Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Selective synthesis of α-olefins by dehydration of fatty alcohols over alumina–thoria mixed catalysts

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Experimental section

Chemicals: The received chemicals (solvents and some metal oxide catalysts) were used without further treatment. Chemicals are stearyl alcohol (Sinopharm Chemical Reagent), *n*-dodecane (>98%, Sinopharm Chemical Reagent), nano sized alumina (99.9%, Maikun Chemical), thorium nitrate (Aladdin Industrial Cooperation), nafion (Alfa Aesar), Nb_2O_5 (Sinopharm Chemical Reagent), alumina acidic (Sinopharm Chemical Reagent), alumina basic (Sinopharm Chemical Reagent), alumina neutral (Sinopharm Chemical Reagent), amberlyst (Aladdin Industrial Cooperation), Y_2O_3 (99.9%, Chengdu Micxy Chemical), TiO_2 (99%, Maikun Chemical), La_2O_3 (Chengdu Micxy Chemical), WO_5 (99.9%, Maikun Chemical), CeO_2 (Aladdin Industrial Cooperation), ZrO_2 (Maikun Chemical), MoO_3 (99%, Chengdu Micxy Chemical), $ZrSO_4.4H_2O$ (Jing Shi Ji), ASA (SiO_2:Al_2O_3=9, The Catalyst Plant (Institute of Green Chemistry) of East China Normal University), *n*-$C_{10}H_{21}$–OH (Sinopharm Chemical Reagent), n-$C_{12}H_{25}$–OH (Sinopharm Chemical Reagent), *cis*-2-methyl cyclohexanol (>98%, Tokyo Chemical Industry), *n*-$C_{14}H_{29}$–OH (Sinopharm Chemical Reagent), *n*-$C_{16}H_{33}$–OH (Sinopharm Chemical Reagent), *trans*-2-methyl cyclohexanol (>98%, Tokyo Chenical Industry), *trans*-2-methyl cyclohexanol (>98%, Tokyo Chemical Industry). Nitrogen and air (99.999 vol. %) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Preparation of catalysts

The alumina (nano sized alumina) catalyst was prepared via calcinations method as received. The calcination was carried out in N_2 at 500 °C (2 °C/min) for an hour with flow of 400 mL min^{-1}. The other kinds of alumina like alumina acidic, alumina basic and alumina neutral were treated the same way.

Likewise, thoria (ThO_2) was prepared from its salt thorium nitrate ($ThN_2O_{12}.6H_2O$) by heat treatment in air. Thorium nitrate was calcined in air at 400 °C (2 °C /min) for 16 h. After this treatment the moist salt thorium nitrate converted into white solid which was ground using mortar and pestle into powdered form. This white powder was used as catalyst.

Catalytic characterization

Powder X-ray diffraction (XRD) patterns were used to investigate the structure and crystal size by Rigaku Ultima IV X-ray diffractometer utilizing Cu-Kα radiation (λ =

1.5405 Å) operated at 35 kV and 25 mA. N_2 adsorption measurements were performed at 77 K on a BEL-MAX gas/vapor adsorption instrument. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. The IR spectra of adsorbed ethanol (IR-ethanol), ethylene (IR-ethylene) and ethanol (IR-ethanol) dehydration were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an in-situ IR cell. The crystal morphology was determined by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100 microscope operating at an accelerating voltage of 200 kV. The IR spectra of the adsorbed pyridine (IR-Py) were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an *in situ* IR cell. The samples were activated in a vacuum at 673 K for 1 h before equilibration with pyridine at 423 K, and then evacuated at 423 K for 1 h.

Typical procedure for selective dehydration of fatty alcohols

Unless stated otherwise, reactions were carried out in an autoclave from Anhui Kemi Machinery Technology Co., Itd. The typical liquid-phase selective dehydration of fatty alcohols to α-olefins were carried out in micro-reactor. In a typical process, 0.6 g alumina catalyst, 0.1 g ThO_2, 3.0 g fatty alcohol and 80 mL of dodecane were placed in micro-reactor. The autoclave was purged with N_2 three times to remove the residual air. After the removal of air, the N_2 was again released to make pressure as zero MPa. Then, the reaction mixture was magnetically stirred to 500 rpm at 300 °C for 6 h. When the above reaction was completed, the autoclave was cooled naturally; the liquid products were analyzed by GC-FID and finally identified by GC-MS.

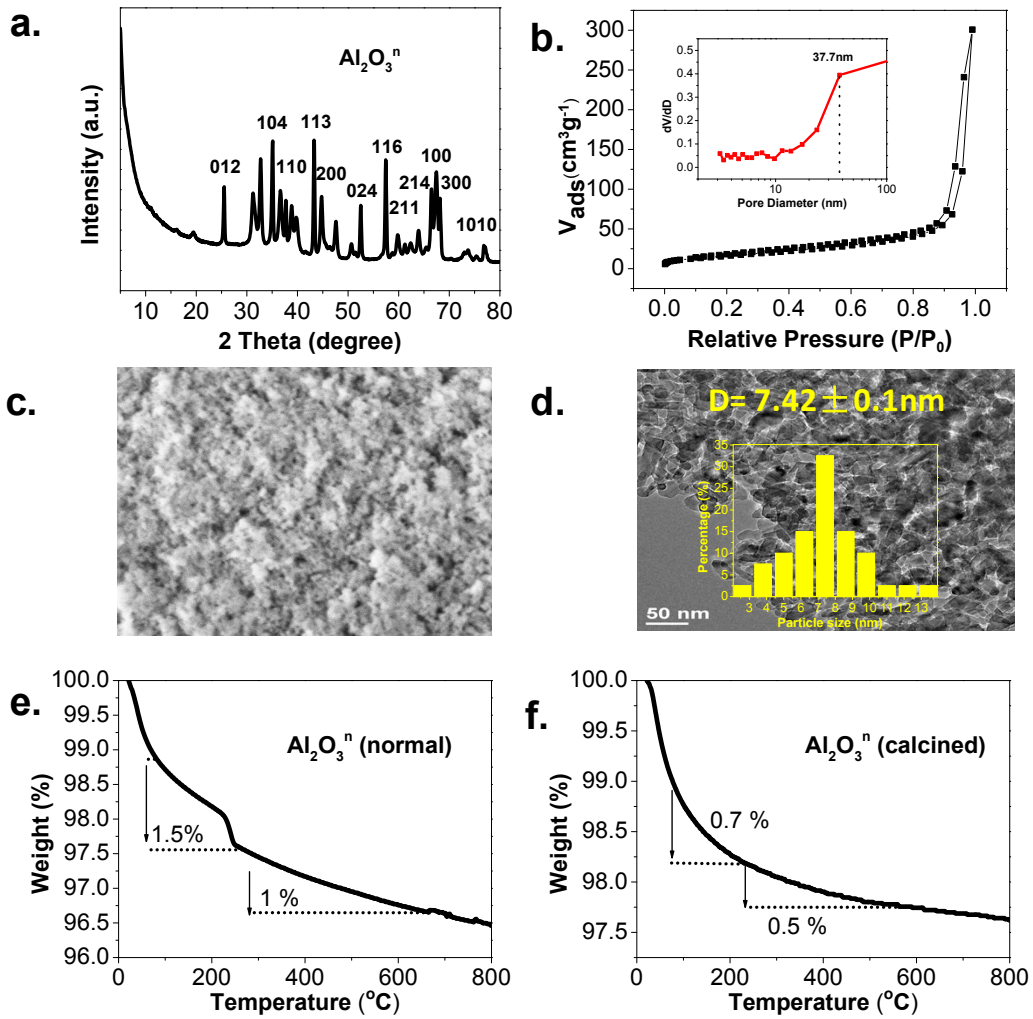

Fig. S1 (a) XRD pattern; (b) N_2 adsorption–desorption isotherms, inlet shows PSD curve; (c) typical SEM and (d) TEM images of $Al_2O_3{}^n$ catalyst; TGA curves of (e) $Al_2O_3{}^n$ (normal) and $Al_2O_3{}^n$ (calcined) catalysts.

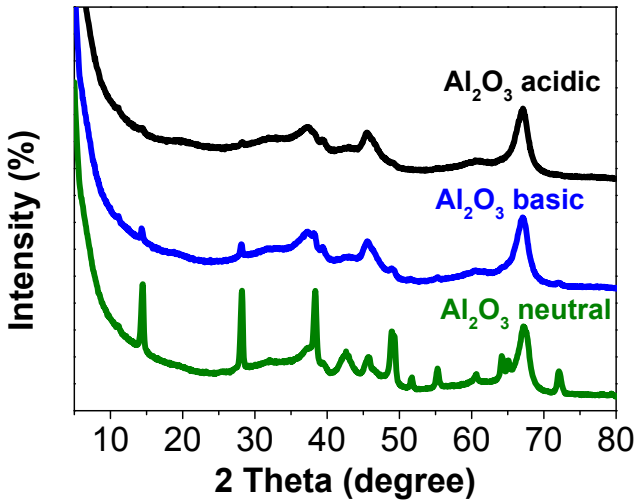

Fig. S2 (a) XRD patterns of Al_2O_3 acidic, Al_2O_3 basic and Al_2O_3 neutral catalysts.

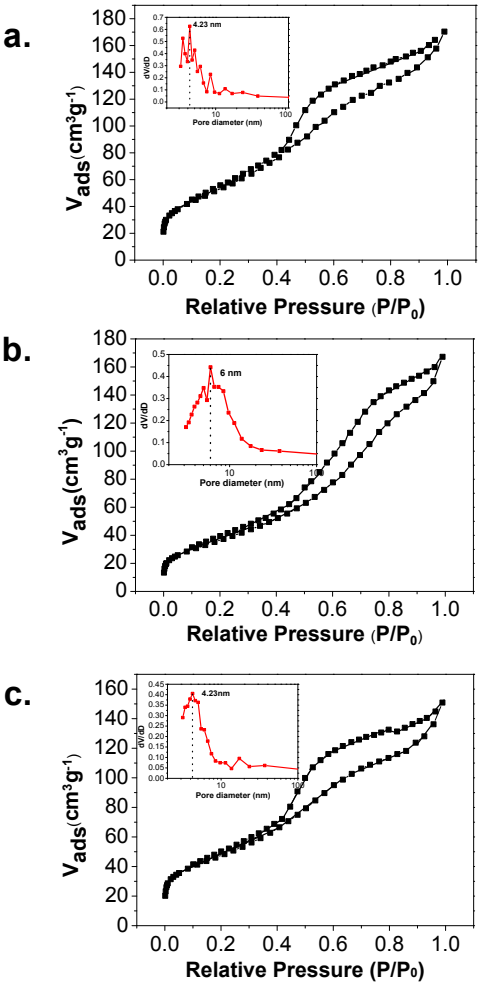

Fig. S3 BET curves of (a) Al_2O_3 acidic, (b) Al_2O_3 basic, (c) Al_2O_3 neutral and (d) ThO_2.

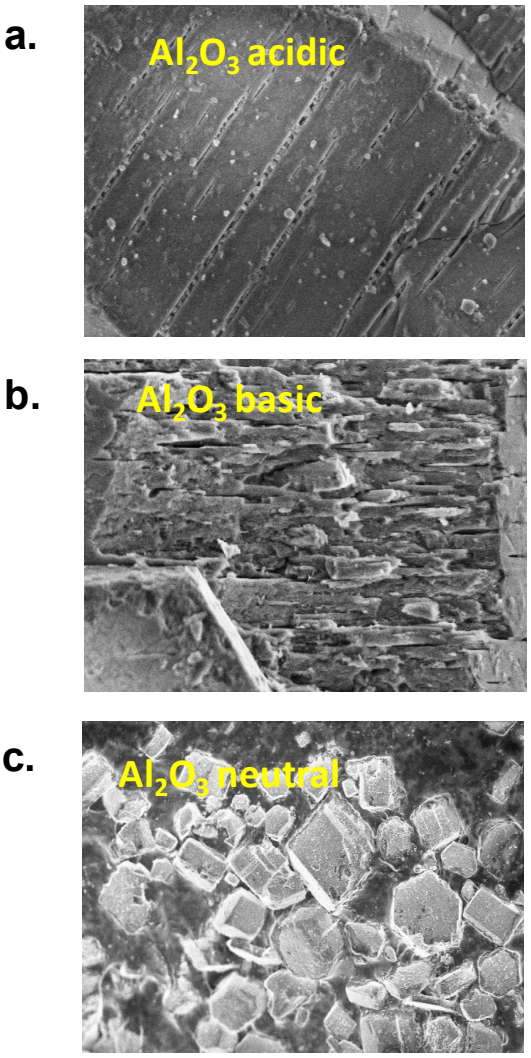

Fig. S4 SEM images of: (a) Al_2O_3 acidic, (b) Al_2O_3 basic, (c) Al_2O_3 neutral, and (d) ThO_2.

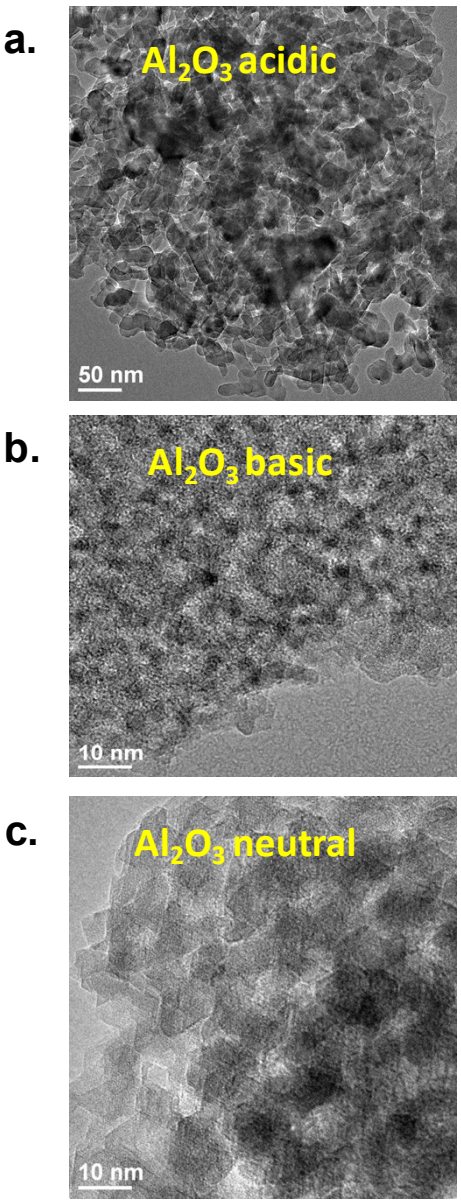

Fig. S5 TEM images of: (a) Al_2O_3 acidic, (b) Al_2O_3 basic and (c) Al_2O_3 neutral.

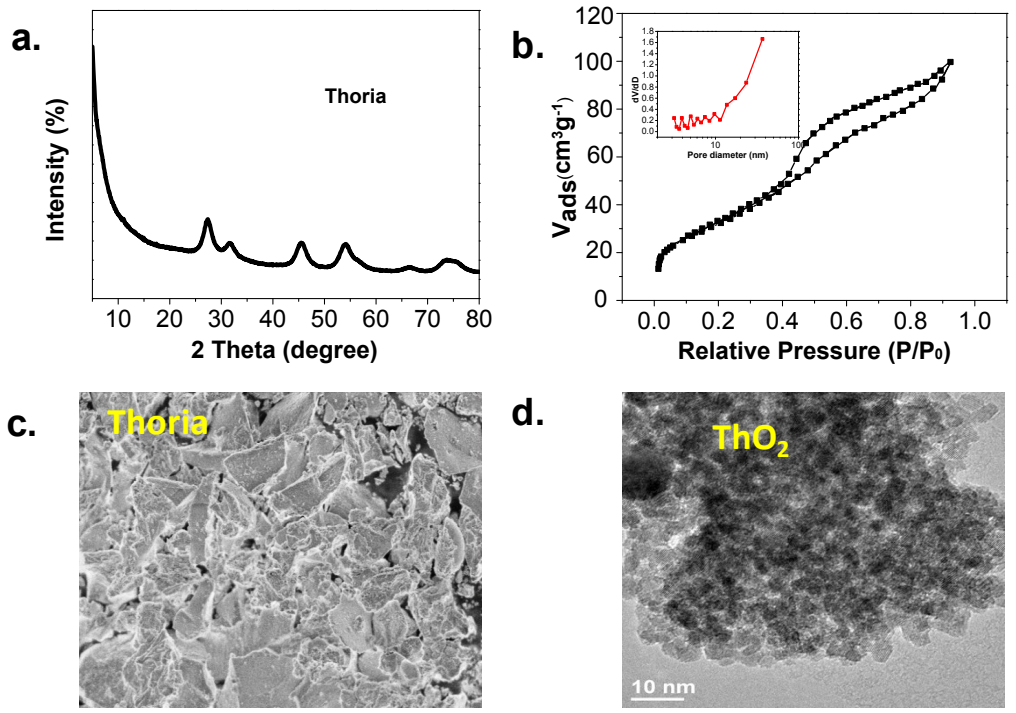

Fig. S6 (a) XRD pattern; (b) N_2 adsorption–desorption isotherms, inlet shows pore size distribution curve; (c) typical SEM and (d) TEM images of ThO_2 catalyst.

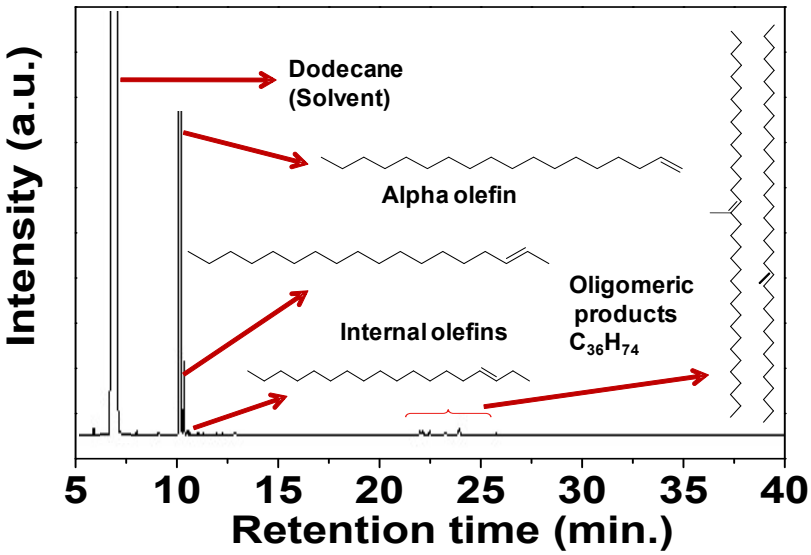

Fig. S7 GC spectra of liquid products obtained by selective dehydration of stearic alcohol. Reaction conditions: 0.6 g $Al_2O_3{}^n$, 0.1 g ThO_2, 3.0 g stearic alcohol, 300°C, 80 mL dodecane, 0.1 MPa N_2, 6 h.

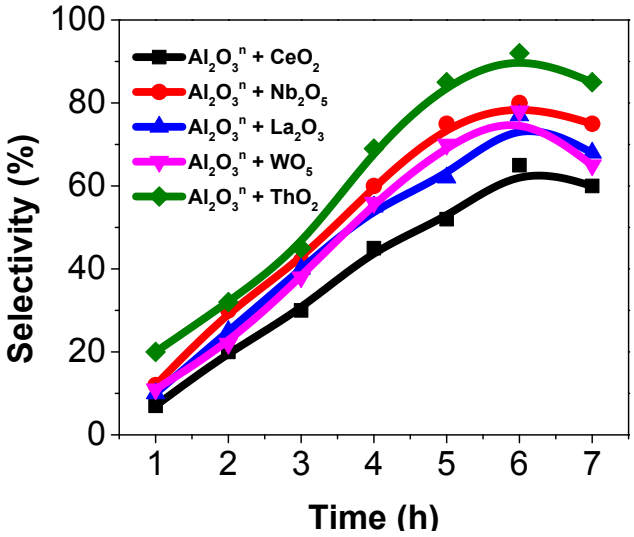

Fig. S8 The recorded selectivity changes as a function of reaction time. Reaction conditions: 3.0 g stearic alcohol, 0.6 g $Al_2O_3^n$ and 0.1 g MO_x (metal oxide) catalysts, 80 mL dodecane, 300°C, 0.1 MPa N_2.

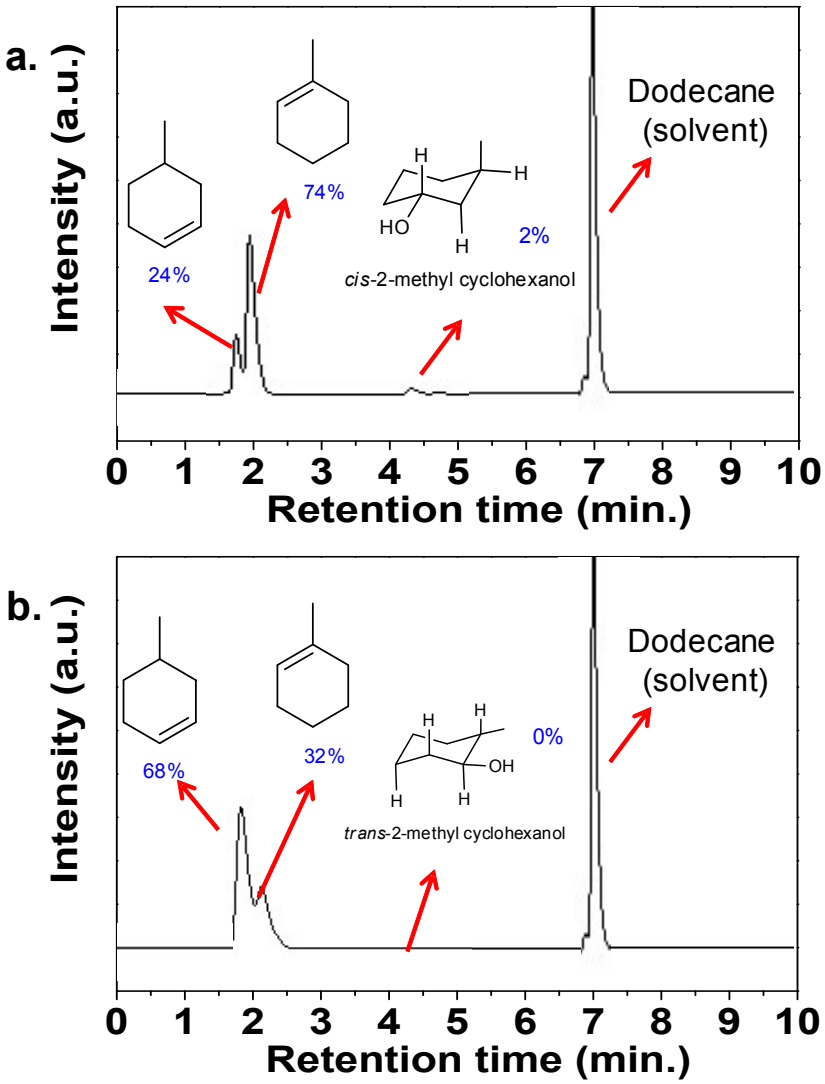

Fig. S9 GC spectra of liquid products identified for the dehydration of (a) *cis*-2-methyl cylcohexanol and (b) *trans*-2-methyl cyclohexanol. Reaction conditions: 0.3 g $Al_2O_3^n$, 3.0 g *cis*-2-methyl cyclohexanol, or 3.0 g *trans*-2-methyl cyclohexanol, 300°C, 80 mL dodecane, 0.1 MPa N_2, and 6 h.

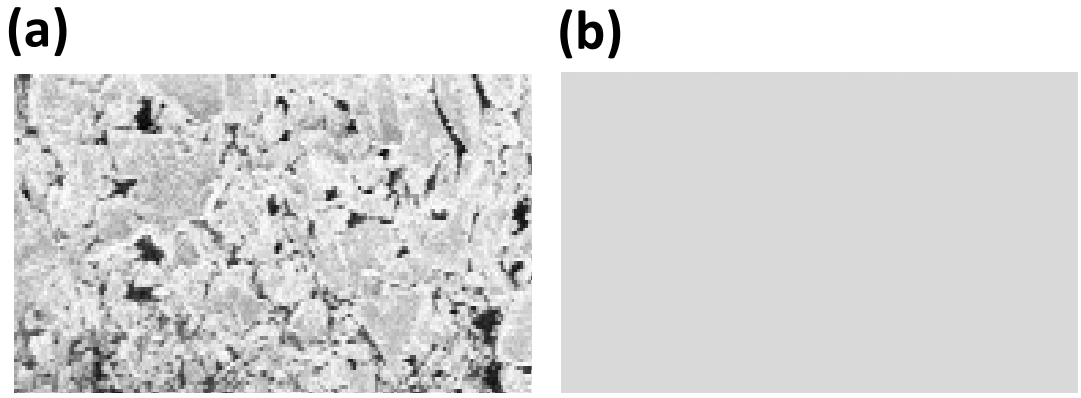

Fig. S10 SEM images of (a) fresh and (b) used ThO_2 catalyst.

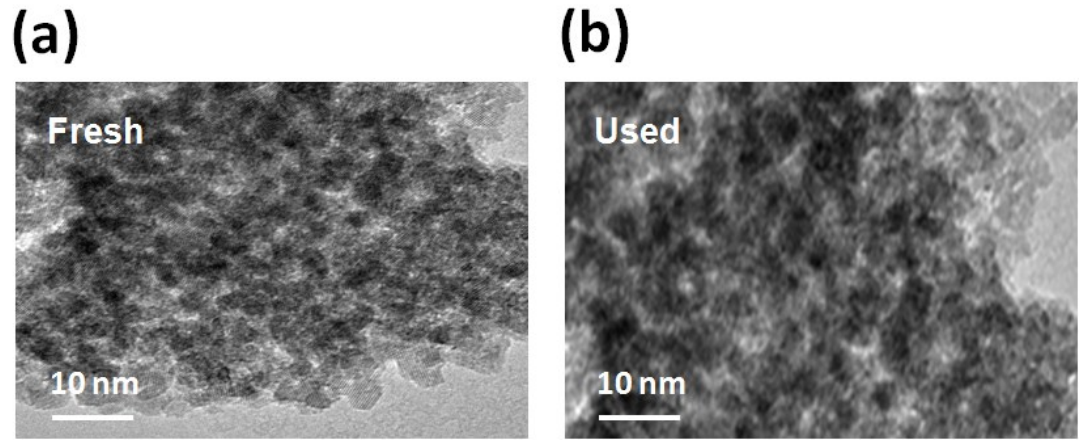

Fig. S11 TEM images of (a) fresh and (b) used ThO_2 catalyst.

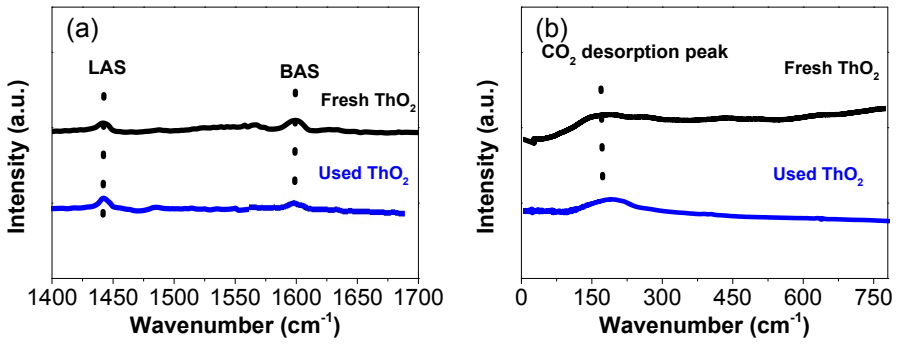

Fig. S12 *In situ* FTIR spectra of (a) pyridine adsorption and (b) CO_2 desorption on fresh and used thoria surfaces.

Table S1 Texture properties of Fresh and Used ThO_2 catalyst.

Catalyst	BET Surface area ($m^2 \bullet g^{-1}$)	Total pore volume ($cm^3 \bullet g^{-1}$)	Pore size (nm)	Acid conc. (IR-Py) ($mmol \bullet g^{-1}$) (LAS)	Base conc. (TPD-CO_2) ($mmol \bullet g^{-1}$) (LBS)
Fresh ThO_2	120	0.3210	3.2	0.047	0.053
Used ThO_2	116	0.2950	2.89	0.041	0.049