

Selective oxidation of methanol to dimethoxymethane under mild conditions over V_2O_5/TiO_2 with enhanced surface acidity†

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Dimethoxymethane was synthesized from the direct oxidation of methanol with high conversion and selectivity over specially designed bifunctional V_2O_5/TiO_2 catalysts with redox and enhanced acidic character, in which the surface acidity played an essential role for inhibiting the formation of formaldehyde through the enhanced condensation reaction of formaldehyde with methanol to produce dimethoxymethane.

Dimethoxymethane (DMM) or methylal has an extremely low toxicity and can be used as an excellent solvent in pharmaceutical and perfume industries, a reagent in organic synthesis¹ and an intermediate for the production of concentrated formaldehyde.² Recently, we found that DMM could be effectively reformed to produce H_2 for fuel cells.³ DMM is usually produced by condensation of formaldehyde with methanol over acidic catalysts.⁴ It can also be synthesized by the direct oxidation of methanol on crystalline $SbRe_2O_6$,⁵ $Re/\gamma-Fe_2O_3$,⁶ heteropolyacid,⁷ RuO_x/SiO_2 ,⁸ and $Cu-ZSM-5$.⁹ The direct synthesis of DMM would be more efficient if the process is industrialized.

The selective oxidation of methanol to DMM may involve two steps: (1) oxidation of methanol to formaldehyde on redox sites and (2) condensation of formaldehyde produced with additional methanol to DMM on acidic sites. Thus, bifunctional catalysts with redox and acidic characters are required for the reaction. In addition, the relative strengths of surface acidity and redox ability of a catalyst may be important in determining the reaction pathways as well as the selectivity to DMM. Among the catalysts reported to date, $Re/\gamma-Fe_2O_3$ was the most effective with 48.4% conversion of methanol and 91% selectivity to DMM at 513 K.⁶ However, there are disadvantages of using rhenium oxides since Re is expensive and rhenium oxides are volatile.¹⁰ Liu *et al.* studied the selective oxidation of methanol over $H_5PV_2Mo_{10}O_{40}/SiO_2$ catalysts. After selective poisoning of surface protons by using an organic base, they were able to inhibit the formation of dimethyl ether (DME) and thereby increase the selectivity of DMM to 80% at 453 K.⁷

The oxidation of methanol over V_2O_5/TiO_2 catalysts has been studied for the production of formaldehyde and methyl formate, and DMM was usually taken as a by-product.^{11–13} In fact, the selectivity to DMM decreased sharply with the increase of conversion of methanol over the traditional V_2O_5/TiO_2 catalysts.¹⁴

Our current work demonstrated that the selectivity of DMM could be greatly increased by simply doping $Ti(SO_4)_2$ onto the traditional V_2O_5/TiO_2 , because of the enhanced condensation reaction between formaldehyde and methanol on the acid sites with enhanced acidity. The performance of the $V_2O_5/TiO_2-Ti(SO_4)_2$ was as good as that of $Re/\gamma-Fe_2O_3$ for the selective oxidation of methanol to DMM.⁶

$Ti(SO_4)_2$ was added onto the V_2O_5/TiO_2 catalysts by the incipient wetness method followed by drying at 383 K and calcination at 673 K. The content of SO_4^{2-} was analyzed to be about 0.5% for the 10% $V_2O_5/TiO_2-Ti(SO_4)_2$ after calcination. (see ESI† for detailed procedure). The titania support used was in the anatase form as determined by X-ray diffraction.

The catalytic reaction for the selective oxidation of methanol was carried out in a glass reactor at atmospheric pressure. Prior to

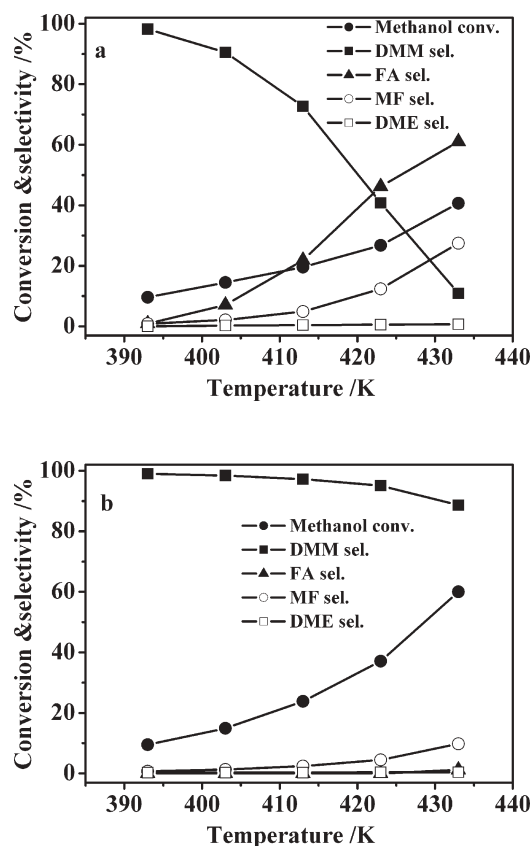


Fig. 1 Selective oxidation of methanol over V_2O_5/TiO_2 (a) and $V_2O_5/TiO_2-Ti(SO_4)_2$ (b) containing 10% V_2O_5 . FA = formaldehyde, MF = methyl formate, DME = dimethyl ether.

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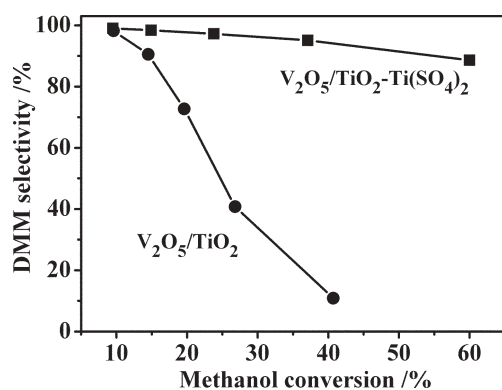
Table 1 Selective oxidation of methanol to dimethoxymethane over V_2O_5/TiO_2 and $V_2O_5/TiO_2(SO_4^{2-})$ catalysts^a

Catalyst	$S_{BET}/m^2 g^{-1}$	T/K	Methanol conv. (%)	Selectivity (%)				Rate ^e /mmol $g^{-1} h^{-1}$	
				DMM	FA ^b	MF ^c	DME ^d	Methanol ^f	DMM ^g
10% V_2O_5/TiO_2	92	433	40.7	10.9	61.0	27.5	0.7	195	7.1
10% $V_2O_5/TiO_2-Ti(SO_4)_2$	82	433	60.0	88.6	1.2	9.8	0.4	287	85
10% $V_2O_5/TiO_2-Ti(SO_4)_2-0.8\%K_2CO_3$	N/A ^h	433	24.0	41.1	43.6	15.0	0.3	115	16
10% $V_2O_5/TiO_2-Ti(SO_4)_2-3\%K_2CO_3$	N/A ^h	433	6.6	33.1	61.5	5.1	0.3	31.4	3.5
5% $V_2O_5/TiO_2-Ti(SO_4)_2$	95	433	48.2	91.6	0.1	6.0	2.4	462	141
10% $Re/\gamma-Fe_2O_3$ ⁱ	16	513	48.4	91.0	2.4	4.6	1.0	319	97

^a Feed conditions: methanol : O_2 : N_2 = 2 : 6 : 30 ml min^{-1} , catalyst loading = 0.2 g. ^b FA = formaldehyde. ^c MF = methyl formate.

^d DME = dimethyl ether. ^e Based on the unit mass of V or Re. ^f Rate of conversion of methanol. ^g Rate of formation of DMM.

^h Not available. ⁱ Data from ref. 6.

**Fig. 2** DMM selectivity vs. methanol conversion over 10% V_2O_5/TiO_2 and 10% $V_2O_5/TiO_2-Ti(SO_4)_2$.

each test, the catalysts were activated at 673 K for 1 h in a flowing gas with O_2 : N_2 = 6 : 30 (ml min^{-1}). The reactants and products were analyzed on line by GC.

Fig. 1 shows the results for the selective oxidation of methanol over 10% V_2O_5/TiO_2 and 10% $V_2O_5/TiO_2-Ti(SO_4)_2$. Fig. 1(a) shows that the selectivity to DMM was high (>90%) on the V_2O_5/TiO_2 at low temperatures (393 and 403 K) with low conversion of methanol (<15%). With the increase of temperature, the selectivity to DMM decreased rapidly with the increased conversion of methanol, due to the increased selectivity to formaldehyde and methyl formate. At 433 K, the products were mainly formaldehyde (61%) and methyl formate (27.5%) with only 10.9% DMM. This result indicated that the surface acidity of the V_2O_5/TiO_2 was not strong enough to effectively catalyze the condensation reaction, leading to the production of a large amount of formaldehyde as well as its oxidation product methyl formate.¹⁵

Fig. 1(b) shows that the selectivity to DMM was greatly improved with the addition of $Ti(SO_4)_2$ onto the V_2O_5/TiO_2 , even at high conversions of methanol. The conversion of methanol increased from 10 to 60% with the increase of temperature from 393 to 433 K, while the selectivity to DMM was maintained at high level (>88%). The production of formaldehyde was greatly inhibited and no formaldehyde was detected for the reaction at the temperatures below 423 K. DMM remained the predominant product in the temperature range used (393–433 K). Fig. 2 presents the curves of selectivity to DMM vs. the conversion of methanol. It is clearly seen that the selectivity to DMM decreased sharply over the V_2O_5/TiO_2 while it remained high over the $V_2O_5/TiO_2-Ti(SO_4)_2$ with the increase of conversion of methanol.

The importance of surface acidity for the synthesis of DMM from the direct oxidation of methanol was further confirmed by poisoning the surface acidity using K_2CO_3 . Data in Table 1 clearly show that the addition of K_2CO_3 greatly decreased the conversion of methanol and selectivity to DMM.

Table 1 also compares the activity of supported vanadia and rhenium oxide for the selective oxidation of methanol to DMM. The rates of conversion of methanol and formation of DMM were found to be about 319 and 97 $mmol g^{-1} h^{-1}$ on the 10% $Re/\gamma-Fe_2O_3$,⁶ and 462 and 141 $mmol g^{-1} h^{-1}$ on our 5% $V_2O_5/TiO_2-Ti(SO_4)_2$ catalyst, respectively, with similar conversion of methanol (48%) and selectivity to DMM (92%). Apparently, vanadia was much more active than rhenium oxide considering the fact that the rate of conversion of methanol was about 50% higher on the 5% $V_2O_5/TiO_2-Ti(SO_4)_2$ than on the 10% $Re/\gamma-Fe_2O_3$ although the reaction temperature was 80 K lower for the reaction on the 5% $V_2O_5/TiO_2-Ti(SO_4)_2$ than on the 10% $Re/\gamma-Fe_2O_3$.⁶

Different sulfates were added into the V_2O_5/TiO_2 for the selective oxidation of methanol to DMM. Similar positive effect was found for the addition of $(NH_4)_2SO_4$ and H_2SO_4 , but the addition of K_2SO_4 greatly decreased the activity and selectivity to DMM. The relevant data are provided in the ESL.[†]

In conclusion, we have demonstrated in this work that the bifunctional V_2O_5/TiO_2 with redox and enhanced acidic character was pertinent for the direct oxidation of methanol to DMM. The reaction involves the oxidation of methanol to formaldehyde which is then condensed with two methanol molecules to produce DMM. Addition of an acidic sulfate, *e.g.*, $Ti(SO_4)_2$ enhanced the surface acidity of V_2O_5/TiO_2 and greatly improved the selectivity to DMM as well as the conversion of methanol, due to the enhanced condensation reaction of formaldehyde with methanol. The selectivity to DMM reached 89–92% with 48–60% conversions of methanol at 433 K over the V_2O_5/TiO_2 modified with $Ti(SO_4)_2$, showing the potential application of the catalysts for the reaction in industry.

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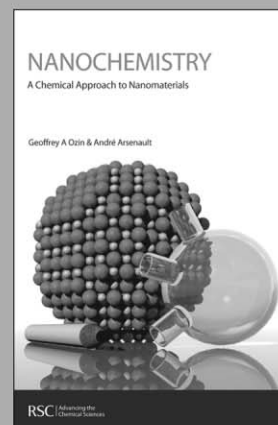
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