

Electronic Supplementary Information

From glycerol to allyl alcohol: Iron oxide catalyzed dehydration and consecutive hydrogen transfer

Yong Liu, Harun Tüysüz, Chun-Jiang Jia, Manfred Schwickardi, Roberto Rinaldi, An-Hui Lu, Wolfgang Schmidt and Ferdi Schüth*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, 45470, Germany. Fax: +49 208-306-2995 E-mail: schueth@mpi-muelheim.mpg.de

Experimental Section

In a typical procedure to prepare Fe_2O_3 with high surface area, 0.33 ml of $0.36 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{H}_2\text{PO}_4)_3$ aqueous solution (Fluka) was added to 15.1 ml of $2.33 \text{ mol}\cdot\text{L}^{-1}$ $\text{Fe}(\text{NO}_3)_3$ solution (Sigma-Aldrich). The mixture was then placed in an oven and heated to 380°C with a heating rate of $4^\circ\text{C}\cdot\text{min}^{-1}$. After 1 hour, the brown powder was collected in a 10 ml bottle and cooled down to room temperature. Finally, 3.04 g of product was obtained. To synthesize Fe_2O_3 with high, reproducible BET surface area without addition of $\text{Al}(\text{H}_2\text{PO}_4)_3$, $0.25 \text{ mol}\cdot\text{L}^{-1}$ Na_2CO_3 aqueous solution was added dropwise to 100 ml of $0.1 \text{ mol}\cdot\text{L}^{-1}$ $\text{Fe}(\text{NO}_3)_3$ solution under stirring at 80°C , until the pH value reached 8.2. After filtration and drying, the precipitate was calcined at 350°C for 6 h.

In a typical procedure to synthesize MgAl_2O_4 with high surface area, 2.54 mL of $3.83 \text{ mol}\cdot\text{L}^{-1}$ $\text{Mg}(\text{NO}_3)_2$ aqueous solution was mixed with 7.98 mL $2.43 \text{ mol}\cdot\text{L}^{-1}$ $\text{Al}(\text{NO}_3)_3$ aqueous solution and 6.7 mL of $4.41 \text{ mol}\cdot\text{L}^{-1}$ citric acid aqueous solution. 6.7 g of carob

tree cernel flour was then added to the mixture to form a gel. The gel was then transferred to an oven and heated up to 550 °C at a heating rate of 4 °C·min⁻¹. After remaining at this temperature for 1 hour, 1.43 g of the MgAl₂O₄ product with amorphous structure and a BET surface area of 175 m²·g⁻¹ was obtained.

In a typical procedure to synthesize MgO with high surface area, 6 g of corn starch was added to 9 mL of 3.83 mol·L⁻¹ Mg(NO₃)₂ aqueous solution under stirring. The mixture was then transferred to an oven and heated up to 550 °C at a heating rate of 4 °C·min⁻¹. After remaining at this temperature for 1 hour, 1.41 g of the MgAl₂O₄ product with periclase structure and a BET surface area of 155 m²·g⁻¹ was obtained.

The conversion of glycerol to allyl alcohol was carried out in a stainless steel fixed bed reactor (7 mm inner diameter). In a typical reaction, 150 mg of Fe₂O₃ was mixed with 2 g of quartz (both sieved, 250-500 µm) and put into the tube reactor. After the temperature of the reactor had reached 320 °C, a 35 wt% glycerol aqueous solution was pumped in at a flow rate of 1 mL·h⁻¹ using a syringe pump (Pharmacia Fine Chemicals P-500). Nitrogen with a flow rate of 15 mL·min⁻¹ was used as carrier gas and after 1 hour, the products were collected hourly in ethanol cooled by an ice-water trap. The samples were analyzed with a HP 5890 Series II gas chromatograph equipped with a DB-WAXetr column (J&W, bonded and cross-linked polyethyleneglycol, 0.25 mm inner diameter, 15 m long) and an FID detector. Butanetriol was selected as the internal standard for the quantification of glycerol and 1-propanol was selected as the internal standard for the quantification of acrolein and allyl alcohol. Since 1-propanol could also be a product of the full hydrogenation of acrolein, all samples were also checked without standard and no 1-propanol was detected in all cases. For reactions between acrolein and different alcohols, acrolein was premixed with the corresponding alcohol at a molar ratio of 1:1, all

mixtures were pumped through the reactor under the same conditions. Since crotonaldehyde and cinnamaldehyde have low solubilities in both glycerol and water, glycerol solution and the aldehyde were pumped using two individual pumps to the same line with 2 meters dipped in a supersonic bath to form a “homogeneous” mixture before entering the reactor. Butanetriol works as internal standard for cinnamaldehyde and cinnamylalcohol, and 2-butanol for crotonaldehyde and crotylalcohol.

BET surface area was measured by nitrogen adsorption on an ASAP 2010 adsorption analyzer (Micromeritics). X-ray diffraction patterns were recorded with a Stoe Stadi P diffractometer. TEM images were obtained with a Hitachi H-7500 microscope. Thermogravimetric analysis was performed on a NETZSCH STA 449C thermobalance.

Carbon balance

Figure S1. gives an original GC spectrum of a representative product. As introduced in the manuscript, quantitative analysis was carried out for glycerol, allyl alcohol, hydroxyacetone and acrolein, which typically add up to 50~60% of the total carbon balance. However, if one simply adds the area of all the other unquantified peaks to the quantitative values, 90.36~98.33% of the total carbon balance can be reached, which indicates that the total carbon balance is actually in an acceptable range. However, the composition of the unknown compounds is extremely complicated. For example, in the spectrum shown in Fig. S1, more than 60 peaks other than the known products are detected as well. The identification of these compounds is unfortunately impossible.

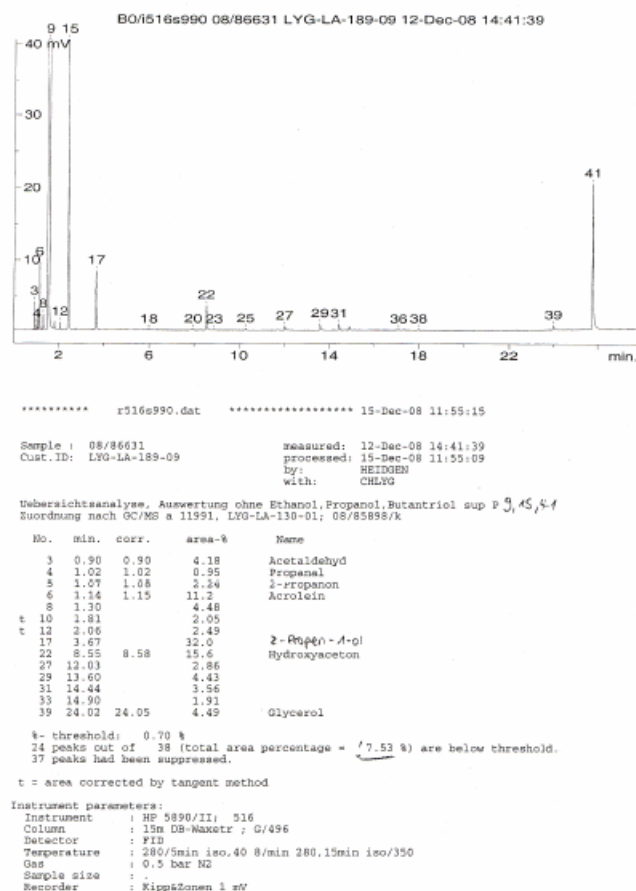


Figure S1. Original GC result of a representative product

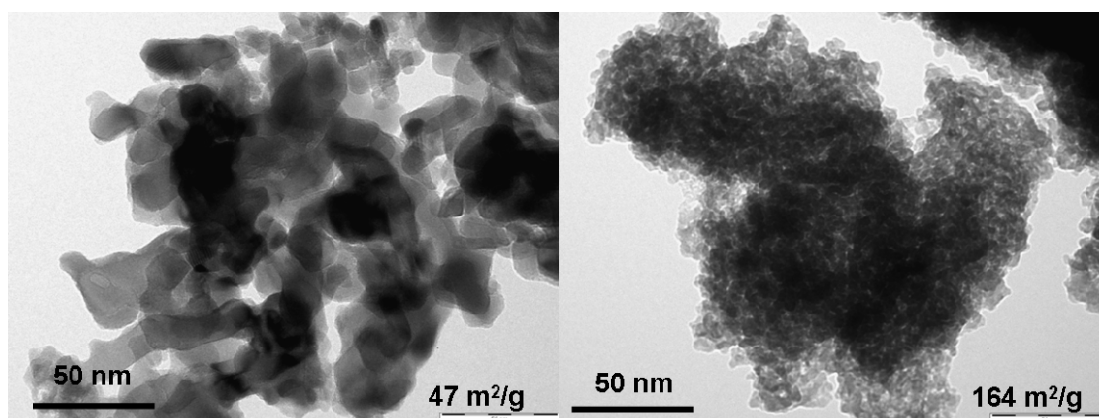


Figure S2. TEM images of Fe_2O_3 materials (a) without the addition of $\text{Al}(\text{H}_2\text{PO}_4)_3$ (b) with 2 mol% of $\text{Al}(\text{H}_2\text{PO}_4)_3$.

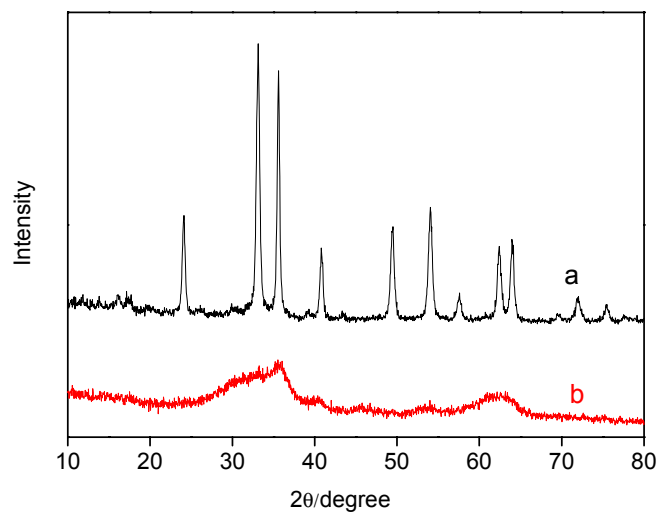


Figure S3. XRD patterns of Fe_2O_3 materials (a) without the addition of $\text{Al}(\text{H}_2\text{PO}_4)_3$ (b) with 2 mol% of $\text{Al}(\text{H}_2\text{PO}_4)_3$

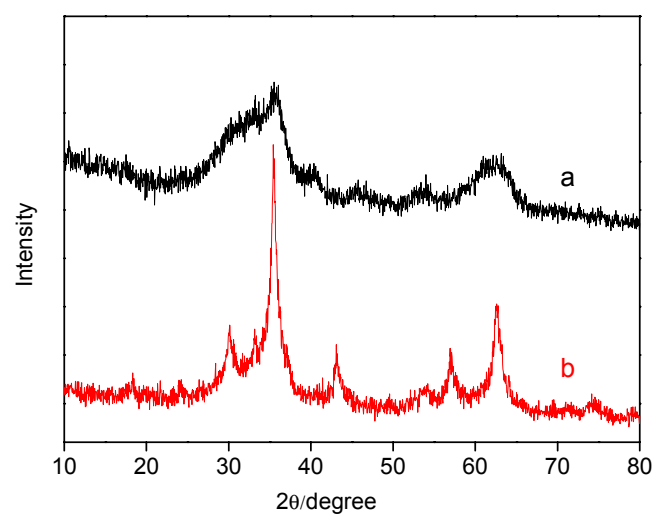


Figure S4. XRD patterns of Fe_2O_3 materials (a) before reaction, (b) after 24 hours

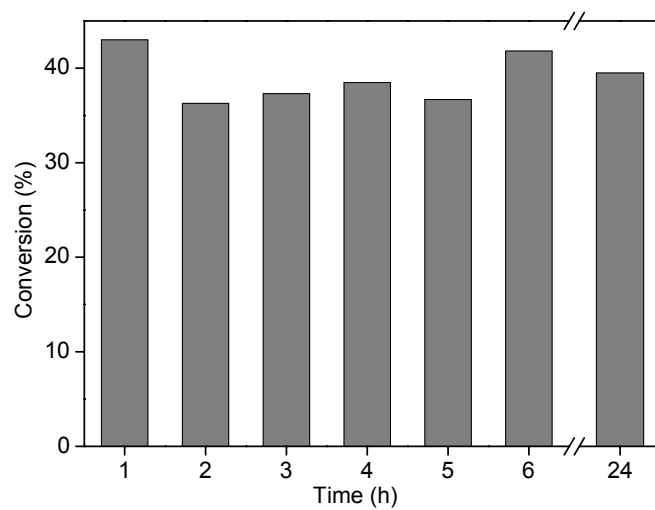


Figure S5. Glycerol conversion at 320°C with a GHSV of 413 h⁻¹

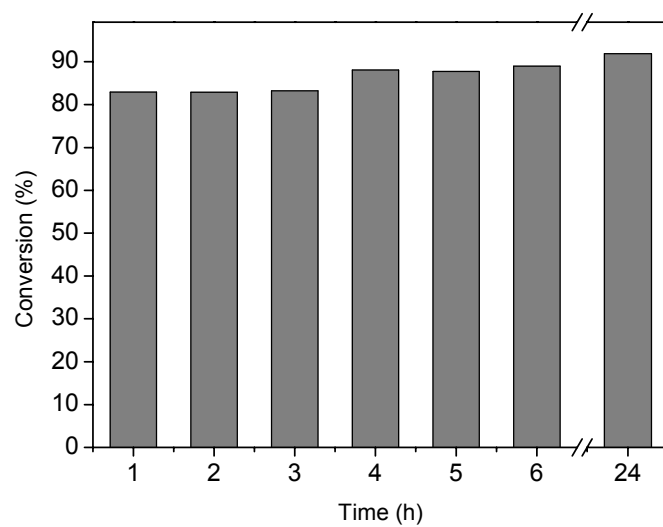


Figure S6. Glycerol conversion of the reused catalyst at 320 °C with a GHSV of 96.4 h⁻¹

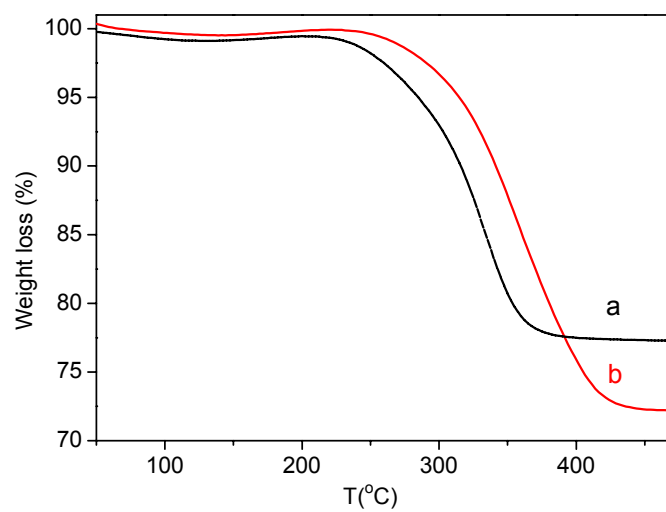


Figure S7. TG results of (a) catalyst after 24 hours, (b) catalyst after 72 hours.

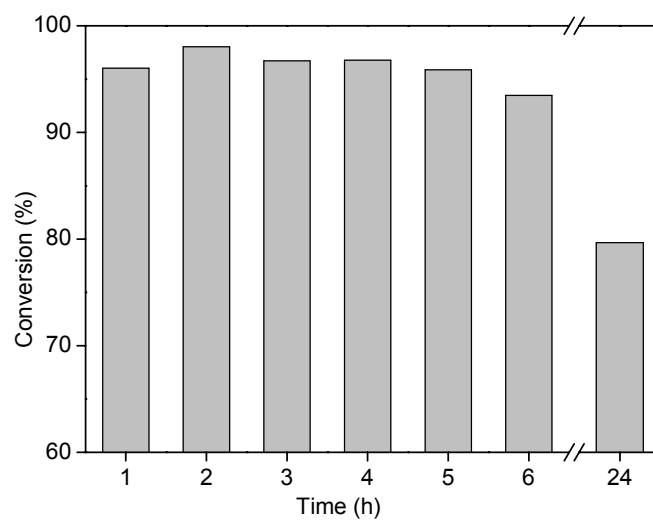


Figure S8. Glycerol conversion using Fe_2O_3 without $\text{Al}(\text{H}_2\text{PO}_4)_3$ as catalyst (320°C , GHSV 96.4 h^{-1}).

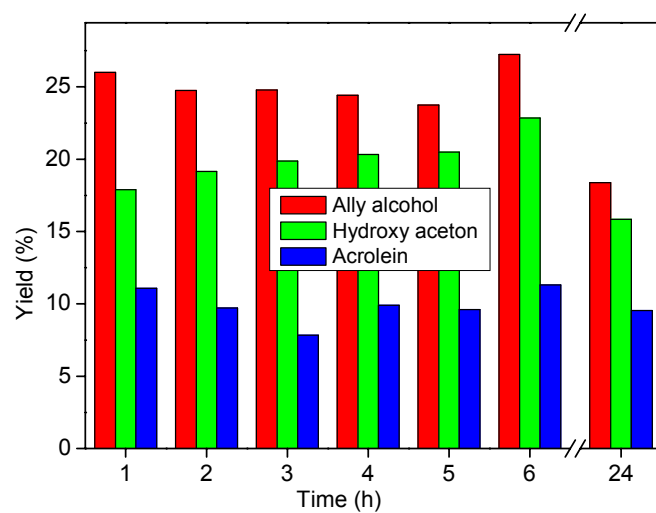


Figure S9. Product distribution of glycerol conversion using Fe_2O_3 without $\text{Al}(\text{H}_2\text{PO}_4)_3$ as catalyst (320°C , GHSV 96.4 h^{-1}).