Available online at www.sciencedirect.com

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