. Abadzhjieva, Appl. Catal. 77 (1991) 55–66.

[6] N. Graciela Valente, L.A. Luis, E. Cadus, Appl. Catal. 205 (2001) 201–214.

[7] I.P. Belomestnykh, E.A. Skrigan, G.V. Isaguliants, Stud. Surf. Sci. Catal. 72 (1992) 256.

[8] A. Pantazidis, A. Burrows, C.J. Kiely, C.J. Mirodatos, J. Catal. 177 (1998) 325;
A. Pantazidis, A. Burrows, C.J. Kiely, C.J. Mirodatos, Stud. Surf. Catal. 101 (1996) 1029.

[9] S.R.G. Carrazan, C. Peteres, J.P. Bernard, M. Ruwer, P. Ruiz, B. Delmon, J. Catal. 158 (1996) 452.

[10] D. Siew Hew San, V. Soenen, J.C. Volta, J. Catal. 123 (1990) 413–417.

[11] H.H. Kung, M.C. Kung, Appl. Catal. A Gen. 157 (1997) 105–116.

[12] D. Creaser, B. Andersson, Catal. Lett. 57 (1999) 121–128;
D. Creaser, B. Andersson, Appl. Catal. 141 (1996) 131.

[13] O.B. Lapina, A.V. Simakov, V.M. Mastikhin, J. Mol. Catal. 50 (1989) 55–65.

[14] W. Oganowsky, J. Hanuza, L. Kepinski, W. Mista, M. Maczka, J. Mol. Catal. A 136 (1998) 91;
W. Oganowsky, J. Hanuza, L. Kepinski, W. Mista, M. Maczka, Bull. Pol. Acad. Sci. Chem. 31 (3–7) (1983) 129–138.

[15] M.F. Gomez, A.A. Luis, M.C. Abello, Ind. Eng. Chem. Res. 36 (1997) 3468–3472.

[16] A. Burrows, C.J. Kiely, J. Perregard, P. Hoojlung-Nielsen, G. Vorbeck, J. Calvino, C. Lopez-Cartes, Catal. Lett. 57 (1999) 121–128.