

**The Critical Role of Hydroxyls on Anatase TiO<sub>2</sub> in the Ring Opening of 2,5-Dimethylfuran to 2,5-Hexanedione**

Table S1. Elemental analysis of sample by XRF

Sample	Element(formula)	Mass fraction(wt.%) <sup>a</sup>
TiO <sub>2</sub> -A	Ti(TiO <sub>2</sub> )	99.84
	Na(Na <sub>2</sub> O)	0.02
	S(SO <sub>3</sub> )	0.03
	Ca(CaO)	0.03
	Mg(MgO)	0.04
	Fe(Fe <sub>2</sub> O <sub>3</sub> )	0.02
	Mn(MnO <sub>2</sub> )	0.02

Table S2. Effect of water content in ethanol on diethyl ether formation over TiO<sub>2</sub>-A catalyst.

Entry	Catalyst	Solvent	Diethyl ether yield (%)
1	TiO <sub>2</sub> -A	ethanol+0 mL H <sub>2</sub> O	3.1
2	TiO <sub>2</sub> -A	ethanol+0.5 mL H <sub>2</sub> O	1.2
3	TiO <sub>2</sub> -A	ethanol+1 mL H <sub>2</sub> O	0.2
4	TiO <sub>2</sub> -A	ethanol+1.5 mL H <sub>2</sub> O	0.1
5	TiO <sub>2</sub> -A	ethanol+2 mL H <sub>2</sub> O	0.1

Reaction condition: catalyst 0.25 g, 2,5-DMF 1 mL, P (N<sub>2</sub>) = 1 MPa, 160 °C, 500 rpm, 1 h

Table S3. Effect of water content in acetonitrile on the 2,5-DMF conversion and product selectivity over TiO<sub>2</sub>-A catalysts under different pretreatment conditions.

Entry	Catalyst	Solvent	2,5-DMF conv. (%)	Sel. (%)	
				2,5-HD	others
1	TiO <sub>2</sub> -A	acetonitrile+0 mL H <sub>2</sub> O	1.3	98.2	1.8
2	TiO <sub>2</sub> -A	acetonitrile+1 mL H <sub>2</sub> O	42.3	96.9	3.1
3	calcined TiO <sub>2</sub> -A <sup>a</sup>	ethanol+1 mL H <sub>2</sub> O	44.6	98.1	1.9
4	reuse regenerated TiO <sub>2</sub> -A <sup>b</sup>	ethanol+1 mL H <sub>2</sub> O	15.2	95.6	4.4
5	Pretreated TiO <sub>2</sub> -A in 2,5-HD <sup>c</sup>	ethanol+1 mL H <sub>2</sub> O	2.1	99.8	0.2
6	Treated reused TiO <sub>2</sub> -A in 2,5-DMF <sup>d</sup>	ethanol+1 mL H <sub>2</sub> O	40.5	98.9	1.1

<sup>a</sup> Calcined TiO<sub>2</sub>-A was the fresh TiO<sub>2</sub>-A calcined in air at 400 °C for 4 h

<sup>b</sup> Reuse regenerated TiO<sub>2</sub>-A was the regenerated TiO<sub>2</sub>-A calcined in O<sub>2</sub> at 400 °C for 4 h

<sup>c</sup> Pretreated TiO<sub>2</sub>-A in 2,5-HD: fresh TiO<sub>2</sub>-A treated with 2,5-HD (1 mL) in ethanol (10 mL) at 25 °C, followed by filtration and drying at 120 °C overnight.

<sup>d</sup> Treated reused TiO<sub>2</sub>-A in 2,5-DMF: reused TiO<sub>2</sub>-A treated with 2,5-DMF (2 mL) in ethanol (10 mL) at 25 °C, followed by filtration and drying at 120 °C overnight.

Reaction condition: catalyst 0.25 g, 2,5-DMF 1 mL, P (N<sub>2</sub>) = 1 MPa, 160 °C, 500 rpm, 1 h

Table S4 BET surface areas of TiO<sub>2</sub>-A, reused TiO<sub>2</sub>-A and calcined TiO<sub>2</sub>-A

catalyst	BET surface area (m <sup>2</sup> /g)
TiO <sub>2</sub> -A	72.9
reused TiO <sub>2</sub> -A	71.1
calcined TiO <sub>2</sub> -A	71.2

Table S5 NH<sub>3</sub> uptake of TiO<sub>2</sub>-A, reused TiO<sub>2</sub>-A and calcined TiO<sub>2</sub>-A

catalyst	NH <sub>3</sub> uptake (μmol/g)
TiO <sub>2</sub> -A	721.4
reused TiO <sub>2</sub> -A	1257.4
calcined TiO <sub>2</sub> -A	615.9

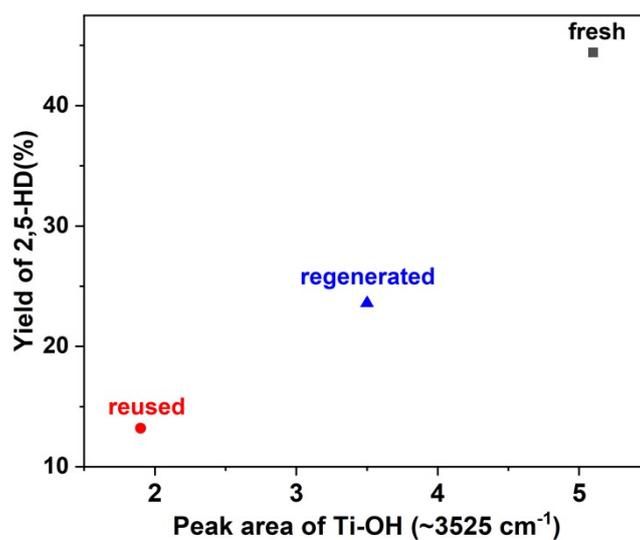


Figure S1. Correlation between the peak area of the Ti-OH band at ~3525 cm<sup>-1</sup> and the catalytic performance in the ring-opening reaction of 2,5-DMF over TiO<sub>2</sub>-A catalysts.