High Temperature Decomposition of Brønsted Acid Sites in Galliumsubstituted Zeolites

Khalid A. Al-majnouni, Nathan D. Hould, William W. Lonergan, Dionisios G. Vlachos* and Raul F. Lobo*

Supporting Information

The SEM images of Ga-ZSM-5 and Ga-beta materials are depicted in Figure S1. The Si to Ga ratio is 16 for Ga-Beta and 29 for Ga-ZSM5 as determined by EDX. Notice that there is no much change in the morphology and composition of Ga-Beta after heating to 800 °C.

S1. MS-TPD Control Experiments

We carry out control experiments to verify that the hydrogen evolves primarily from the zeolite samples. We monitor the evolved gases from the empty quartz tube and quartz tube filled with quartz ships in the range of 550 to 800 °C. The quartz ships are used to hold the sample bed since it is stable at the testing temperature. We follow m/e of 2 and 18 for H₂ and H₂O respectively. We can not compare quantitatively the ion current of H₂ to H₂O directly since they have different specific concentration factor. We can compare however the ion current of H₂ or H₂O from different samples since all measurements are recorded at the same conditions, e.g ionization voltage.

Figure S2 shows that there is no H_2 or H_2O evolved from the empty reactor. The same result is observed for the sample with quarts ships (not shown here). Further control experiments are reported in the supporting information of Nash et. al. for other samples considered such as mordenite in Na form. We conclude that the H_2 and H_2O detected by MS come from the zeolite samples. Figure S3 shows a snapshot of the ion current in analog signal versus m/e taken during Ga-Beta dehydroxylation. The H_2 (m/e=2) and H_2O (m/e= 17 & 18) are observed clearly in well resolved peaks. The m/e of 4 is for the He which is used as inert.

S2. FTIR Control Experiment and D₂ Experiments

The IR gas system was modified by including a moisture trap "safe glass moisture trap from Chromatography Research Supplies" in the line of H₂ to remove any water impurities that could be associated with H_2 in the tank. We repeated the acid site recovery experiment and observe that both silanol and BAS are partially recovered (Figure S4). The relative area of BAS is increased by 27% compared to 32% before the moisture trap was installed. Therefore we conclude that the recovery of BAS and silanol group is in indeed from the H_2 gas.

Figure S5 shows the exchange of BAS from Si-OH-Ga to Si-OD-Ga after exposing the sample to 3% D₂ in N₂ at 500 °C. Both the silanol groups and the BAS absorption area decrease after the exchange. This is due to the difference in the molar absorption coefficient between OH and OD. To study the reactivity of D₂ with the dehydroxylated samples, dehydroxylated Ga-ZSM5 was exposed to D₂. The residual BAS were exchanged for OD but there is no BAS recovery. The same result is also obtained when a Ga-ZSM5 with slightly lower Si/Ga ratio is used. The silanol groups do recover in a small fraction in these experiments (Figure S6). See the main text for more details.

S3. Decomposition of Hydroxyl Groups Monitored by FTIR

The hydroxyl groups in zeolite represent mainly the silanol groups and the Bronsted acid sites. Figure S7 shows the normalized integrated area of BAS and silanol group plotted against temperature. The best fit models are shown as inserts in the figures. These groups do not decompose at the same rate with respect to temperature. In fact, the BAS decomposes linearly whereas the silanol group decomposes exponentially with temperature. It is expected that not all BAS have the same stability since there are at least nine T-atoms with potentially different geometry in zeolite beta and more in zeolite ZSM-5. The least energetic bonds are expected to decompose first. The rate of decomposition of BAS is also related to the pathway, e.g dehydrogenation or dehydration. See text for more details.

S4. EXAFS Fittings

Figure S8 shows the Fourier transform EXAFS magnitude in radial space for Ga-Beta and Ga-ZSM5 in as-synthesis and ammonium forms plotted along with the fit. These spectra are measured at room temperature. In all cases, we fixed the passive reduction factor at 0.95 while the other parameters are optimized including the coordination number. For gallium a coordination number of four is obtained in all cases. Therefore, we fixed the coordination number at four and we reported the interatomic distance and the Debye-Waller factor to keep consistence throughout the fitting with high temperature data.

Figure S9 shows the reduced chi-square of the fits of Ga-Beta and Ga-ZSM5 calcined at 550 and 850 °C plotted against either distorted (550 °C) or symmetric (850 °C) tetrahedral coordination environments. The optimal fit is the one with the minimum reduced chi-square. Figure S10 shows the corresponding Fourier transform EXAFS magnitude in radial space of the optimal fit.

Figure Captions

Figure S1

SEM images of as-synthesis a) Ga-Beta & b) Ga-ZSM5.

Figure S2

MS-TPD traces of empty quartz tube reactor. There is no H_2 evolved from the reactor when it is heated from 550-800 °C in a flowing He under atmospheric pressure.

Figure S3

A snapshot of ion current scan in analog signal is taken for Ga-Beta during dehydroxylation process.

Figure S4:

FTIR spectra for Ga-ZSM5 exposed to H_2 after excessive dehydroxylation to study the effect of the hydrogenation on BAS after installing a moisture trap.

Figure S5:

FTIR spectra for Ga-ZSM5 exposed to D_2 after calcination at 500 °C in order to exchange the Si-OH-Ga to Si-OD-Ga

Figure S6:

FTIR spectra for Ga-ZSM5 exposed to D_2 after dehydroxylation to study the reactivity of D_2 with the dehydroxylated sample

Figure S7

The normalized integrated area of a) BAS vibration & b) silanol vibration plotted as a function of temperature. The line represents the fitting of the experimental data. The fitting models and the parameters are inserted in the graph.

Figure S8

The k^3 -weighted Fourier transform EXAFS magnitude for Ga-Beta and Ga-ZSM5 in assynthesis and ammonium forms taken at room temperature along with the fittings. No phase correction was applied and fitting range was 1-2 Å

Figure S9

The reduced χ -square as a function of weighted fraction of distorted or symmetrical tetrahedral species for Ga-Beta and Ga-ZSM5 heated at 530-550 and 850-860 °C. The global minimum is taken as the optimal fitting.

Figure S10

The k^3 -weighted Fourier transform EXAFS magnitude for Ga-Beta and Ga-ZSM5 calcined at 530-550 and 850-860 °C along with the fittings that correspond to minimum reduced χ -square. No phase correction was applied and fitting range was 1-2 Å



Figure S1



Figure S2





Figure S4



Figure S5







Figure S7



Figure S8







Figure S10

