Electronic Supplementary Information

High-loading Ga-exchanged MFI zeolites as selective and coke-resistant catalysts for nonoxidative ethane dehydrogenation

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EDH reactions

The conversion, selectivity, and carbon balance values were determined based on the following equations.

$$Conv.\,[\%] = \frac{[ethane]_{init} - [ethane]}{[ethane]_{init}} \times 100$$

$$Selec.\,[\%] = \frac{[ethylene]}{[ethylene] + [methane]} \times 100$$

$$Carbon\ balance\,[\%] = \frac{([ethane] + [ethylene] + [methane])}{[ethane]_{init}} \times 100$$

Note that the gas line from the reactor to GC was heated at 200 °C and that the amounts of other products, such as C4 and C6 hydrocarbons, are relatively low compared to ethylene and methane in all the case. The deactivation rate based on a first-order deactivation mechanism (k_d^{-1}) was calculated according to the previous paper as follows:

$$k_d(h^{-1}) = \frac{ln\left(\frac{1 - Conv._{end}}{Conv._{end}}\right) - ln\left(\frac{1 - Conv._{start}}{Conv._{start}}\right)}{t}$$

where $Conv._{start}$ and $Conv._{end}$ denote the conversion at the start and the end, and t represents the reaction time in hours. Lower k_d values are indicative of slower deactivation. For the reuse experiment, the Ga-MFI-1.0(800) after 20 h reaction was treated with 10 mL/min of 5% O_2/He at 600 °C for 90 min to calcine the coke and then treated with 10 mL/min of 10% H_2/He to regenerate the Ga hydrides in MFI. The dehydrogenation was performed in the same reaction conditions for 20 h. The kinetic study was conducted in the following reaction conditions. For the formation rate dependency on $p(C_2H_6)$: $p(C_2H_6)$ = 0.02–0.08, balanced with He (total flow rate: 50 mL/min), and 600 °C. For the formation rate dependency on reaction temperature: $p(C_2H_6)$ = 0.04, balanced with He (total flow rate: 50 mL/min), and 550–610 °C.

Figures

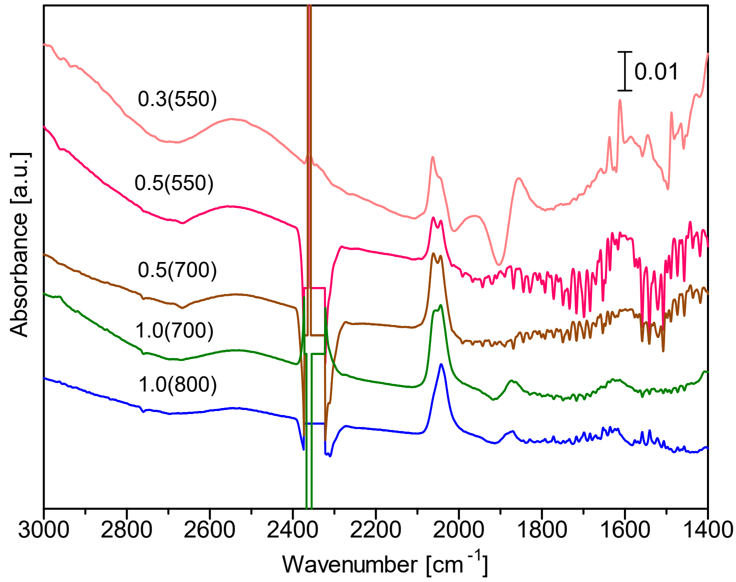

Figure S1. Wide-range difference IR spectra obtained at 50 °C without exposure to air. The IR spectra after H^2 treatment at different temperature was recorded at 50 °C and then the sample was further treated at 800 °C under He flow followed by cooling to 50 °C to record the spectra. The difference IR spectra were obtained by subtracting the spectra after He treatment from the ones after H_2 treatment.

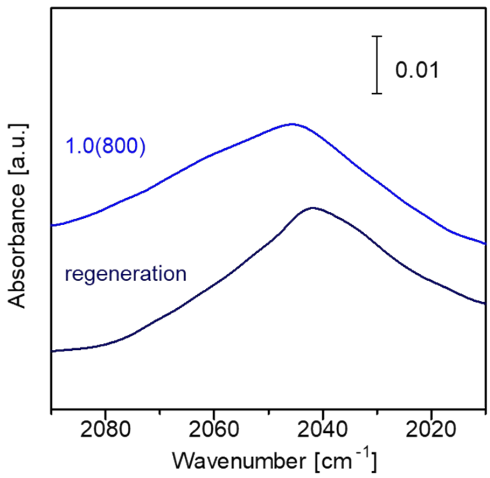

Figure S2. IR spectra of regenerated Ga-hydrides by H_2 treatment of the He-treated Ga-MFI-1.0(800). The difference spectrum was obtained in a similar manner.

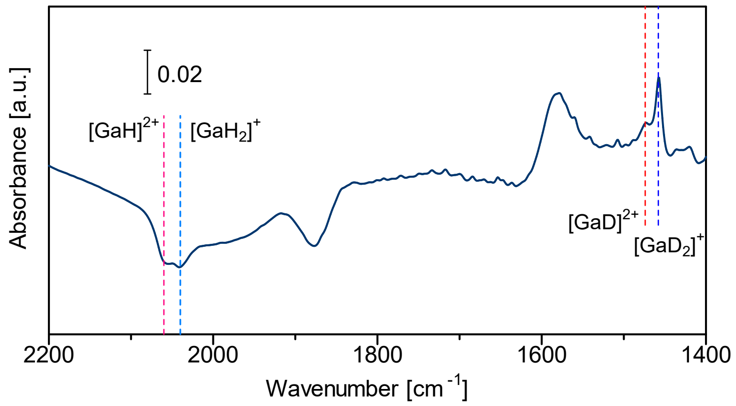

Figure S3. IR spectra for exchange reaction of Ga hydrides with D_2 at 300 °C. After the RSSIE reaction for Ga-MFI-1.0(800) (H_2, 800 °C), the temperature decreased to 50 °C to take the background spectrum. Next, the sample was exposed to D_2 at 300 °C and then the temperature decreased to 50 °C again for measurement.

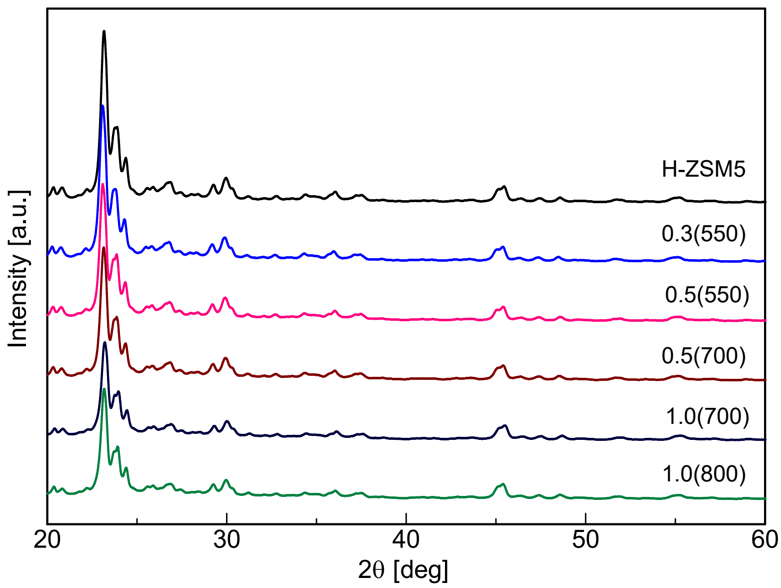

Figure S4. XRD patterns of a series of Ga-MFI after RSSIE. The XRD measurements were performed under room temperature and air atmosphere.

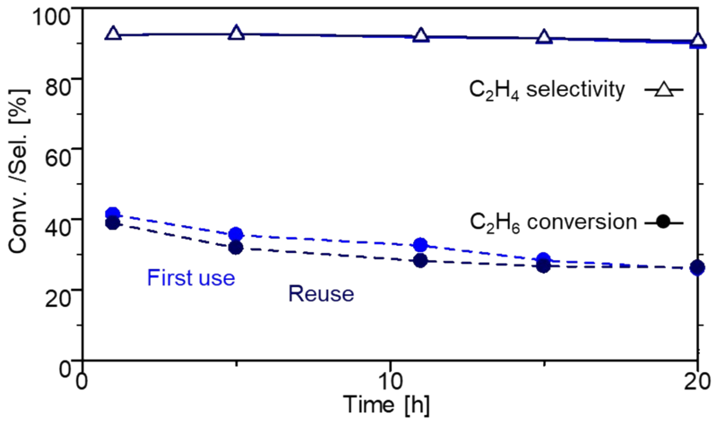

Figure S5. Time on stream of reuse experiment. Reaction conditions: 100 mg of Ga-MFI-1.0(800), 10% C_2H_6/He (10 mL/min), 660 °C. Regeneration treatment: (1) 5% O_2/He (10 mL/min), 600 °C. (2) 10% H_2/He (10 mL/min), 800 °C.

Table S1. Comparison of conversion, selectivity, and deactivation rate of Ga-MFI and previously reported Pt-free catalysts in C_2H_6 dehydrogenation without oxidant.

Catalyst	Temp. [°C]	Cat. [mg]	Flow [mL/min]	C_2H_6 Conc. [%]	C_2H_6 Conv. [%]	C_2H_4 Sel. [%]	C_2H_4 Formation Rate [mmol/(g·h)]	Deactivation Rate (k_d) [h^{-1}]	Reference
Ga-MFI-1.0(800)	660	100	10	10	43.1	89.7	10.4	0.024 (15 h)	This work
	660	50	10	50	28.5	92.6	72.1	0.014 (30 h)	This work
Ga-MFI-0.3(550)	660	100	10	10	79.1	55.0	11.7	0.190 (15 h)	This work
In-CHA	700	100	7.5	13	37.4	95.1	9.2	0.0025 (20 h)	*J. Am. Chem. Soc.*, 2020, 142, 4820
Cr0.8MFI	650	100	10	10	36.2	> 99	19.2	0.0046 (40 h)	*ACS Cat.*, 2021, 11, 3988
Fe-containing MFI siliceous zeolite	600	200	6.6	30	26.3	97.5	10.4	n.a.	*J. Am. Chem. Soc.*, 2020, 142, 16429
0.10Ba-Ga-α-Al_2O_3	700	100	143	12.6	1	98	4.7	n.a.	*Appl. Catal. A General*, 2019, 581, 23
FeZSM5	600	100	60	9	28	71.6	29.0	0.071 (4.5 h)	*Applied Catalysis B: Environmental*, 2019, 256, 117816
Ga/SiO_2-doped TiO_2	650	200	30	3	46.0	84.9	4.7	0.81 (6 h)	*Fuel Process Tech.*, 2018, 177, 246
5Cr/MCM-41E	650	160	50	15	23	99	28.6	n.a.	*J. Mol. Cat. A Chem.*, 2009, 301, 159
Cr/MgAlOx	700	500	70	29	15	84	13.5	n.a.	*Catal. Comm.*, 2007, 8, 2186
Cr/Al_2O_3	580	200	22	9	27	94	6.8	0.676 (1 h)	*Catal. Lett.*, 2005, 103, 143
Co-MFI	650	200	30	3	54.5	87.8	5.8	0.078 (6 h)	*Microporous Mesoporous Mater.*, 2021, 312, 110791
Ni_3Ga/Al_2O_3	600	100	20	10	10.0	94.0	5.0	0.018 (30 h)	*ACS Catal.*, 2019, 9, 10464
Pd-In-0.8/SiO_2	600	200	50	5	24.0	>99	8.0	0.090 (3 h)	*Catal. Sci. Tech.*, 2016, 6, 6965