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Supporting information for

Synthesis of Trioxane from Formaldehyde Catalyzed by [Ga, Al]-MFI Zeolite

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Method part

X-ray diffraction (XRD) patterns were recorded with a PANanalytical X'Pert Pro diffractometer operated at 40 kV and 40 mA and using Cu Kα radiation in the 2θ angular range of 5–55°.

The content of Ga/Al/Si in the sample was determined using ICP-OES collected by Agilent 5110. The sample was put in hydrothermal reactor and 30% concentrated alkali solution was added for digestion. It is completely dissolved after being kept at 120℃ for 6 hours, and then the pH was adjusted to neutral with hydrochloric acid.

The N_2 adsorption-desorption isotherms, pore volumes, surface areas were evaluated at liquid nitrogen temperature after dehydration under vacuum at 423 K for 10 h using Micromeritics Tristar 3020. The pore volume was taken by a single point method at $p/p_0 = 0.99$.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250XI photoelectron spectrometer with Al Ka radiation.

The electron microscope used in the experiment was produced by the German company ZEISS and the model was Gemini SEM 300.

Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out one the Micromeritics AutoChem II 2920. The procedure for the NH_3-TPD test was as follows: a 100 mg sample was placed in a U-shaped glass tube and pretreated by heating from room temperature to 300 °C at a rate of 10 °C/min under a He atmosphere (flow rate of 30 mL/min), after which the sample was maintained for 1 h. The sample was then reduced to 100 °C and purged with a 5% NH_3-95% He gas mixture (flow rate of 30 mL/min) until the baseline was stable. After saturation, the adsorption was purged with He (flow rate of 30 mL/min) until the baseline was stable again. Start the programmed temperature rise and record the data. Increase the temperature at a rate of 10 °C/min to 550 °C, maintain the temperature for 30 min and then complete the test.

Infrared spectra of adsorbed pyridine (Py-IR) was collected at 150℃ by Nicolet FTIR 6700 infrared spectrometer.

The amount of Brønsted acid and Lewis acid were determined by the integrated intensities of the infrared bands at 1450 $cm^{-1}$and 1550 cm^{-1} respectively.

Solid-state nuclear magnetic resonance (NMR) spectra were collected on a Bruker AVANCE III 400 MHz spectrometer. The ^{27}Al MAS NMR and ^{71}Ga MAS NMR were recorded at a resonance frequency of 600 MHz, spinning rate of 14 kHz and a recycle delay of 1 s. Quantitative ^{29}Si MAS NMR spectra were recorded at a resonance frequency of 99.35 MHz, spinning rate of 10 kHz and a recycle delay of 20 s.

The glass reactor for the continuous experiment was the same as that for the intermittent experiment, as shown in Figure S1. Experimental procedure: 37% aqueous formaldehyde solution was concentrated to 60% by dehydration, then 100 g of aqueous formaldehyde solution and 3 g of catalyst were placed in a 250 ml reactor. The reaction temperature is controlled by an oil bath heating system at 98-100 °C, while condensation is carried out using 45 °C circulating water. Every two hours the reactor is replenished with the same mass of raw material (60% formaldehyde solution) as the extracted distillate. Component analysis of the distillate is performed every 8 hours.

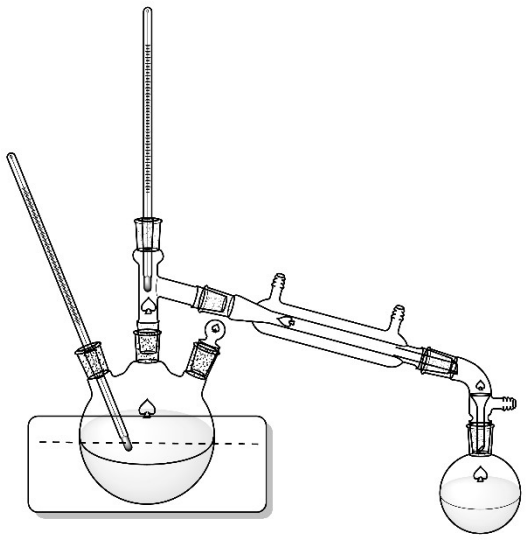

Fig. S1 Glass reactor unit

Formaldehyde analysis process: formaldehyde reacts with excess sodium sulfite solution to produce sodium hydroxide, thymolphthalein is used as a referent and titrated with sulfuric acid standard titration solution. According to the consumption of sulfuric acid standard solution, the mass fraction of formaldehyde is calculated.

The process of formic acid analysis: NaOH standard solution was titrated, bromothymol blue was used as indicator, and the mass fraction of formic acid was calculated according to the consumption of NaOH standard solution.

The TOX and by-products methylal, methanol and methyl formate were analyzed by Agilent GC-7890B gas chromatograph. Chromatographic conditions: hydrogen flame ion detector, column type HP-1 quartz capillary column: (30 m×0.320 mm×0.25 μm) with inert gas nitrogen as carrier gas. The detector temperature was 300 °C and the injection port temperature was 280 °C. The column was programmed to ramp up to 40 °C and to remain at that temperature for 5 min, and then to 250 °C at a rate of 30 °C-min-1 and to remain at that temperature for 5 min.

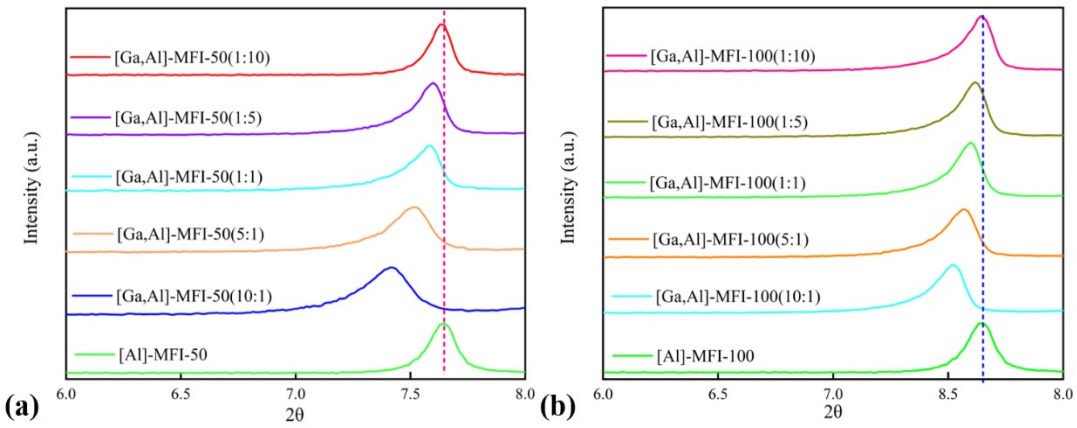

Fig. S2 XRD patterns of the enlargement of the 2θ region from 6.0° to 8.0°

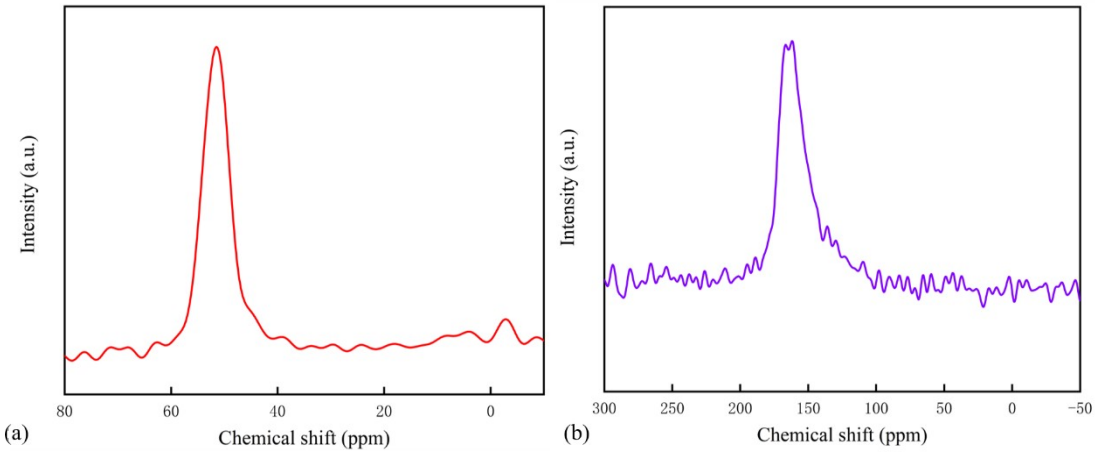

Fig. S3 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-50(5:1)

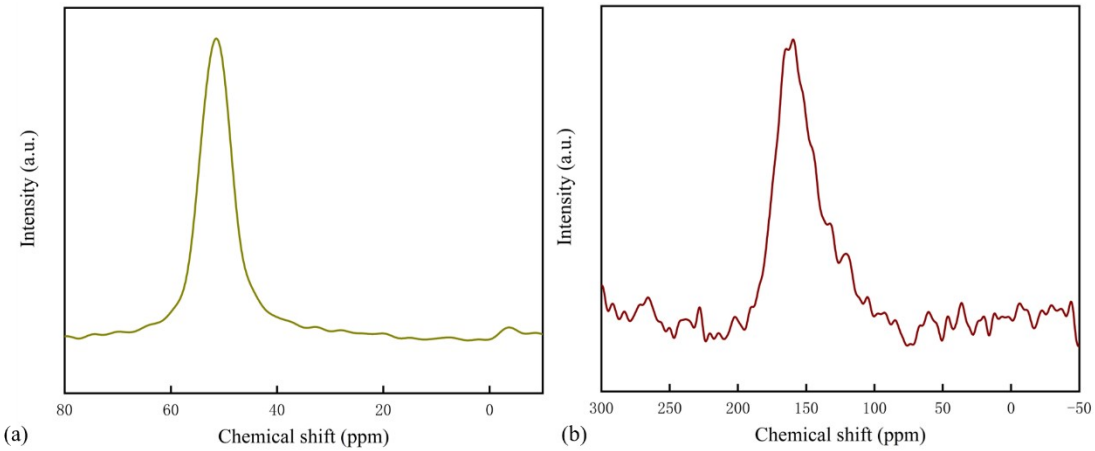

Fig. S4 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-50(1:5)

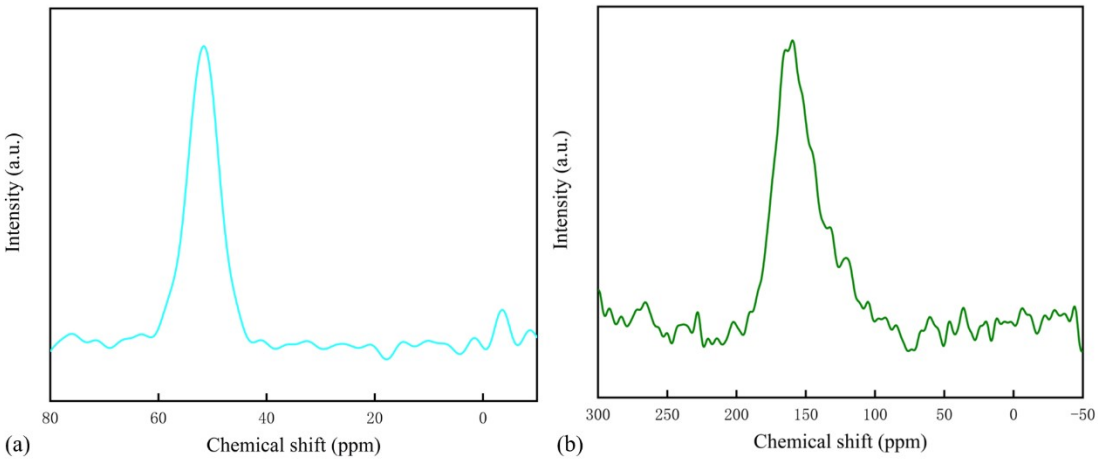

Fig. S5 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-50(10:1)

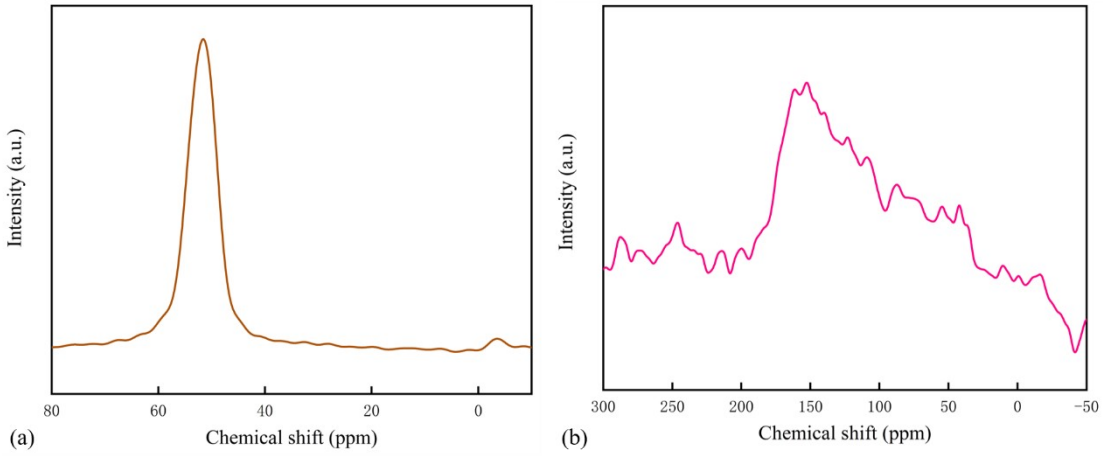

Fig. S6 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-50(1:10)

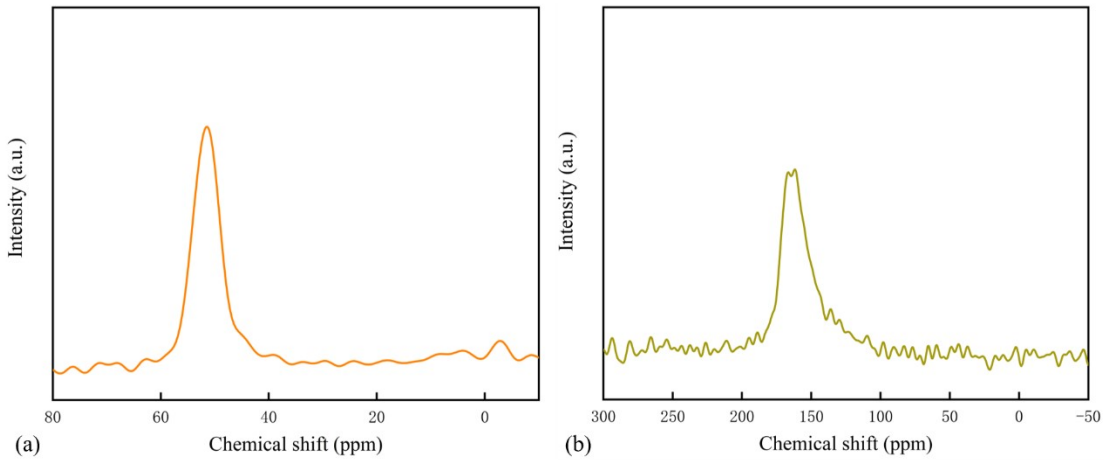

Fig. S7 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-100(5:1)

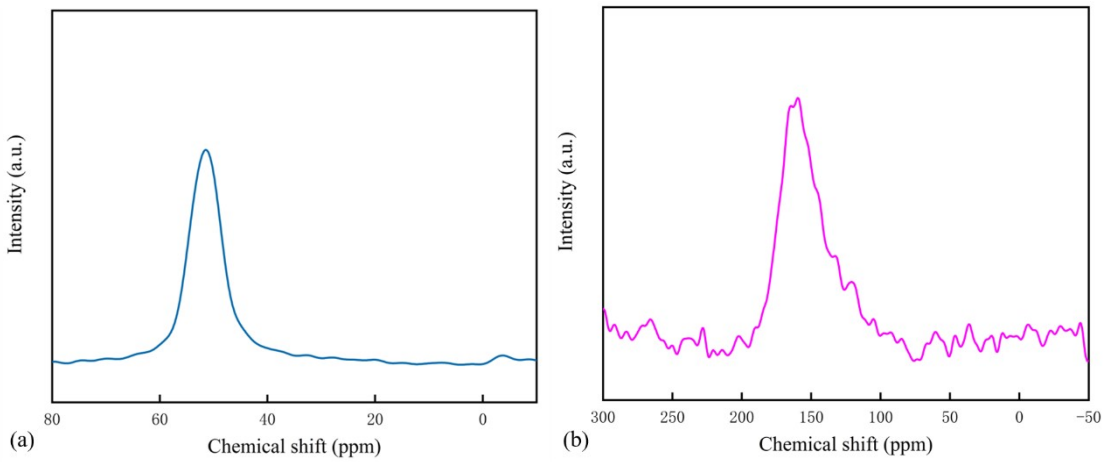

Fig. S8 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-100(1:5)

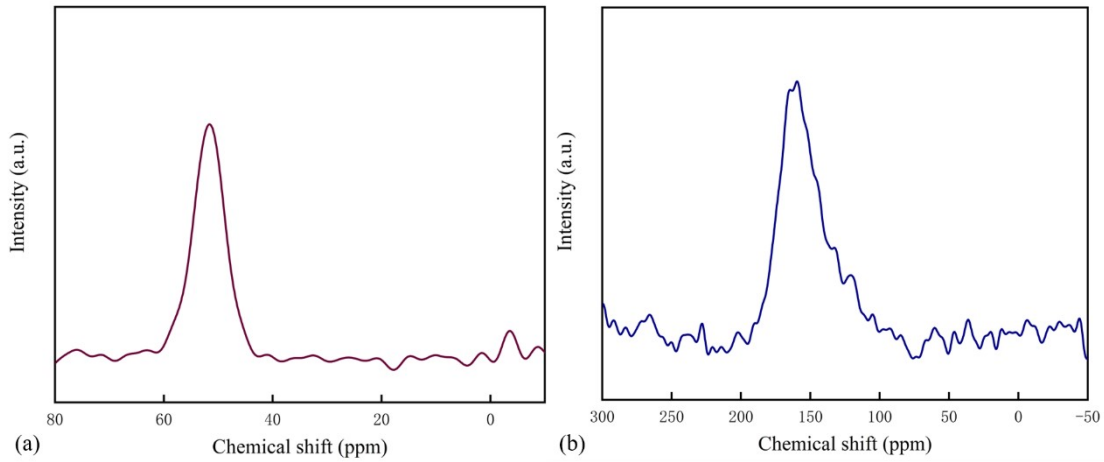

Fig. S9 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-100(10:1)

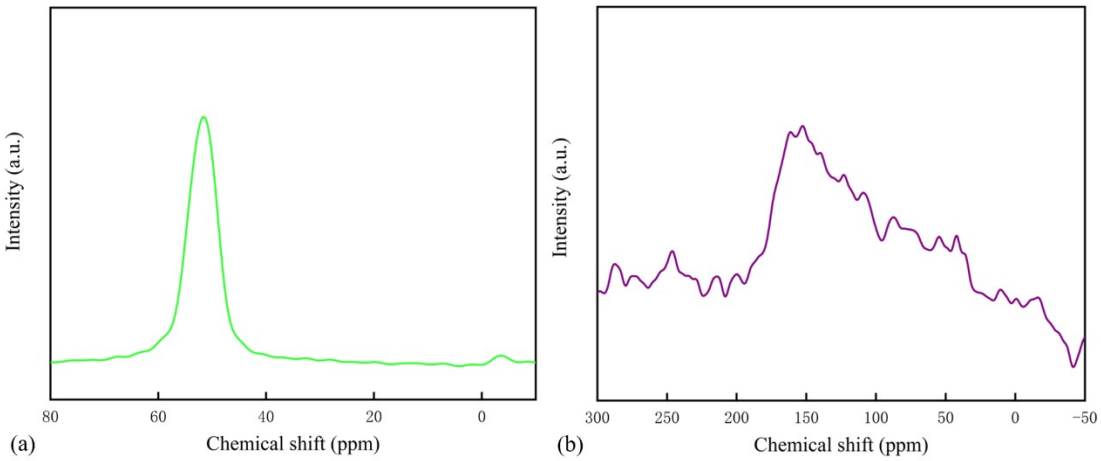

Fig. S10 ^{71}Ga MAS NMR spectra(a) and ^{27}Al MAS NMR spectra(b) of [Ga, Al]-MFI-100(1:10)

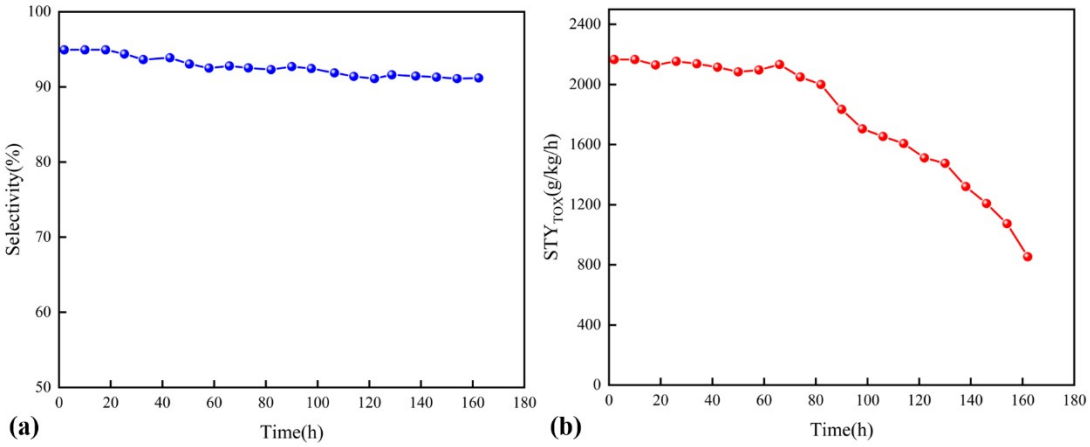

Fig. S11 Selectivity (a) and STY (b) of [Ga, Al]-MFI-50(1:1) zeolite to TOX in continuous reactions

Table S1 Catalytic performance data of [Al]-MFI-50 zeolite

Catalyst	STY_{TOX}(g/kg/h)	Selectivity of TOX (%)
[Al]-MFI-20	1283	54.28
[Al]-MFI-30	1198	67.99
[Al]-MFI-50	1129	74.53
[Al]-MFI-70	903	81.11
[Al]-MFI-80	815	85.24
[Al]-MFI-100	742	88.53