Supporting Information

Glycerol Dehydration to Acrolein Catalyzed by ZSM-5 Zeolite in Supercritical Carbon Dioxide Medium

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Supporting Information

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1. Catalyst material

ZSM-5 (CBV 2314) in its ammonia form was purchased from Zeolyst International (Valley Forge, PA, USA). ZSM-5 in its hydrogen form (HZSM-5) was obtained by calcining the purchased ZSM-5 at 500 °C in air atmosphere for 4 h. Then the zeolite powder was pelletized at 35 MPa for 5 min, followed by crushing and sieving to 40-60 mesh (0.25-0.42 mm). Before use, the HZSM-5 particles were calcined again at 500 °C in air atmosphere for 4 h to remove impurities.

2. Catalytic reaction test

The setup of reaction system is depicted in Fig. SI 1. Reaction conditions have not been systematically optimized due to long reaction time.

3. Catalyst characterization via NH₃-TPD and titration

Temperature-programmed desorption of ammonia (NH₃-TPD) was conducted in a ChemBET Pulsar TPR/TPD unit (Quantachrome Instruments, Boynton Beach, FL, USA) equipped with a thermal conductivity detector (TCD) to measure the NH₃ desorption. A quartz sample U-tube loaded with 0.1 g of catalyst was pretreated from room temperature to 650 °C at a rate of 10 °C/min with helium flow (27 mL/min) and maintained at the end temperature for 1 h.
Then the sample was cooled down to 150 °C and titrated by injecting known amount of ammonia pulses until the saturation point was passed, followed by flushing with helium for 1 h to remove physically adsorbed ammonia. Subsequently, the sample was heated to 650 °C at a rate of 10 °C /min with helium flow (27 mL/min), and maintained at 650 °C for 30 min. The TCD detector recorded the signal of desorbed ammonia as a function of temperature.

The acquired NH₃-TPD curve (Fig. SI 2) was background corrected and deconvoluted to analyze the distribution of acid strength. The deconvolution was performed using the built-in software of TPRWin to resolve the curve into three components (Split-Gaussian method) centered around 250 °C, 350 °C, and 450 °C, representing weak, medium, and strong acids respectively. The results are presented in Table SI 1 together with the data of manufacturer specifications.

![NH₃-TPD profile of fresh HZSM-5 catalyst](image)

**Fig. SI 2.** NH₃-TPD profile of fresh HZSM-5 catalyst

| ZSM-5 determined by NH₃-TPD | Acid strength by deconvoluting NH₃-TPD curve |
|-----------------------------|------------------------------------------|
| Total acid (mmol/g)          | Weak (%)                                 |
| 0.567                       | 36.7                                    |
| Weak (%)                    | Medium (%)                               |
| 42.8                        | Strong (%)                               |
| Strong (%)                  | 20.5                                    |

**Table SI 1.** Specification of ZSM-5 and acidic properties
4. Catalyst characterization via DRIFTS and infrared pyridine adsorption

To analyze chemical depositions on the spent HZSM-5, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was conducted using a Varian 3100 FTIR spectrometer equipped with a research grade diffuse reflection accessory (DiffusIR™, PIKE Technologies, Madison WI, USA). A catalyst sample (15 mg) was diluted with KBr in a proportion of 1:25 and loaded into a DRIFTS cell. IR spectra of fresh and spent HZSM-5 (Fig. 2b) were recorded at room temperature with 128 scans and a resolution of 4 cm⁻¹, revealing supporting information of the depositions on the spent HZSM-5. The most important regions of the FTIR spectra are (i) 1300–1700 cm⁻¹, and (ii) 2800–3100 cm⁻¹. The vibrations in the first range correspond to polycondensed aromatics, conjugated olefins, plus some bending modes of aliphatics, while the second range corresponds to aliphatics (asymmetric and symmetric stretching) and single-ring aromatics [1]. According to Yoda et al. [2], glycerol is adsorbed to the zeolite as confirmed by the IR band at 1461 cm⁻¹. The interaction between the glycerol with the bridging OH groups on the zeolite is observed around 2900 cm⁻¹ and a broad band around 2478 cm⁻¹. The adsorption of water on the bridging zeolite OH groups also gives rise to the bands around 2900 cm⁻¹ and 2478 cm⁻¹. Some bands can also be observed between 1600 cm⁻¹ and 1700 cm⁻¹, which are considered as νC=O and νC=C of the products of glycerol dehydration. Two strong peaks appeared at 1380 cm⁻¹ and 1657 cm⁻¹ are attributed to adsorbed acetol.

The same device was used to perform infrared pyridine adsorption for the analysis of acid types on HZSM-5. Before pyridine adsorption, a self-supported sample without KBr dilution was filled in a DRIFTS cell and pretreated at 400 ºC under vacuum and flow of helium for 2 h. The sample was cooled down to room temperature and then pyridine vapor was admitted to the cell through a vacuum line at room temperature for 2 h. After evacuating the weakly-bound pyridine at 150 ºC for 2 h, the sample was cooled down to room temperature and the IR spectra were recorded with 128 scans and a resolution of 4 cm⁻¹. It should be pointed out that the spent catalyst was diluted with quartz sand of the same size that was difficult to be separated out. Therefore, it is difficult to compare the pyridine adsorptions by directly comparing the IR peak height or area. Nonetheless, the ratio of the peak height or area clearly shows that Bronsted acids decreased after reaction, especially at the pyridine–Brønsted acid site complex as indicated by IR vibrations at 1636 and 1609 cm⁻¹ (Fig. 2a). The IR spectra were interpreted according to Kim et al. [3] and Stevens et al. [4].
5. Determination of coke amount via thermogravimetry

Thermogravimetric and differential thermal analysis (TG-DTA) of the spent catalysts was performed using a Perkin Elmer Diamond TG/DTA system (Waltham, MA, USA), and the results are shown in Fig. SI 3. Using 15 mg of spent catalyst, the temperature was programmed from room temperature up to 750 °C at a heating rate of 5 °C/min with a flux of air at 20 mL/min. Before the test, all samples were washed with deionized water and centrifuged for three times, and then the collected solids were dried at 105 °C overnight.

![Graphs showing TG-DTA analysis](image)

**Fig. SI 3.** Results of TG-DTA analysis of spent HZSM-5

Water was inadvertently adsorbed onto the HZSM-5 in earlier runs during the handling and transfer of the samples, as indicated by the first peak around 150 °C (this was corrected in Run 2). Therefore, this peak was not used for the calculation of coke amount. For the runs in SC-CO₂, the decomposition temperature of stable coke was approximately centered at ~530 °C, while for the gas-phase reaction, this peak shifted ~50 °C higher, indicating that “harder” coke was formed in the gas-phase reaction.
6. Analysis of product distribution and coking using GC and GC-MS

The gas and liquid samples were quantified using a Agilent 7820A gas chromatography equipped with a FID detector (GC-FID) and a VB-WAX capillary column (Valco Instruments, Houston, TX, USA). To ensure the identification of the products and coke precursors, Gas Chromatography Mass Spectrometry (GC-MS) was also carried out using a HP 5890A GC-MS system equipped with the same capillary column.

Glycerol conversion, product selectivity and yield, and carbon balance are defined below. The carbon balance in Table 1 was calculated based on the summation of the gas products and the aqueous products.

\[
\text{Glycerol conversion (mol\%) } = \left(1 - \frac{\text{moles of glycerol collected in aqueous sample}}{\text{moles of glycerol in feed}} \right) \times 100\% \quad (1)
\]

\[
\text{Product yield (mol\%) } = \left( \frac{\text{moles of carbon in gas sample or aqueous sample}}{\text{moles of carbon in glycerol feed}} \right) \times 100\% \quad (2)
\]

\[
\text{Product selectivity (mol\%) } = \left( \frac{\text{product yield}}{\text{glycerol conversion}} \right) \times 100\% \quad (3)
\]

\[
\text{Carbon balance (mol\%) } = \left( \frac{\text{moles of carbon in all quantified compounds}}{\text{moles of carbon in glycerol feed}} \right) \times 100\% \quad (4)
\]

Typical GC spectra for the quantification of gas samples and aqueous samples are shown in Fig. SI 4 and Fig. SI 5, respectively. Distribution of major byproducts is shown in Fig. SI 6.
**Fig. SI 4.** Typical GC spectrum of gas samples
(Shown here is sample collected at TOS = 72 h)

**Fig. SI 5.** Typical GC spectrum of aqueous samples
(Shown here is sample collected at TOS = 72 h. The four small peaks around 14 min were identified as dioxane derivatives including 1,4-dioxane-2,6-diyldimethanol and 1,4-dioxane-2,5-diyldimethanol for which 1,4-dioxane-2,5-diyldimethanol was used as standard calibration.)
Fig. SI 6. Distribution of major reaction byproducts (Shown here is the average yield between TOS of 222–246 h)

The oil phase in liquid product was attached to sidewall inside the collection vial. The complex chemicals were dissolved in methanol and qualitatively analyzed using GC-MS (Fig. SI 7).

Fig. SI 7. Typical GC-MS spectrum of oil-phase samples (Shown here is sample collected at TOS = 296 h)
The spent catalyst was extracted with methanol and the extract was qualitatively analyzed using GC-MS (Fig. SI 8).

![GC-MS spectrum of methanol extract from spent HZSM-5 catalyst](image)

**Fig. SI 8.** GC-MS spectrum of methanol extract from spent HZSM-5 catalyst

7. Characterization of catalysts via TEM

Transmission electron microscopy (TEM) was performed on a ZEISS Libra 200 MC TEM/STEM system, and the results are shown in Fig. SI 9. The clear lattice fringes confirm the high crystallinity of the zeolite particles, and the crystallinity was well preserved after the 528-hour long reaction.
Fig. SI 9. TEM micrograph of fresh HZSM-5 (A) vs. spent HZSM-5 after 528 h reaction (B)

References

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[4] R. W. Stevens Jr, S. S. C. Chuang, B. H. Davis, *Applied Catalysis A: General* **2003**, *252*, 57-74.