# Supplementary Material (ESI) for Chemical Communications

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

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## Preparation of catalysts

$TiO_2$ was prepared by the precipitation of $Ti(OH)_4$ from an ethanol solution of $TiCl_4$ with an aqueous solution of ammonia. Specifically, 30 g $TiCl_4$ was dissolved in 100 ml anhydrous ethanol to obtain a light yellow solution, which was then added dropwise into the ammonia solution until pH=7.0. A white precipitate of $Ti(OH)_4$ was formed during the process and was aged for 1 h in an ice-water bath under stirring. The precipitate was washed thoroughly to remove $Cl^-$. Then, it was added into 300 ml n-butanol and heated at 353 K until it was dried. It was then further dried at 383 K for 5 h and calcined at 673 K for 6 h. The sample thus obtained was an anatase $TiO_2$ with a surface area of 107 $m^2$ $g^{-1}$.

$V_2O_5/TiO_2$ catalysts were prepared according to the method described in literature [G. C. Bond, Appl. Catal. A, 1997, **157**, 91]. Briefly, $NH_4VO_3$ was dissolved in the solution of oxalic acid, and impregnated onto the $TiO_2$. After drying at 383 K for 12 h and calcining at 673 K for 6 h, $V_2O_5/TiO_2$ catalysts with different loadings of $V_2O_5$ were obtained. The 10%$V_2O_5/TiO_2$ catalyst had the surface area of 92 $m^2$ $g^{-1}$.

$Ti(SO_4)_2$ was doped onto $V_2O_5/TiO_2$ by the incipient wetness impregnation method. After impregnation, the samples were dried at 383 K and calcined at 673 K for 3 h. The amount of $SO_4^{2-}$ added was adjusted to 5% by weight in a sample. After calcination, the content of $SO_4^{2-}$ was different for different samples. Chemical analysis showed that the catalyst 5%$V_2O_5/TiO_2$-$Ti(SO_4)_2$ contained about 3.6% of $SO_4^{2-}$, while the 10%$V_2O_5/TiO_2$-$Ti(SO_4)_2$ contained only 0.5% of $SO_4^{2-}$. The $V_2O_5/TiO_2$ catalysts containing $SO_4^{2-}$ through the addition of $(NH_4)_2SO_4$ and $H_2SO_4$ were prepared in the same way.

$K_2CO_3$ was added into the 10%$V_2O_5/TiO_2$-$Ti(SO_4)_2$ by the impregnation method, too. The 10%$V_2O_5/TiO_2$-$Ti(SO_4)_2$ was impregnated with an aqueous solution of $K_2CO_3$ with desire amount of $K_2CO_3$, followed by drying at 383 K and calcining at 673 K for 3 h.

Table S1 Selective oxidation of methanol to dimethoxymethane over the $V_2O_5/TiO_2$

catalysts doped with $(NH_4)_2SO_4$, $H_2SO_4$ and $K_2SO_4$ [a]

| | | Methanol | Rate/mmol $g^{-1}h^{-1}$ [b] | | Selectivity /% | | | |
|---|---|---|---|---|---|---|---|---|
| | $T$/K | conv. /% | Methanol | DMM | DMM | FA | MF | DME |
| 10%$V_2O_5/TiO_2$ | 393 | 8.7 | 41 | 14 | 98.8 | 0 | 0.9 | 0.2 |
| -$(NH_4)_2SO_4$ | 403 | 14.7 | 70 | 23 | 97.8 | 0 | 1.9 | 0.3 |
| | 413 | 23.4 | 112 | 36 | 96.8 | 0 | 2.8 | 0.3 |
| | 423 | 36.6 | 175 | 55 | 94.5 | 0.2 | 5.0 | 0.4 |
| | 433 | 55.8 | 267 | 79 | 88.8 | 1.4 | 9.3 | 0.5 |
| 10%$V_2O_5/TiO_2$ | 393 | 8.2 | 39 | 13 | 98.9 | 0 | 0.8 | 0.3 |
| -$H_2SO_4$ | 403 | 14.5 | 70 | 23 | 98.0 | 0 | 1.6 | 0.4 |
| | 413 | 23.7 | 113 | 37 | 96.9 | 0 | 2.7 | 0.4 |
| | 423 | 40.5 | 194 | 61 | 93.9 | 0.1 | 5.6 | 0.4 |
| | 433 | 61.7 | 296 | 84 | 85.1 | 1.7 | 12.6 | 0.5 |
| 10%$V_2O_5/TiO_2$ | 393 | 0.4 | 1.9 | 0.5 | 81.6 | 18.4 | 0 | 0 |
| -$K_2SO_4$ | 403 | 0.7 | 3.2 | 0.8 | 72.3 | 27.7 | 0 | 0 |
| | 413 | 1.2 | 5.7 | 1.2 | 64.6 | 34.6 | 0.8 | 0 |
| | 423 | 2.8 | 13 | 1.9 | 43.3 | 55.7 | 1.0 | 0 |
| | 433 | 5.6 | 27 | 3.1 | 35.1 | 63.1 | 1.8 | 0 |

[a] Feed conditions: methanol/$O_2/N_2$=2/6/30 ml $min^{-1}$, catalyst loading=0.2 g. [b] Based on the unit mass of V. [c] FA=formaldehyde. [d] MF=methyl formate. [e] DME=dimethyl ether. No CO or $CO_2$ was detected at the reaction temperatures used.