

Sulfated Mesoporous Au/TiO₂ Spheres as a Highly Active and Stable Solid Acid Catalyst

Cheng Chao Li,^a Yan Ping Zheng^b, Tai Hong Wang^{*a}

^aKey Laboratory for Micro-Nano Optoelectronic Devices of Ministry of Education and State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, 410082, P. R. China

^bState Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

* Tel: +86-0731-88823407; Fax: +86-0731-88822137.

E-mail address: thwang@aphy.iphy.ac.cn (T. H. Wang).

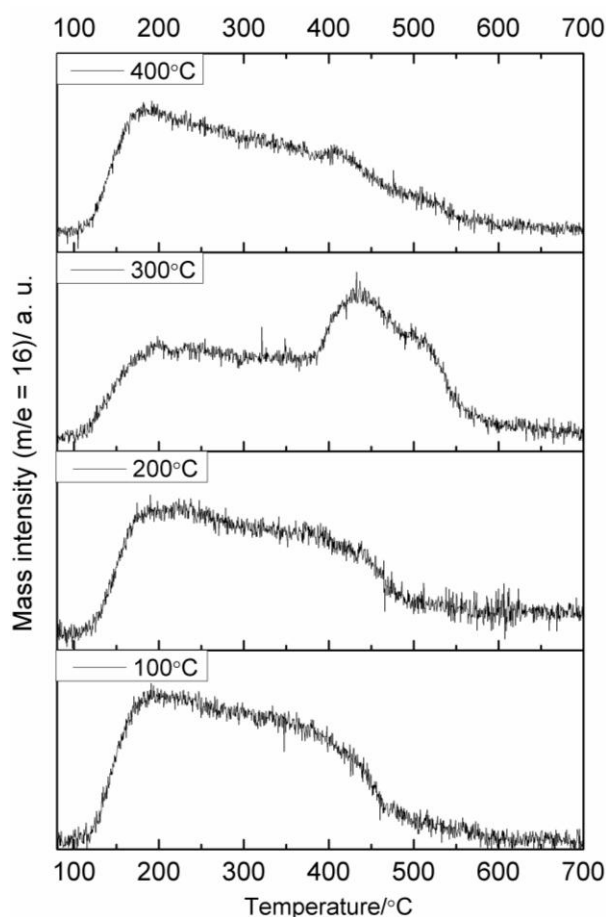


Figure SI-1. NH₃-TPD (m/e=16) curves for sulfated MTOS-based solid acid catalysts (heat-treated at 100 °C to 400 °C respectively for 4 h).

Supporting Information

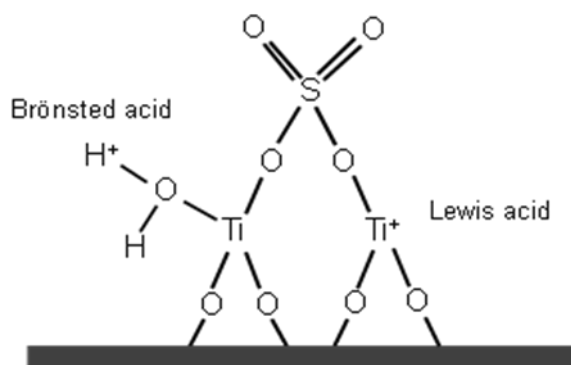


Figure SI-2. Lewis and Brønsted acid sites of a sulfated titania.¹⁻⁴

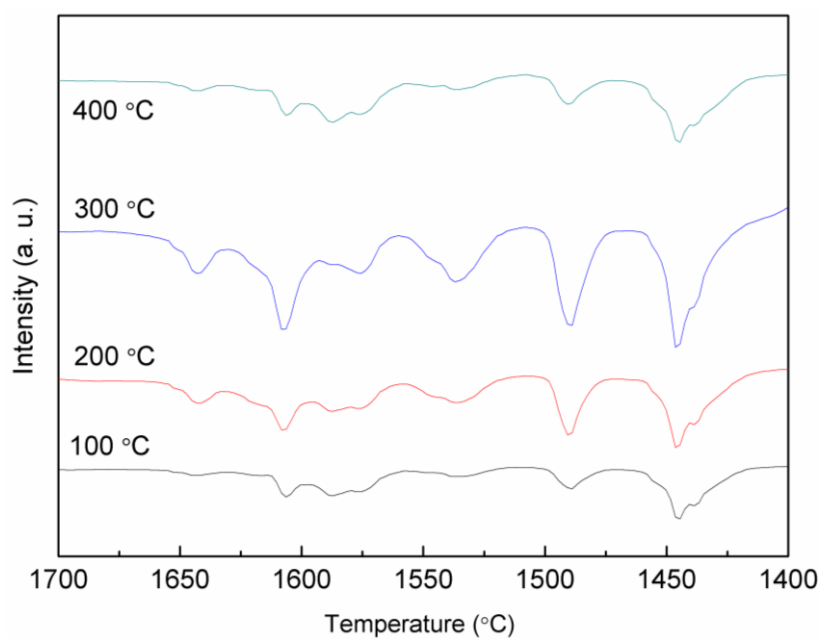


Figure SI-3. Adsorbed pyridine infrared spectra of as-prepared catalysts.

Supporting Information

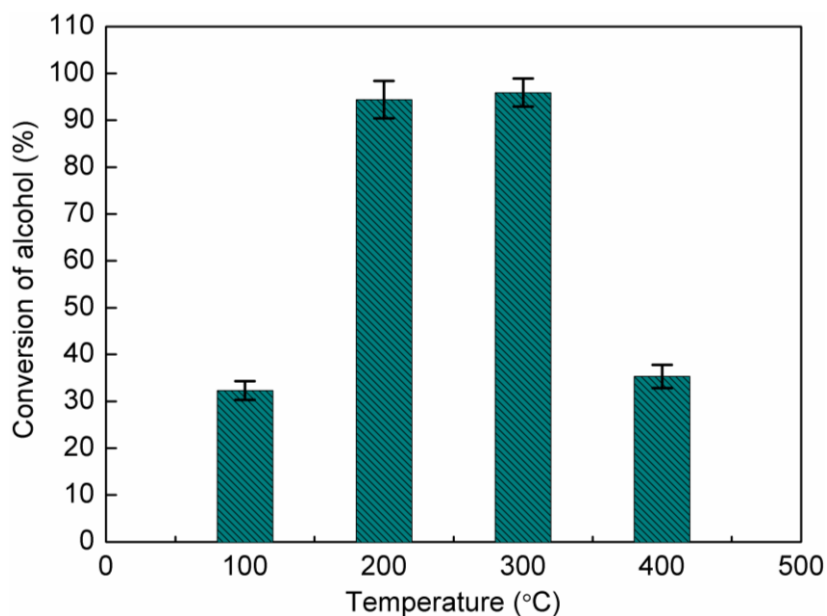


Figure 11. The catalytic activity of the sulfated MTOS treated at 100 to 400 °C.

Table 1. Friedel-Crafts Alkylation of toluene using our mesoporous TiO₂-based solid acid catalysts

Reaction conditions: 50.0 mL of toluene + 5.0 mL of benzyl alcohol + 0.5 g of catalyst + 0.5 mL of hexadecane (internal standard) at 130°C. Selectivity of methyl-diphenylmethane (i.e., the total sum of 1-methyl-4-(phenylmethyl)-benzene, 1-methyl-2-(phenylmethyl)-benzene, and 1-methyl-3-(phenylmethyl)-benzene) was determined at (a) 30 min and (b) 1 h after the reaction.

Catalyst	S _{BET} (m ² ·g ⁻¹)	Acid amount (mmol·g ⁻¹)	Conversion (%) ^a	Reaction rate (mmol·g ⁻¹ ·h ⁻¹)	Selectivity (methyl-diphenylmethane, %)
Sulfated MTOS-400°C	123.4	1.83	36.5	58.3	24.8, ^a 45.0 ^b
Sulfated MTOS-300°C	153.3	3.28	>99	189.7	45.0, ^a 84.3 ^b
Sulfated MTOS-200°C	148.9	2.94	>99	189.7	45.2, ^a 82.2 ^b
Sulfated MTOS-100°C	155.0	1.61	30.1	64.9	20.2, ^a 26.8 ^b

Supporting Information

Table 2. Esterification of Acetic Acid with Ethanol and Hydrolysis of Ethyl Acetate

Reaction conditions:

Esterification: 0.1 mol of acetic acid + 1 mol of ethanol + 0.2 g of catalyst, at 70 °C for 4 h.

Hydrolysis: 50 mmol of ethyl acetate + 10.0 mL of water + 0.1 g of catalyst, at 70 °C for 4 h. TOF is defined as the number of moles of reactants that one mol of acid sites converts to products in per unit of time.

Catalyst	S _{BET} (m ² ·g ⁻¹)	Acid amount (mmol·g ⁻¹)	Esterification of acetic acid		Hydrolysis of ethyl acetate	
			Reaction rate (mmol·g ⁻¹ ·min ⁻¹)	TOF (h ⁻¹)	Reaction rate (mmol·g ⁻¹ ·min ⁻¹)	TOF (h ⁻¹)
Sulfated MTOS-400°C	123.4	1.83	1.20	39.3	0.28	9.2
Sulfated MTOS-300°C	153.3	3.28	1.35	24.7	0.32	5.9
Sulfated MTOS-200°C	148.9	2.94	1.32	26.9	0.32	6.5
Sulfated MTOS-100°C	155.0	1.61	1.28	47.7	0.30	11.2

References:

- [1] A. Corma, *Chem. Rev.* **1995**, *95*, 559.
- [2] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, **1986**.
- [3] T. Yamaguchi, *Appl. Catal. A: Gen.* **1990**, *61*, 1.
- [4] K. Arata, *Advance in catalysis* **1990**, *37*, 165.