

Supporting Information

Methods and Materials

Catalyst preparation

γ -Al₂O₃ was obtained from STREM Chemicals and was pre-treated at 648 K in 60 cm³ (STP) min⁻¹ helium (Airgas, industrial grade) for 3 hours before use. Amorphous SiO₂-Al₂O₃ was obtained from Grace Davison (SIAL 3113, Si/Al=3.40) and was pre-treated at 723 K in 100 cm³ (STP) min⁻¹ air (Airgas, industrial grade) for 2 hours before use.

The tungstated alumina catalysts were prepared by incipient wetness impregnation of γ -Al₂O₃ with an aqueous solution of ammonium metatungstate (Sigma-Aldrich, 99.99% trace metals basis). After impregnation, the material was dried at 383 K overnight followed by calcination at 723 K for 5 hours in static air. Before reaction studies, the catalysts were further pre-treated at 648 K in 60 cm³ (STP) min⁻¹ helium (Airgas, industrial grade) for 3 hours. Catalyst containing 4 wt% WO₃ (calculated value) is denoted as 4W-Al.

The Magnesium Oxide (MgO) catalyst was obtained from NanoScale Materials, Inc. and was activated at 500K under 60 cm³ (STP) min⁻¹ helium (Airgas, industrial grade) for 3 hours before reaction studies.

Catalytic activity measurements

Reaction studies were conducted in 6.4 mm (0.25 inch, wall thickness = 0.028 inch) outer diameter stainless steel tube. The reactor was packed with 100mg ~ 2g of catalyst diluted with fine fused silica powder (Sigma-Aldrich). Two quartz wool plugs were used to seal both ends of the reactor. The reactor was heated by an insulated furnace (Applied Test Systems Series 3210), and temperature was monitored using a K type thermocouple (Omega) and was controlled with a PID temperature controller (Love Controls, Series 16A). An HPLC pump (Lab Alliance) was used to deliver aqueous γ -valerolactone solution to the reactor. For γ -octalactone and γ -undecalactone study, two syringe pumps were used to deliver water and lactone to the reactor due to the low solubility of γ -octalactone and γ -undecalactone in water. In the 1-butene isomerization study, 1-butene (Airgas, 5% in helium) was diluted with helium to obtain the targeted partial pressure needed in the feed. Gas flow was regulated using a mass flow controller (Brooks 5850 model), and the system pressure was maintained at 1 bar. The effluent liquid was collected in a gas-liquid separator maintained at room temperature and was drained periodically for analysis by HPLC or GC. The effluent gas was analyzed by two online GCs equipped with an FID (Shimadzu, 2010) detector and a TCD detector (Shimadzu GC-8A), respectively. Products were identified using a gas chromatograph/mass spectrometer system (Shimadzu GCQP-2010) and quantifications were performed using a gas chromatograph (Shimadzu GC-2010) equipped with an FID. Yields and conversions were defined as:

$$\text{Conversion} = \frac{\text{moles of lactones converted}}{\text{moles of lactones fed}}$$

$$\text{Selectivity} = \frac{\text{moles of product}}{\text{moles of lactones converted}}$$

$$\text{Yield} = \frac{\text{moles of product}}{\text{moles of lactones fed}}$$

Temperature-programmed desorption

Temperature-programmed desorption of NH₃ or CO₂ was used to determine the total acid site density or total basic site density, respectively. 100-200 mg of catalyst was loaded in a glass flow-through cell. Before NH₃ or CO₂ adsorption, samples were treated at 648 K for 1 h under flowing helium (120 cm³ (STP) min⁻¹) to remove adsorbed moisture. In the case of NH₃ adsorption, 1 mol% NH₃ in He (Airgas, 100 cm³ (STP) min⁻¹) was then passed through the sample at 423 K for ca. 45 min. Physisorbed NH₃ was removed by holding the sample at 423 K under flow helium (120 cm³ (STP) min⁻¹) for 45 min. In the case of CO₂ adsorption, 10 mol% CO₂ in He (Airgas, 100 cm³ (STP) min⁻¹) was then passed through the sample at 298K for ca. 45 min. Physisorbed CO₂ was removed by holding the sample at 298 K under flow helium (120 cm³ (STP) min⁻¹) for 45 min. Temperature-programmed desorption was performed using a temperature ramp of 10 K min⁻¹ from room temperature to 1073 K under flowing He (50 cm³ (STP) min⁻¹). The desorbed NH₃ or CO₂ was quantified by an online mass spectrometer (OmniStar).

N₂ adsorption

Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 analyzer. The samples were degassed at 423K for 5 hours prior to analysis. The specific surface areas of the materials were determined using the Brunauer-Emmett-Teller (BET) approach. The surface areas of catalysts used in this study are presented in Table S1.

Table S1. Surface area of catalysts used in this study

Catalyst	Surface Area (m ² /g)
SiO ₂ /Al ₂ O ₃	450
γ-Al ₂ O ₃	200
4W-Al	195
8W-Al	193
20W-Al	188
MgO	78

Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) was carried out using a Thermogravimetric Analyzer Q500 in oxygen atmosphere ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) with a rate of 20 K min^{-1} to 973 K . The temperature was maintained at 973 K for 10 minutes for each experiment. Approximately 42 mg of sample was used in each experiment.

FTIR spectroscopy of adsorbed pyridine

The ratio of Brønsted and Lewis acid sites on the solid acid catalysts studied was determined from infrared spectroscopic measurements of adsorbed pyridine. Approximately 10 mg of catalyst was placed in a 1.2 cm die and pressed into a self-supporting wafer, which was placed in a treatment/sampling cell where it was heated to 648 K under flowing dry helium (Airgas, industrial grade) for 2 h. A reference spectrum of the catalyst was then taken. Pyridine was introduced into the cell through a bubbler for 30 min at room temperature, followed by purging under flowing helium for 1 h before another spectrum was taken. The areas of the pyridine peaks at 1455 , and 1540 cm^{-1} , assigned to Lewis and Brønsted acid sites, respectively,^[1] were determined by subtracting the spectra of the sample before and after pyridine exposure. The Brønsted/Lewis acid ratios were obtained by normalizing the areas with integrated molar extinction coefficients reported in the literature: $1.67 \text{ cm} \mu\text{mol}^{-1}$ for Brønsted sites and $2.22 \text{ cm} \mu\text{mol}^{-1}$ for Lewis sites.^[1]

[1] C. A. Emeis, *J. Catal.* **1993**, *141*, 347-354.