

Appendix A. Supplementary Data

Catalytic Oxidation of HCHO over the Sodium-Treated Sepiolite-Supported Rare Earth (La, Eu, Dy, and Tm) Oxide Catalysts

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Catalyst preparation

The sepiolite raw material was purchased from the Liuyang Sepiolite Mining Industry Company of China. Its chemical composition, which was determined using the X-ray fluorescence (XRF) spectroscopic technique, was 64.0 wt% SiO₂, 6.6 wt% Al₂O₃, 16.0 wt% MgO, 2.33 wt% Fe₂O₃, 9.2 wt% CaO, 0.26 wt% TiO₂, 0.48 wt% K₂O, 0.13 wt% Na₂O, and trace amounts of other compounds. Sodium modification of sepiolite can improve the thermal stability of the sample, the cation exchange capacity was significantly enhanced, and the original structure of sepiolite was not changed. The support was prepared using the sodium-leached sepiolite. The leaching treatment was carried out in an aqueous solution containing 2.0 wt% sepiolite by adding Na₂CO₃ at a Na/Sep mass ratio of 0.04 at 60 °C for 2 h. The sodium-treated sepiolite was in turn aged at room temperature for 24 h, filtered, washed with deionized water, and dried at 80 °C for 24 h. The obtained sodium-treated sepiolite support was denoted as NaSep.

Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using Bruker D8-Advance in the 2θ range of 5–80 ° ($\lambda = 0.15404$ nm at a scan rate of 5 °/min). The crystallite sizes of the samples were calculated using the Scherrer equation. Fourier transform Infrared (FT-IR) spectra of the samples were determined on a Perkin-Elmer One FTIR spectrometer with a resolution of 4 cm⁻¹ operating in the range of 500–2000 cm⁻¹ with 4 scans per spectrum. N₂ adsorption–desorption isotherms of the

samples were measured via nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ on an ASAP 2010 analyzer (Micromeritics). Before measurement, the sample was degassed at $200\text{ }^{\circ}\text{C}$ for 2 h. BET (Brunauer–Emmett–Teller) surface areas of the samples were calculated according to the BET method. X-ray photoelectron spectroscopic (XPS) spectra of the samples were recorded on an ESCALAB 250 XI spectrometer using Al $K\alpha$ as an excitation source. Ammonia temperature-programmed desorption (NH_3 -TPD) of the samples was performed on a Builder PCA-1200 analyzer. 100 mg of the sample was pretreated at $400\text{ }^{\circ}\text{C}$ and saturated with NH_3 (1 vol% NH_3/He , 30 mL/min) at $100\text{ }^{\circ}\text{C}$. After being purged with pure He (30 mL/min) at $100\text{ }^{\circ}\text{C}$ for 1 h, NH_3 desorption took place at a ramp of $10\text{ }^{\circ}\text{C}/\text{min}$ in a He flow of 30 mL/min and the temperature range of $30\text{--}500\text{ }^{\circ}\text{C}$.

Catalytic activity evaluation

Catalytic activity measurements of the samples for the oxidation of HCHO were carried out in a continuous flow fixed-bed quartz tubular microreactor at atmospheric pressure. 50 mg of the sample (40–60 mesh) and 50 mg of quartz sand (40–60 mesh) were well mixed and put into the tubular microreactor. A N_2 flow of 5.0 mL/min was passed through a HCHO-containing tubular saturator at $45\text{ }^{\circ}\text{C}$, and then mixed with an air flow, thus giving a total flow rate of 200 mL/min and a space velocity (SV) of 240,000 mL/(g h). In the feed gas mixture, the HCHO concentration was 2000 ppm. The reaction products were analyzed online on a Techcomp GC-7900 gas chromatograph equipped with a flame ion detector (FID) for HCHO analysis. The

conversion of HCHO was calculated according to the changes of HCHO concentration in the inlet and outlet gas mixture.

$$X_{\text{HCHO}} = \frac{C_{\text{HCHO,inlet}} - C_{\text{HCHO,outlet}}}{C_{\text{HCHO,inlet}}} \times 100 \%$$

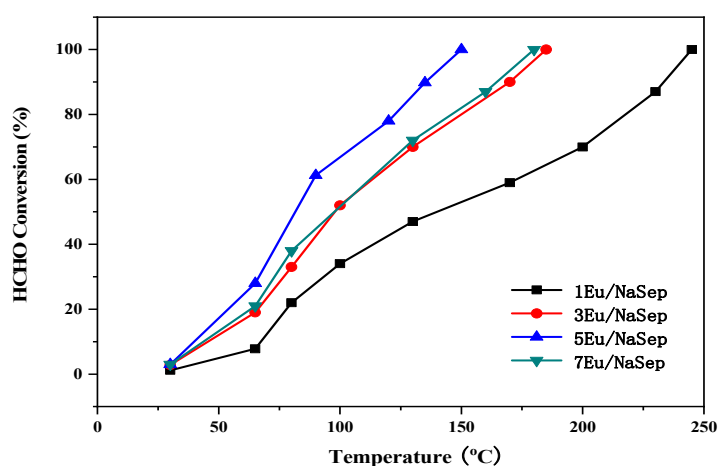


Figure S1. HCHO conversion as a function of temperature over the x wt% Eu/NaSep sample under the conditions of 2000 ppm HCHO + 20 vol% O₂ + N₂ (balance) and GHSV = 240000 mL/(g h).

The catalytic oxidation activity of the supported Eu/NaSep catalyst (Eu loading = 1.0 wt%, 3.0 wt%, 5.0 wt%, and 7.0 wt%) on HCHO was shown in Figure S1. It can be seen that 5.0 wt% Eu/NaSep was capable of completely converting HCHO at a lower temperature, so in the following experiments, a loading of 5.0 wt% was employed.

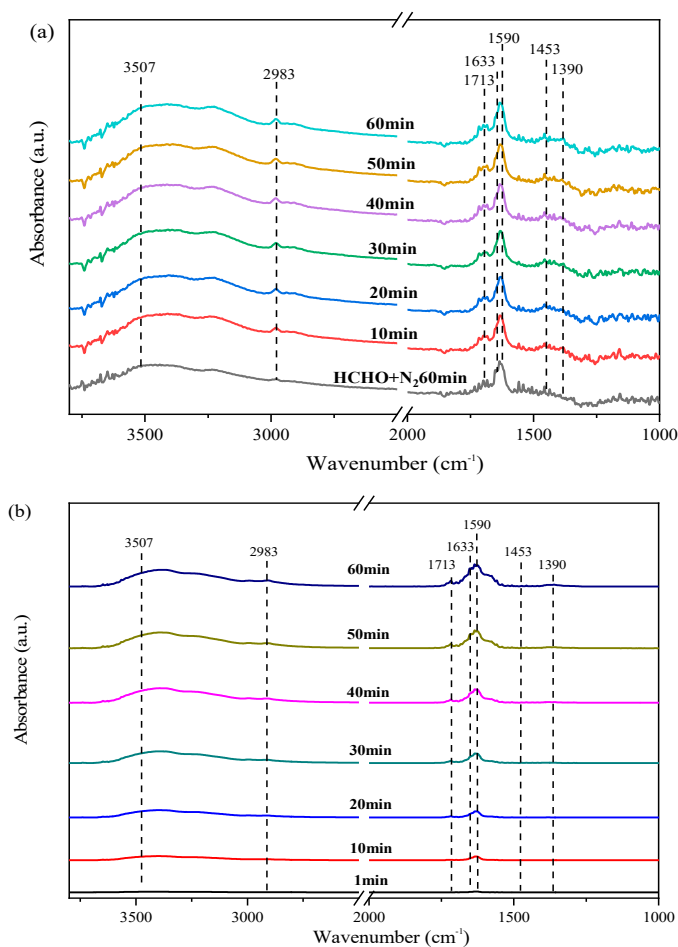


Figure S2. In situ DRIFTS spectra of (a) Eu/NaSep, and (b) NaSep exposed to the flow of 2000 ppm HCHO + 20 vol% O₂ + N₂ (balance) at 30 °C and different time.

Figure S2 shows in situ DRIFTS and catalytic oxidation mechanism of HCHO at 30 °C over Eu/NaSep, and NaSep. It can be concluded that the intermediate products for catalytic oxidation of HCHO over NaSep (Fig. S2 (b)) were the same as that over Eu/NaSep (Fig. S2 (a)), but the strength of intermediate products over NaSep was lower than that of Eu/NaSep.