Supporting Information

Introduction of TiO_2 enhancing the catalytic performance of the $Ti(SO_4)_2/SiO_2$ for dimethyl ether oxidation

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1. Experimental section

1.1 Materials

$Ti(SO_4)_2$ was purchased from the Aladdin Industrial Co. (Shanghai, China). Silicon dioxide was purchased from Qingdao Ocean Chemical Co, and tetrabutyl titanate was purchased from Sinopharm. All other regents were analytical grade and were used without further purification.

1.2 Synthesis of TiO_2/SiO_2(TS) supports

Firstly, 10 ml of tetrabutyl titanate was added to 55 ml of anhydrous ethanol solution and stirred for 8 min, followed by the addition of 9 g of SiO_2 and continued stirring for 8 min to form solution A. After the stirring was completed, 5ml of deionized water and 5ml of anhydrous ethanol solution were mixed. Then nitric acid solution was added drop by drop in order to adjust the pH of the mixed solution to 1. The solution obtained is the aqueous ethanol solution with pH=1. Then, the above solution was added to solution A and stirred for 30 min, and all stirring processes were carried out under the condition of a 35°C water bath. The stirred solution was aged at room temperature for 24h and then evaporated on a rotary evaporator, the dried solid was continued to be dried at 105°C for 12h, and calcined in a muffle furnace at different temperatures (300 °C,400 °C, 500 °C, 600 °C) for 4 h. The obtained support was defined as TS-X °C, where X stands for the calcination temperature.

1.3 Synthesis of $Ti(SO_4)_2$/TS catalysts

$Ti(SO_4)_2$/TS catalysts were prepared by an incipient wetness impregnation method. The TS support was impregnated with an aqueous solution of $Ti(SO_4)_2$ at 25 °C for 6 h and dried overnight at 120 °C, where the theoretical loading of titanium sulfate is 10%. The catalysts were then calcined at 240 °C for 4 h under a flow of O_2.

2. Catalytic oxidation of DME

The catalytic oxidation of DME was performed in a continuous-flow fixed-bed reactor. The catalyst (1 mL, 20–40 mesh) was diluted with ground quartz to prevent over-heating. The catalyst was pretreated in an O_2 flow (30 mL/min) for 2 h before a reaction. The reactant mixture consisted of DME and O_2 at nO_2:nDME = 1:1. The reaction products were analyzed by using a gas chromatography instrument (Shimadzu Co., Kyoto, Japan) equipped with a flame ionization detector (DB-1 column, 60 m × 0.25 mm, Agilent Technologies Inc., USA). A GC-2014 instrument (Shimadzu Co., Kyoto, Japan) with a thermal conductivity detector (Porapak T column, Waters Corporation, USA) and a GC-4000A (TDX-01 column, East & West Analytical Instruments, Inc., China) with a thermal conductivity detector were also used to analyze products. The data were calculated based on the carbon balance and the carbon balances for most experiments were within 95%–99%.

3. Catalyst characterization

3.1 Surface areas of the samples were measured by a BET nitrogen adsorption method at -195.65 °C using a TriStar 300 machine (Micromeritics, Atlanta, GA, USA). The samples were treated at 200 °C under vacuum conditions for 8h before BET test.

3.2 X-ray diffraction (XRD) measurements were carried out on a Bruker D2 phaser X-ray Diffractometer in the range of 5-90° with the scan rate of 4°/min using Cu Kα radiation source.

3.3 Diffuse reflectance UV–vis spectra were recorded on a Cary100 (Agilent Technologies, Inc.) in the range of 200-800 nm with polytetrafluoroethylene coating as the reference.

3.4 X-ray photoelectron spectra (XPS) were measured on Kratos Axis Ultra Dld spectrometer equipped with Al anode (Al Kα hv = 1486.6 eV) powered at 150 W.

3.5 Morphology of the sample was measured by a JEM-F200 transmission electron microscope (TEM) operated at 200 keV. The sample powder was dispersed in ethanol by ultrasonic for 20 min. Then, the suspension was dropped onto a carbon coated copper TEM grid (200 mesh) and dried in air before measurement.

3.6 Ammonia-Temperature programmed desorption (NH_3-TPD) profiles were obtained in the TP-5080 type automatic adsorption instrument from Tianjin XianQuan Co. Ltd.

3.7 Fourier Transform Infrared Spectrometer (FT-IR) spectrum of the supports and catalysts were collected on a VERTEX 80V spectrometer (Bruker, Germany) in a wavenumber range of 4000-400 cm^{-1}.

3.8 Low-temperature electron spin resonance (ESR) spectra were recorded on a Bruker EMX plus-10/12 spectrometer, operating in the X-band(at 9.41 GHz) with 100 kHz magnetic field modulation at -173 ºC.

3.9 The Ti content was measured by a NexION 5000 inductively coupled plasma mass spectrometer (ICP-MS).

Table S1

The structural parameters of TS supports with different calcinations temperatures.

Support	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
TS-300 ^oC	547.23	0.44	4.68
TS-400 ^oC	574.57	0.67	4.56
TS-500 ^oC	563.73	0.58	4.85
TS-600 ^oC	544.65	0.48	4.37
SiO_2	589.33	0.69	4.42

Table S2

The structural parameters of $Ti(SO_4)_2$/TS catalysts.

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
$Ti(SO_4)_2$/TS-300 ^oC	286.52	0.43	6.04
$Ti(SO_4)_2$/TS-400 ^oC	259.07	0.39	6.15
$Ti(SO_4)_2$/TS-500 ^oC	303.76	0.43	5.69
$Ti(SO_4)_2$/TS-600 ^oC	346.97	0.51	5.87

Table S3

Ti content of different TS supports by ICP-MS.

Support	Ti (%)
TS-300 ^oC	3.5
TS-400 ^oC	3.4
TS-500 ^oC	3.5
TS-600 ^oC	3.4

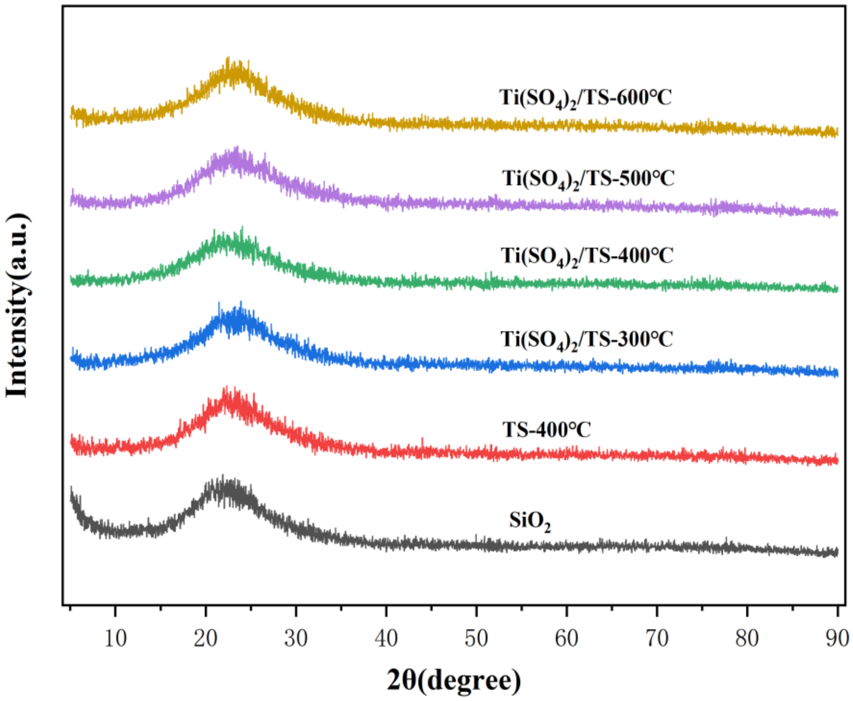

Figure S1. XRD spectra of different supports and catalysts.

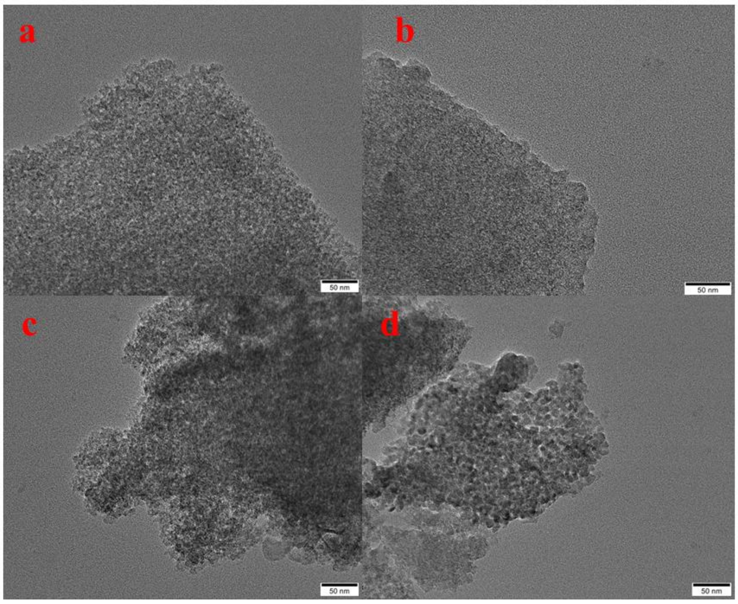

Figure S2. TEM images of TS supports calcined at different temperatures: (a) TS-300 ^{o}C; (b) TS-400 ^{o}C; (c)TS-500 ^{o}C; (d)TS-600 ^{o}C.

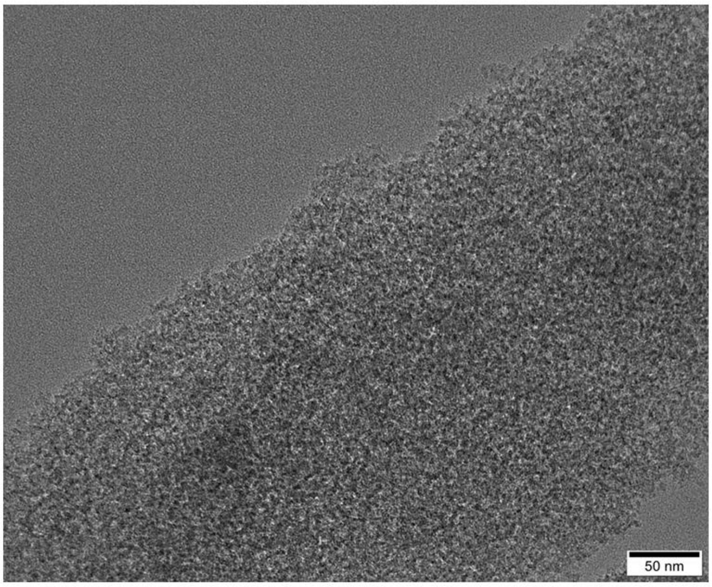

Figure S3. TEM image of SiO_2 material.

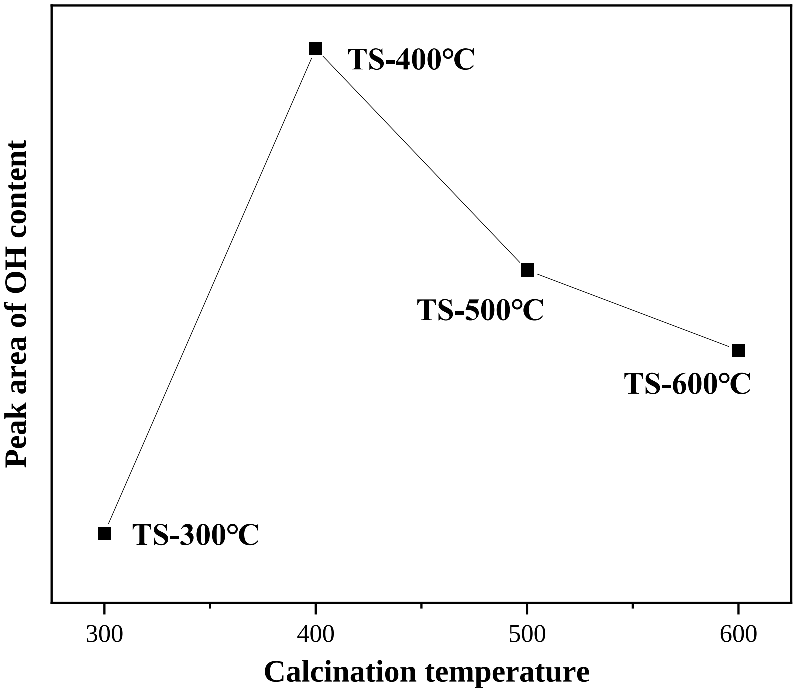

Figure S4. Relationship between calcination temperature and hydroxyl content of supports.

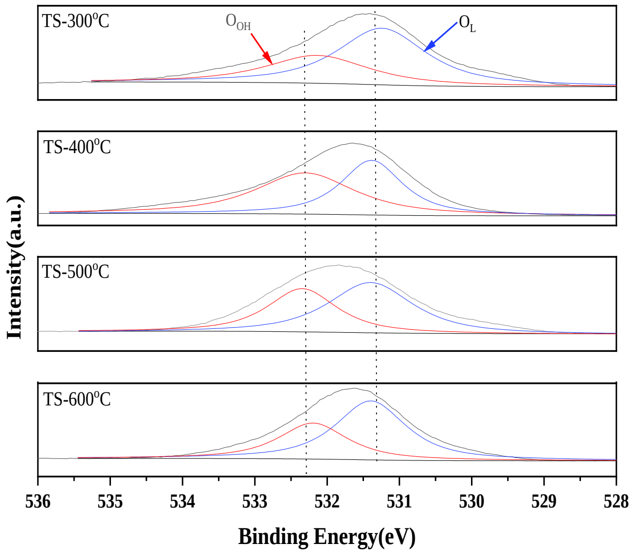

Figure S5. XPS analysis of O 1s for TS supports.

Table S4

Quantitative analysis of surface oxygen species over TS supports from XPS.

Support	$O_{OH(\%)}$	$O_{L(\%)}$
TS-300 °C	32.7	67.3
TS-400 °C	54.9	45.1
TS-500 °C	40.8	59.2
TS-600 °C	37.3	62.7

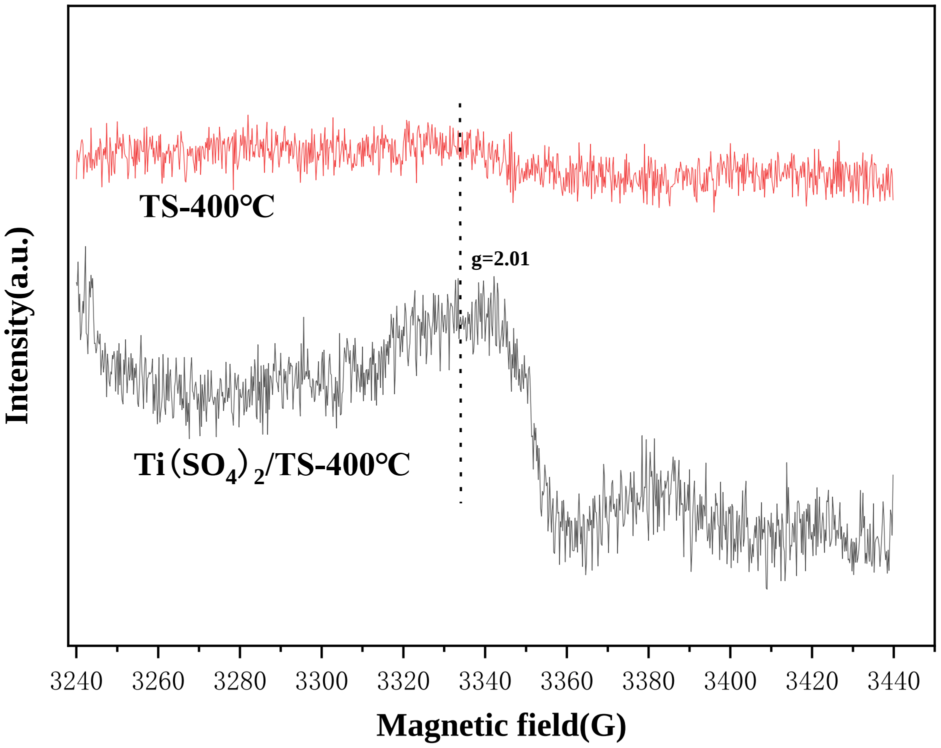

Figure S6. Low-temperature ESR spectra of different samples.

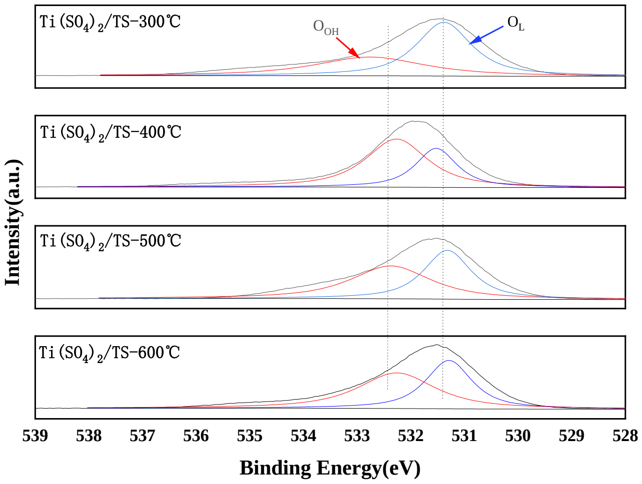

Figure S7. XPS analysis of O 1s for catalysts.

Table S5

Quantitative analysis of surface oxygen species over different catalysts.

Catalyst	$O_{OH(\%)}$	$O_{L(\%)}$
$Ti(SO_4)_2$/TS-300 ºC	41.4	58.6
$Ti(SO_4)_2$/TS-400 ºC	69.5	30.5
$Ti(SO_4)_2$/TS-500 ºC	59.1	40.9
$Ti(SO_4)_2$/TS-600 ºC	55.2	44.8