Supporting Information

Selective oxidation of methanol to dimethoxymethane over bifunctional VO_x/TS-1 catalysts

Shuang Chen, Shengping Wang, Xinbin Ma* and Jinlong Gong*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Emai: jlgong@tju.edu.cn; xbma@tju.edu.cn

1 Catalysts preparation

TS-1 zeolites (200 mesh, 2.5wt.% Ti) were acquired from Nankai Catalyst (Tianjin, China). Reagents used in this work include NH_4VO_3, $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ (≥ 99%, Tianjin DaMao Chemical Reagent Factory, China), oxalic acid (≥ 99.8%, Tianjin Chemical Reagent Factory, China), methanol (AR, Tianjin Kermel Chemical Co., Ltd), nitrogen and oxygen (99.99%, Tianjin Sixon Gas Co.,Ltd).

Vanadium oxide supported on TS-1 zeolite (commercial) was prepared by impregnation, using ammonia vanadate (NH_4VO_3) as a metal precursor and oxalic acid as a complexing agent. The resultant solids were dried at 393 K for 2 h and then calcined in air at 673 K for 6 h. The catalyst was named VO_x/TS-1 with theoretical amount of vanadia loading (20 wt%).

VO_x/TS-1-SO_4^{2-} and VO_x/TS-1-PO_4^{3-} catalysts were prepared by incipient wetness impregnation of the prepared VO_x/TS-1 with an aqueous solution containing the theoretical percentage of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ respectively overnight to achieve 5 wt.% SO_4^{2-} and 7.5 wt.% PO_4^{3-} loadings. The resulting solids were dried at 393 K for 2 h and then calcined in air at 673 K for 4 h.

2 Catalytic reactions

Catalytic test was carried out at atmospheric pressure in a fixed-bed micro-reactor made of quartz with an inner diameter of 6 mm. Methanol was introduced into the reaction zone by bubbling O_2/N_2 (1/3) through a glass saturator filled with methanol (99.9%) at 288 K. The feed composition was maintained as methanol/O_2/N_2 (v/v)=1/2.5/7.5. In each test, 0.3 g of catalyst was loaded. Reaction products were analyzed by on-line gas chromatography (SP-2100) using a Propack T column connected to a FID detector and a TCD detector.

3 Characterization

NH_3-TPD spectra were recorded on a 2910 Chemisorption Instrument (Micromeritics). The catalyst (50 mg) was pretreated at 673 K under Ar flow (30 ml min^{-1}) for 2 h, and was then cooled down to 333 K. NH_3 was then introduced into the flow system. The TPD spectra were recorded at a ramp rate of 10 K min^{-1}.

Pyridine adsorption infrared spectra (Py-FTIR) were recorded on a Nicolet-6700 FT-IR spectrophotometer (DTGS detector). The spectra were obtained in the 4000–400 cm^{-1} range with a resolution of 2 cm^{-1} and 128 scans. Self-supporting wafer (10–30 mg, 18 mm diameter) was first evacuated at 623 K for 30 min and then exposed to pyridine at 333 K for 5 min. Desorption of pyridine was carried out by evacuation at 333 K for 30 min.

Temperature-programmed reduction (TPR) measurements were carried out in a continuous mode using a U-type quartz microreactor equipped with a thermal conductivity detector (TCD). The sample (50 mg) was contacted with a H_2:Ar mixture (10vol.% H_2) at a flow rate of 40 ml min^{-1}. The sample was heated at a rate of 10 K min^{-1} from room temperature to 1100 K.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-1600 instrument (Physical Electronics) equipped with a hemispherical electron analyzer and an Mg Kα X-ray source (1253.6 eV). The energy region of the photoelectrons was scanned at a passing energy of 29.35 eV. The binding energies were referenced to the C1s band at 284.6eV. The data was treated on PHI Multipack Program, Gauss.

X-ray diffraction (XRD) patterns were collected on a D/Max-2500 diffractometer using C-filtered Cu Ka radiation, operated at 40 kV and 200 mA, 2θ= 5- 90°.

Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature using a Micromeritics ASAP 2020. Pore size distribution and pore volume were calculated by the T-plot method according to the desorption isotherms.

4. The results of characterization

4.1 Nitrogen adsorption–desorption

Table S1 Surface areas, pore volumes, and pore sizes of the catalysts.

Sample	Surface Area/ m^2g^{-1}	pore volume $/cm^3g^{-1}$	average pore diameter /nm
TS-1	438.2	0.11	1.2
VO_x/TS-1	334.7	0.10	1.0
VO_x/TS-1-SO_4^{2-}	313.5	0.10	1.0
VO_x/TS-1-PO_4^{3-}	295.9	0.09	1.0

4.2 X-ray diffraction XRD

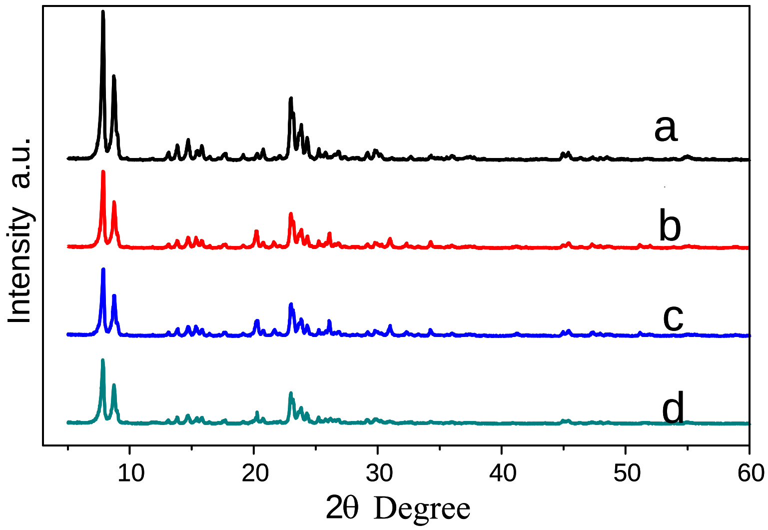

Fig S1 X-ray diffraction (XRD) patterns of catalysts (a) TS-1; (b) VO_x/TS-1; (c) VO_x/TS-1-SO_4^{2-}; (d) VO_x/TS-1-PO_4^{3-}

4.3 The V $2p_{3/2}$ peak-fitting from XPS spectra

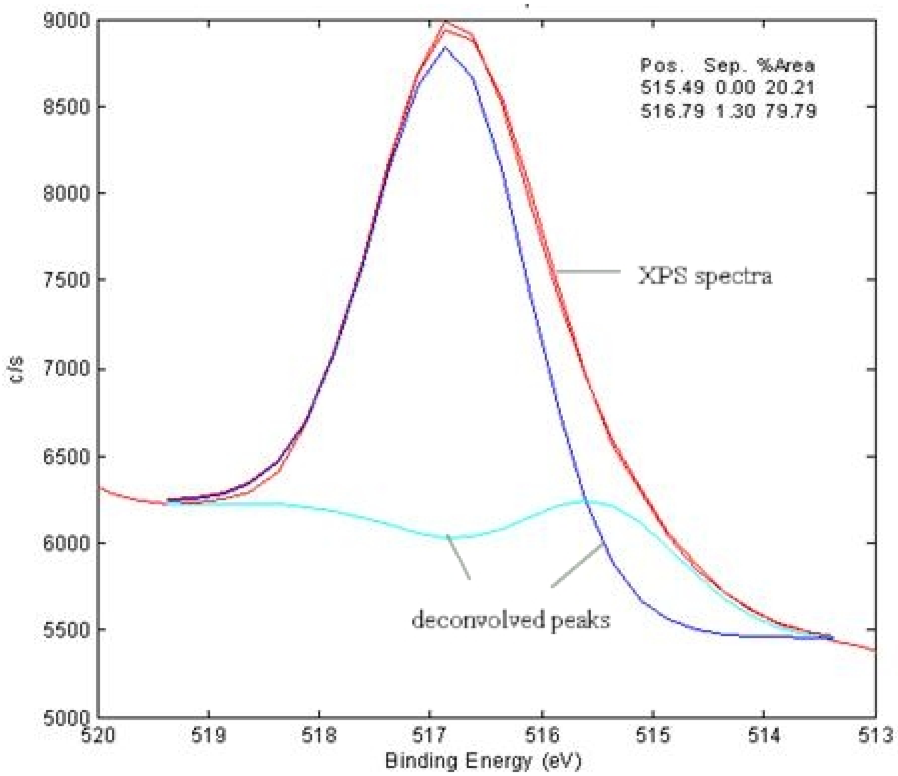

Fig S2 Peak-fitting of the V2p3/2 photoelectronic peak of VO_x/TS-1 sample

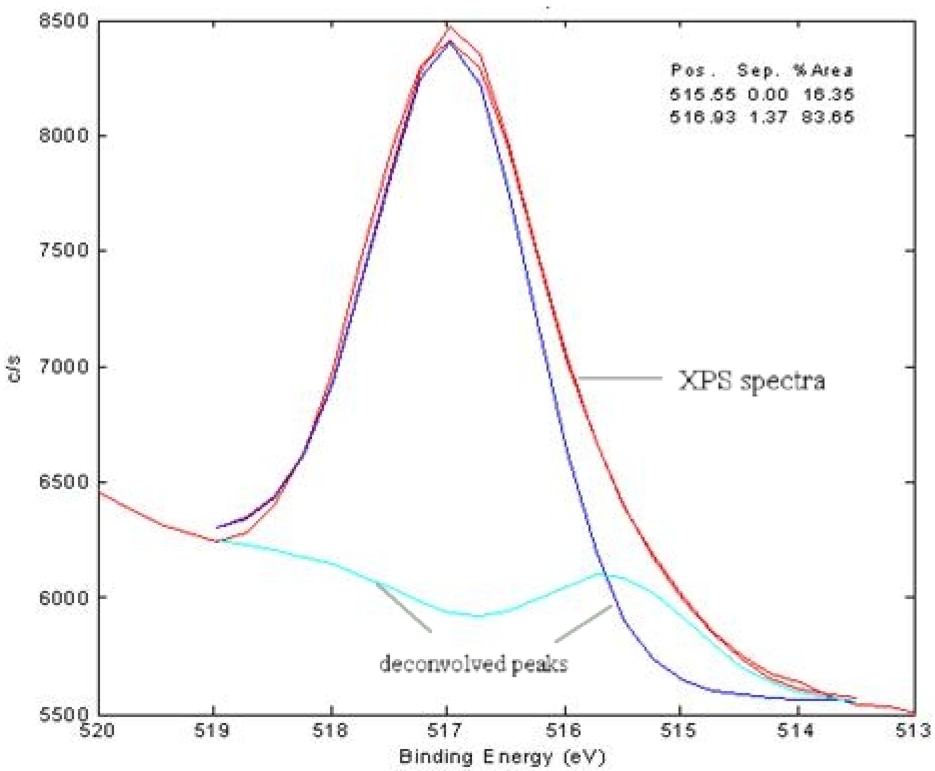

Fig S3 Peak-fitting of the V2p3/2 photoelectronic peak of VO_x/TS-1-SO_4^{2-} sample

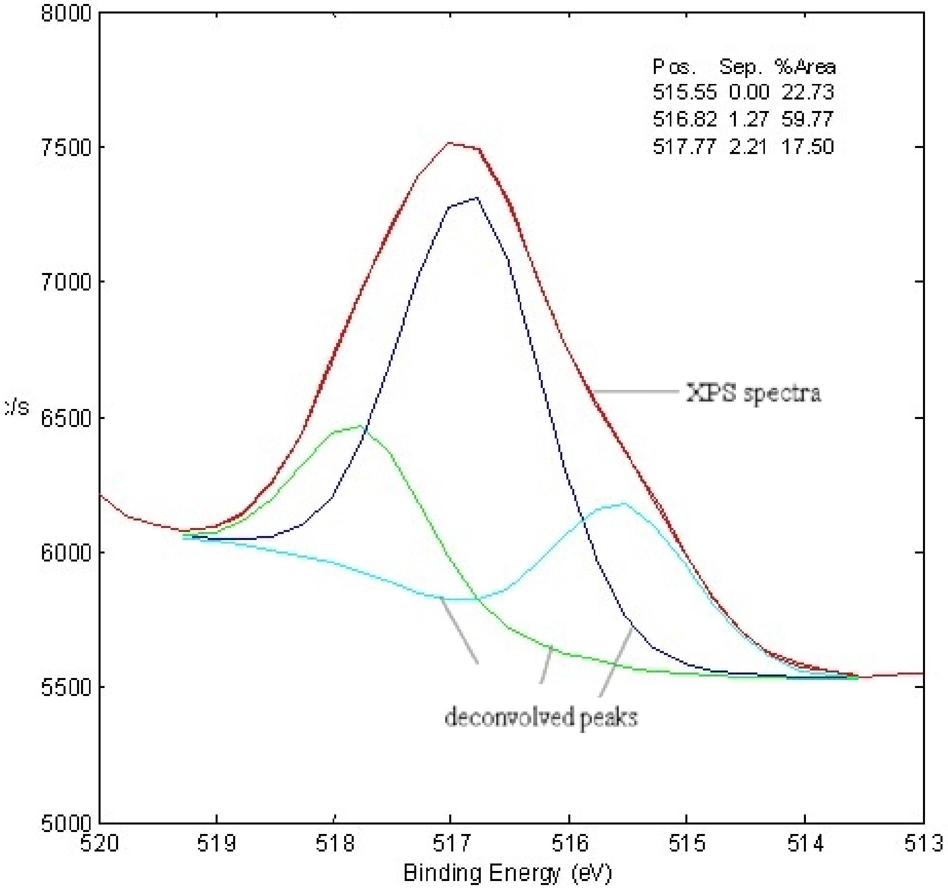

Fig S4 Peak-fitting of the V2p3/2 photoelectronic peak of VO_x/TS-1-PO_4^{3-} sample