



## Research on catalytic oxidation of dimethyl ether to dimethoxymethane over MnCl<sub>2</sub> modified heteropolyacid catalysts

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### ABSTRACT

The catalytic oxidation of dimethyl ether (DME) to dimethoxymethane (DMM) was carried out over MnCl<sub>2</sub> modified different heteropolyacid catalysts. Kinds of supports and the catalyst packing structure were investigated. Besides, the possible reaction pathway of DME direct-oxidation to DMM was also discussed. The results showed H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> modified with MnCl<sub>2</sub> exhibited a better catalytic performance than other heteropolyacids. SiO<sub>2</sub> is the better supporting materials than the materials used as support. The synergistic effects of the acid sites offered by H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and the redox sites mainly offered by MnO<sub>2</sub> significantly improve the catalytic activity of the catalyst.

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### 1. Introduction

Dimethoxymethane (DMM, CH<sub>3</sub>OCH<sub>2</sub>OCH<sub>3</sub>) is an important chemical. Because of the high content of oxygen and high cetane number, DMM can improve the thermal efficiency of diesel and reduce the emission of the pollutant when it is used as diesel fuel additive. Therefore, it is considered as a promising diesel fuel additive [1].

At present, DMM is produced in industrial scale via acetalization of methanol with formaldehyde over acidic catalysts [2]. There also exist some other synthesis routes: direct CO hydrogenation from synthesis gas [3] and selective oxidation of methanol [4,5]. The synthesis of DMM from DME (CH<sub>3</sub>OCH<sub>3</sub>) and methanol in a microreactor using H<sub>3+n</sub>V<sub>n</sub>Mo<sub>12-n</sub>PO<sub>40</sub> as the catalyst was reported [6], but the DME conversion is very low.

DME is a potential chemical feedstock like methanol, and also known as a very clean substitute for diesel fuel because of its high cetane number (55–60). It is not easy to directly blend DME with diesel due to the low boiling point of DME (–23.7 °C). In the near future, DME will be produced in industrial scale via one-step synthesis process from syngas. Therefore, using DME as the starting material to synthesize a variety of organic compounds with high value will be as important as using methanol. Direct oxidation of DME to DMM is one of the attractive uti-

lization routes to develop value added downstream products of DME.

In our previous study [7,8], we have carried out some work on the synthesis of DMM via the direct oxidation of DME over Mn modified H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> catalysts.

In the present work, the catalytic performance of different heteropolyacid catalysts, kinds of supports and the catalyst packing structure have been investigated. More importantly, the possible reaction pathway of DME direct-oxidation to DMM has been also discussed.

### 2. Experimental

#### 2.1. Catalyst preparation

MnCl<sub>2</sub> modified heteropolyacid catalysts were prepared by an incipient wetness impregnation method: firstly, an aqueous solution of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (Shanghai Chemical Co.) was impregnated in SiO<sub>2</sub> (Shanghai Chemical Co. 20–40 mesh) at 298 K for 4 h, then was dried in ambient air at 393 K for 12 h, after that, it was calcined for 4 h at 673 K; secondly, an aqueous solution of MnCl<sub>2</sub> (Tianjin Chemical Co.) was added to the above calcined sample, then dried and calcined as the same conditions as the above. Thus, MnCl<sub>2</sub>(5 wt%)-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub>, MnCl<sub>2</sub>-(5 wt%)-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub> or MnCl<sub>2</sub>(5 wt%)-H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>-(40 wt%)/SiO<sub>2</sub> was prepared. Besides, when other supports were used instead of SiO<sub>2</sub>, the modified catalysts were denoted as

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MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/TiO<sub>2</sub>, MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/Al<sub>2</sub>O<sub>3</sub>, MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>, MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/NaY and MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/La<sub>2</sub>O<sub>3</sub>.

## 2.2. Catalytic oxidation of dimethyl ether

The catalytic oxidation reactions were carried out in a continuous flow type fixed-bed reactor. The catalyst (4.8–5.0 g, 20–40 mesh) was diluted with ground quartz in order to prevent overheating of the catalyst due to the exothermic reaction. The catalyst was treated in flow of O<sub>2</sub> (15 ml/min) for 1 h before reaction. The reactant mixture consisted of DME and O<sub>2</sub> with ratio of  $n_{\text{DME}}/n_{\text{O}_2} = 1:1$ . The outlet stream line from the reactor to the gas chromatograph was heated at 423 K. The reaction products were analyzed by on-line gas chromatography (GC-9A) equipped with Porapak T column and thermal conductivity detectors. The carbon balances of the experiments are within the range of 95–99%.

## 2.3. Catalyst characterization

Surface areas of the samples were measured by a BET nitrogen adsorption method at 77.35 K using a TriStar 3000 machine.

X-ray diffraction (XRD) patterns were measured on a Bruker Advanced X-ray Solutions/D8-Advance using Cu K $\alpha$  radiation. The anode was operated at 40 kV and 40 mA. The 2 $\theta$  angles were scanned from 5° to 70°.

The ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) spectra were recorded in a fixed-bed reactor system equipped with a gas chromatograph. The catalyst (100 mg) was pretreated at 773 K under Ar flow (40 ml/min) for 2 h and then cooled down to 373 K under Ar flow. Then NH<sub>3</sub> was introduced into the flow system. The TPD spectra were recorded at a temperature rising rate of 10 K/min from 373 to 1273 K.

## 3. Results and discussion

### 3.1. Catalytic oxidation of DME over different heteropolyacid catalysts

Table 1 shows DME conversion and DMM selectivity over different heteropolyacid catalysts. H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub> catalyst is highly active for DME oxidation with DME conversion of 94.9%, but the targeted-product DMM is not detected. In general, as for the acidity, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> > H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> ~ H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, but H<sub>3</sub>-PMo<sub>12</sub>O<sub>40</sub> takes on much stronger oxidizability than H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Therefore, DME strongly absorbs on the surface of the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub> catalyst and is easily oxidized to CO. The H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub> catalyst gives a little higher selectivity for DMM and a lower DME conversion than H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>(40 wt%)/SiO<sub>2</sub>. Compared to MnCl<sub>2</sub>-H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> and MnCl<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub>, MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> markedly achieves much higher selectivity to DMM (39.1%) and lower CO<sub>x</sub> selectivity (6.6%). Due to the different acidity and oxidizability, the heteropolyacids have distinctive effects on the DME oxidation reaction.

Strong acidity of the catalyst easily results in the deep oxidation of DME. For MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub>, its acidity is weaker than MnCl<sub>2</sub>-H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> and MnCl<sub>2</sub>-H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub>, which can be found in Fig. 1 (NH<sub>3</sub>-TPD spectra). Evidently, the synergistic effects of MnCl<sub>2</sub> and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> greatly promotes DMM synthesis from the direct oxidation of DME.

### 3.2. Effects of different supports on MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> catalyst

DME conversion, product selectivity over MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> supported on different supports are shown in Table 2. Comparatively, it is very evident that SiO<sub>2</sub> as support demonstrates excellent catalytic performance, because SiO<sub>2</sub> with high surface area can help to highly disperse MnCl<sub>2</sub>-H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and distribute more active sites on itself, besides, it has also good thermostability and high oxidation activity. When NaY is used as support, the catalyst only gives DMM selectivity as low as 1.6%. Due to its strong acidity of NaY, DME absorbs on the surface of the catalyst and is mainly deep-oxidized to CO<sub>x</sub>, which results in lower DMM selectivity, although the catalyst has higher BET surface area of 294.9 m<sup>2</sup>/g. When TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> are used as acidic supports instead of much weaker acidic support of ZrO<sub>2</sub>, higher DMM selectivity is obtained at 24.7%, 24.1%, although the surface area of the sample supported on TiO<sub>2</sub> is only 7.8 m<sup>2</sup>/g, it is reported that TiO<sub>2</sub> has weak acidity and better catalytic activity [9]. The La<sub>2</sub>O<sub>3</sub> supported catalyst does not show DMM selectivity, and La<sub>2</sub>O<sub>3</sub> is very easy to react with the heteropolyacid, and this leads to the decrease of acidic sites and the change of Keggin structure of heteropolyacid (XRD patterns of catalysts can be found in Fig. 2).

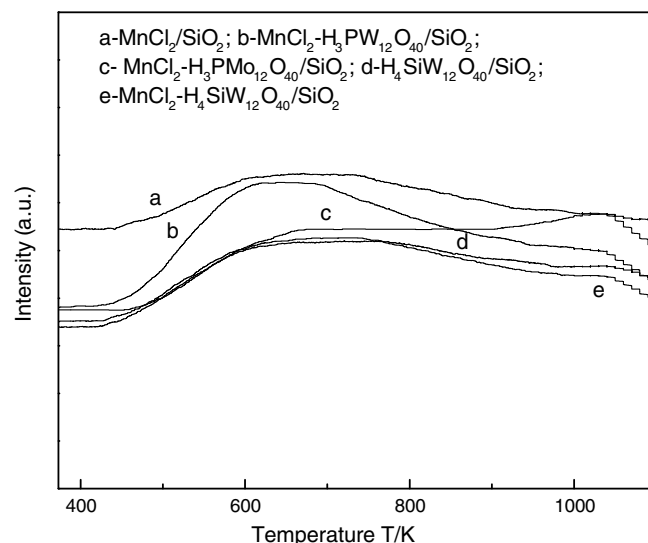


Fig. 1. NH<sub>3</sub>-TPD spectra of different modified heteropolyacid catalysts.

Table 1

DME oxidation catalyzed over different heteropolyacid catalysts

Catalyst	DME conversion (%)	Selectivity (mol%)							
		DMM	HCHO	MF	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>4</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (40 wt%)/SiO <sub>2</sub>	55.7	2.9	5.4	5.3	19.3	0.5	45.7	17.2	3.8
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> (40 wt%)/SiO <sub>2</sub>	94.9	0	3.0	2.6	5.4	0.1	79.2	6.5	2.6
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> (40 wt%)/SiO <sub>2</sub>	21.5	5.5	8.5	6.1	41.8	1.9	28.9	6.3	0.9
MnCl <sub>2</sub> (5 wt%)-H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	8.6	39.1	8.5	9.3	33.0	3.6	3.2	3.4	0
MnCl <sub>2</sub> (5 wt%)-H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	52.0	0	7.8	5.2	10.5	0.7	36.6	36.6	2.6
MnCl <sub>2</sub> (5 wt%)-H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /SiO <sub>2</sub>	14.9	12.0	15.2	9.6	28.9	0.9	17.2	16.2	0

Reaction conditions: T = 593 K, atmospheric pressure, SV = 360 h<sup>-1</sup>, t = 30 min.

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