



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec1 The role of oxygen species in the selective oxidation of methanol to
2 dimethoxymethane over VO_x/TS-1 catalyst

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ARTICLE INFO

Article history:

Received 14 April 2016
Received in revised form 25 June 2016
Accepted 24 September 2016
Available online xxx

Keywords:

Methanol
Dimethoxymethane
Selective oxidation
Vanadium oxide
Oxygen

ABSTRACT

VO_x-based catalysts showed good performance in selective oxidation of methanol to dimethoxymethane (DMM). For VO_x/TS-1 catalyst, the experiments of Temperature Programmed Surface Reaction (TPSR), *in situ* Infrared spectrometer (*in situ* IR) and X-ray photoelectron spectroscopy (XPS) were carried out to investigate the products distribution of the methanol oxidation reaction and the adsorb-desorption process at active centers. Furthermore, the role of oxygen species during the reaction process over VO_x/TS-1 catalyst and the surface reaction mechanism was explored.

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6 Introduction

7 Q2 Dimethoxymethane (DMM) is an important chemical interme-
8 diate [1]. It has been widely used as an organic synthesis reagent
9 and a diesel fuel additive. It also can be an excellent solvent in
10 pharmaceutical and perfume industries due to its low toxicity
11 [2,3]. One-step selective oxidation of methanol to DMM has
12 attracted much attention for its economical and environmental
13 advantages. Recently, numerous efforts have been made to develop
14 catalysts for selective oxidation of methanol to DMM. Catalysts
15 such as rhenium oxide [4–6], heteropoly acids [7], Cu-ZSM-5 [8],
16 V₂O₅/TiO₂ catalysts [9–15], modified VO_x/TS-1 [16] and V-complex
17 oxides catalysts [17–19] have been reported active for the reaction.

18 VO_x-based catalysts showed good performance in selective
19 oxidation of methanol to dimethoxymethane (DMM). Wachs and
20 Weckhuysen [20] and Kaichev et al. [21] studied the catalytic
21 properties of supported vanadium catalysts, determined the role of
22 Q3 carriers in methanol oxidation. Kropp et al. [22] and Goodrow and
23 Bell [23] investigated the mechanism of methanol oxidation on
24 vanadium oxide catalysts by DFT method. In our previous study
25 [16], bifunctional VO_x/TS-1 catalyst was prepared, in which the TS-
26 1 (2.5 wt% Ti) was chosen for its moderate acidity, high surface area
27 and stability as acidic sites, while the VO_x deposited on the surface
28 of TS-1 served as redox sites. The optimal vanadium loading was

29 20 wt.%. The cascade reaction (oxidation and acetalization) process
30 over VO_x/TS-1 catalyst was as follows: (1) Methanol was adsorbed
31 on the catalyst surface and oxidized to formaldehyde on VO_x redox
32 sites. (2) Formaldehyde and methanol conducted dehydration
33 condensation on the acid sites provided by the carrier TS-1 zeolite
34 to generate DMM. The relationship between the surface nature of
35 the catalyst and the reaction activity has been discussed. However,
36 the in-depth study of the active sites, as well as adsorb-desorption
37 process on the surface of the catalyst is still lacking. The role of
38 oxygen in the oxidation reaction also needs further clarification.

39 In this paper, the experiments of the TPSR and *in situ* IR were
40 carried out to explore the reaction process over VO_x/TS-1 catalyst.
41 The reaction mechanism of the methanol oxidation to synthesis
42 DMM as well as the role of oxygen species in the oxidation reaction
43 was investigated. It may provide further theoretical guidance for
44 the design of high efficient catalyst.

45 To explore the reaction of methanol on VO_x/TS-1 catalyst, the
46 methanol TPSR Experiments were carried out under anaerobic
47 conditions, with He gas as a carrier gas. The results are shown in
48 Fig. 1.

49 From Fig. 1, we can see that the desorption temperature of the
50 methanol and formaldehyde is about 150 °C. At the same time, the
51 reaction also produced a small amount of dimethyl ether, DMM
52 and methyl formate as well. The peaks of DMM are below 200 °C,
53 indicating that lower temperature is required for methanol
54 conversion to DMM.

55 CH₃OH and O₂ TPSR experiments were carried out with the
56 same steps of methanol TPSR, except that the carrier gas for

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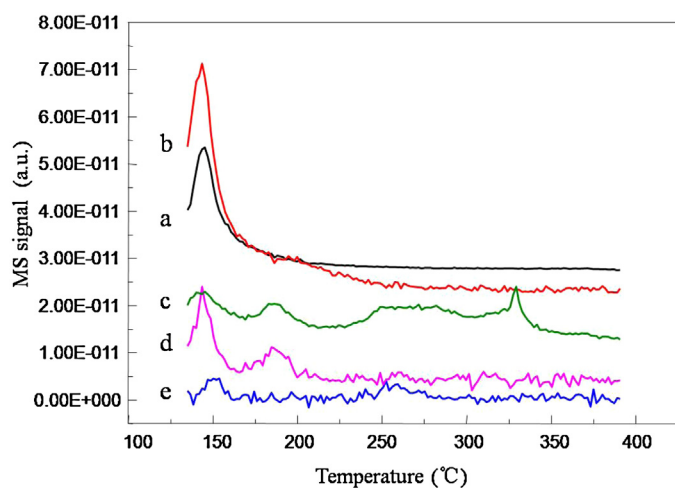


Fig. 1. CH_3OH -TPSR over $\text{VO}_x/\text{TS-1}$ ((a) CH_3OH , (b) FA, (c) DME, (d) DMM, (e) MF).

temperature programmed surface reaction step was 10% vol. O_2/He . The results are shown in Fig. 2.

The products distribution of the reaction is similar as it is under anaerobic conditions. However, the desorption temperature of the methanol and formaldehyde is about 130°C . The decrease of the reaction temperature indicates that the methanol oxidation reaction is more easily performed in the presence of oxygen. There is also a small amount of dimethyl ether, DMM, and methyl formate in products. On the one hand, the desorption peak of DMM is mainly below 200°C , which shows that lower temperature may be suitable for the conversion of methanol to DMM. On the other hand, the formation of dimethyl ether and methyl formate has sudden increase at higher temperatures, indicating that the high temperature may be more suitable for the formation of dimethyl ether and methyl formate in the presence of oxygen. Furthermore, the simultaneous desorption of these species is an indication that they could be originated from the same surface intermediate. It also proves that the methanol oxidation process and dehydration condensation process take place at different active sites.

The IR spectra of methanol adsorption on catalysts under anaerobic conditions, 150°C , were shown in Fig. 3. It reflects not

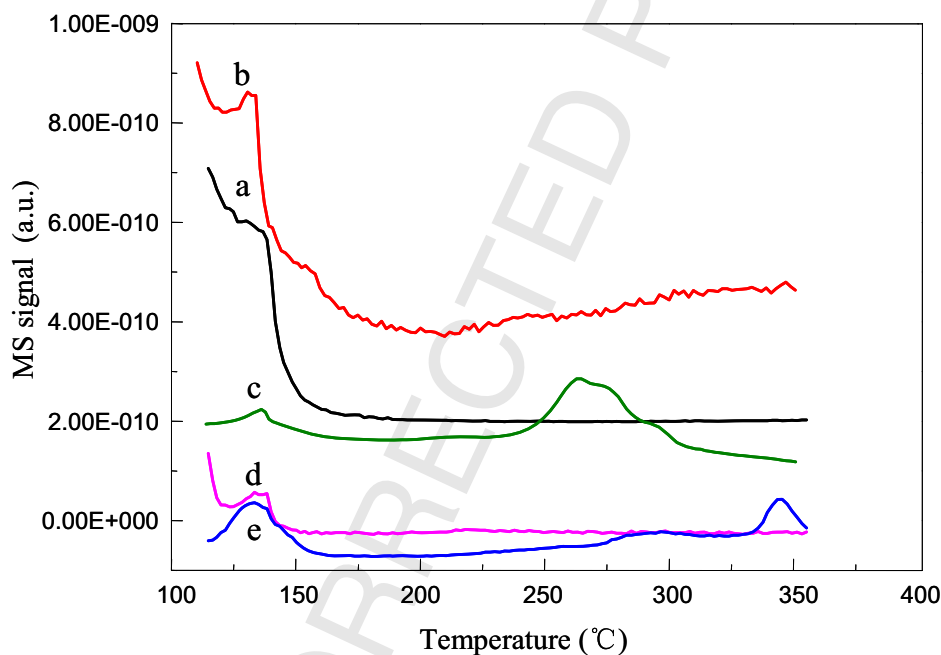


Fig. 2. $\text{CH}_3\text{OH}/\text{O}_2$ -TPSR over $\text{VO}_x/\text{TS-1}$ ((a) CH_3OH , (b) FA, (c) DME, (d) DMM, (e) MF).

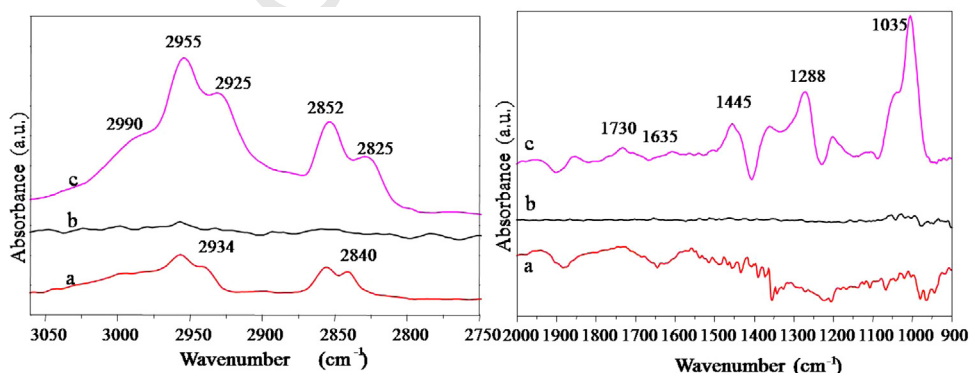


Fig. 3. FT-IR spectra of methanol adsorbed at 150°C at catalysts (a) TS-1, (b) V_2O_5 , (c) $\text{VO}_x/\text{TS-1}$.

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