Supplementary Information

Promoting effect of boron oxide on FeO$_x$/Si$_3$N$_4$ catalyst for oxidative dehydrogenation of ethylbenzene

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Chemical reagents

Ferric nitrate ($Fe(NO_3)_3·9H_2O$, 99%, Sinopharm), boric acid (H_3BO_3, 99%, Sinopharm), and silicon nitride (Si_3N_4, α phase, 99.9%, Aladdin, denote as SiN) were used as purchased.

Catalyst preparation

Iron oxide (1wt% Fe_2O_3) was introduced into SiN by an impregnation method. SiN support was immersed in an aqueous solution of ferric nitrate and stirred for 2 h at room temperature. The slurry was then dried at 80 °C for 12 h. The powdery sample was finally calcined in the air at 600 °C (5 °C min^{-1}) for 2 h to obtain the FeO_x/SiN sample. The B_2O_3-modified FeO_x/SiN catalysts were prepared by impregnation of the FeO_x/SiN with an aqueous solution of boric acid (0.1-5wt% B_2O_3) followed by drying and calcination with the same procedure described above.

Catalyst characterizations

X-ray powder diffraction (XRD) was performed on an X'Pert-3 Powder diffractometer (Cu Kα, λ = 0.15406 nm, PANalytical). Nitrogen adsorption isotherms (ASAP 3000, Micromeritics) were measured at −196 °C. The sample was pretreated at 200 °C in a vacuum for 6 h before the test. The specific surface areas (S_{BET}) were calculated by the BET method. The S_{BET} of $1FeO_x$/SiN and xB_2O_3-$1FeO_x$/SiN catalysts were less than 10 m^2 g^{-1}. The UV-vis diffuse reflectance spectra (UV-vis DRS) were tested from 200-800 nm using $BaSO_4$ as a reference. Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 F30 S-Twin at an accelerating voltage of 300 kV. H_2-TPR was tested on an AutoChem II 2920 apparatus (Micromeritics) with a

TCD detector. Before H_2-TPR, the samples were pretreated at 150 °C for 1 h under Ar flow and then cooled to ambient temperature, then TPR was performed in the 8%H_2/Ar at 10 °C min^{-1} up to 800 °C. CH_3OH-TPD experiments were measured on a self-built device using a mass spectrometer for the online detection of desorbed products (m/z=31 and 30, respectively for CH_3OH and HCHO). Typically, 100 mg of catalyst was pretreated under 20%O_2/Ar (25 mL min^{-1}) mixture at 400 °C for 1 h then cooled to 50 °C under Ar flow. After adsorption of CH_3OH/Ar mixture (19.7 kPa, 25 mL min^{-1}) at 50 °C for 0.5 h and Ar purging for 1 h, then TPD was performed in Ar (25 mL min^{-1}, 10 °C min^{-1}) up to 500 °C. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer (Al Kα X-ray source). The binding energy was calibrated using the C 1s photoelectron peak at 284.8 eV.

Catalytic tests

Catalytic tests were performed in a fix-bed quartz tube reactor (i.d. 8 mm, length 420 mm) under atmospheric pressure at 500 °C. The reactants (5.6 kPa EB, O_2/EB=2, N_2 as balance, 10 mL min^{-1}) were fed into the reactor through a saturator (54 °C). The compositions of the effluent stream were analyzed by an online gas chromatograph (GC7900, Themcomp) equipped with TCD and FID detectors. Heyesep D and molecular sieve 5A column were attached to TCD for the analysis of O_2, N_2, CO, and CO_2. A PEG capillary column was attached to FID for the detection of hydrocarbons and oxygenates (ethylbenzene, styrene, benzene, benzaldehyde, etc.). The ethylbenzene conversion and styrene selectivity were calculated by the following equations:

$$X_{EB}(\%) = \frac{\sum n_i^{out}}{n_{EB}^{out} + \sum n_i^{out}} \times 100$$

$$S_i(\%) = \frac{n_i^{out}}{\sum n_i^{out}} \times 100$$

$$Carbon\ balance = \frac{\sum moles\ of\ carbon\ in\ outlet}{\sum mols\ of\ carbon\ in\ feed}$$

where n_i is the mole of the products obtained during the oxidative dehydrogenation of ethylbenzene (i = styrene, benzaldehyde, benzene, CO, and CO_2). The carbon balance was 100±5% in all runs, and the EB conversion of the blank experiment (quartz sand) was less than 1% at 500 °C.

To measure the kinetic behaviors, the corresponding ethylbenzene conversions were tuned to less than 15% to exclude mass transfer limitations. Mass and heat transfer calculations were carried out using the $1FeO_x/SiN$ catalyst in this reaction. The Weisz-Prater criterion (C_{WP}) and Mears' criterion (C_M) were respectively

$$C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff}C_s} = 1.43 \times 10^{-2} < 1 \text{ and } C_M = \frac{r_{obs}\rho_b R_p n}{k_c C_{Ab}} = 1.32 \times 10^{-2} < 0.15,$$ indicating the absence of internal and external diffusion limitations during the tests. The Mears'

criterion (C_M) was $$C_M = \left| \frac{-\Delta H\ r_{obs}\ \rho_b\ R_p\ Ea}{h\ T^2\ R_g} \right| = 1.35 \times 10^{-2} < 0.15,$$ suggesting the absence of heat transport limitations. These mathematical calculations confirmed that the mass and heat transfer limitations could be neglected in our measurements.
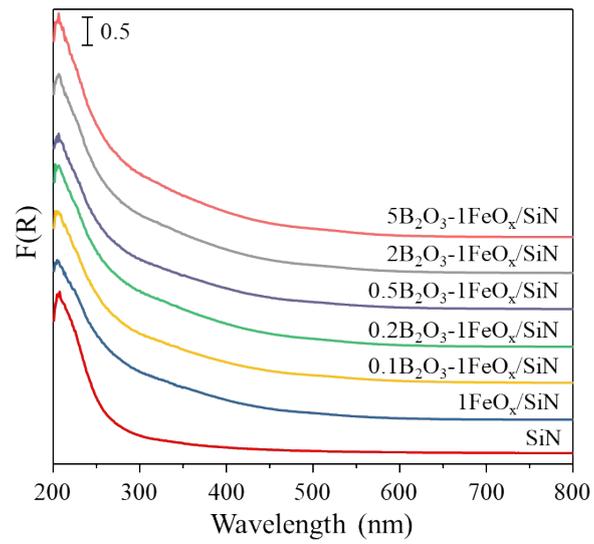
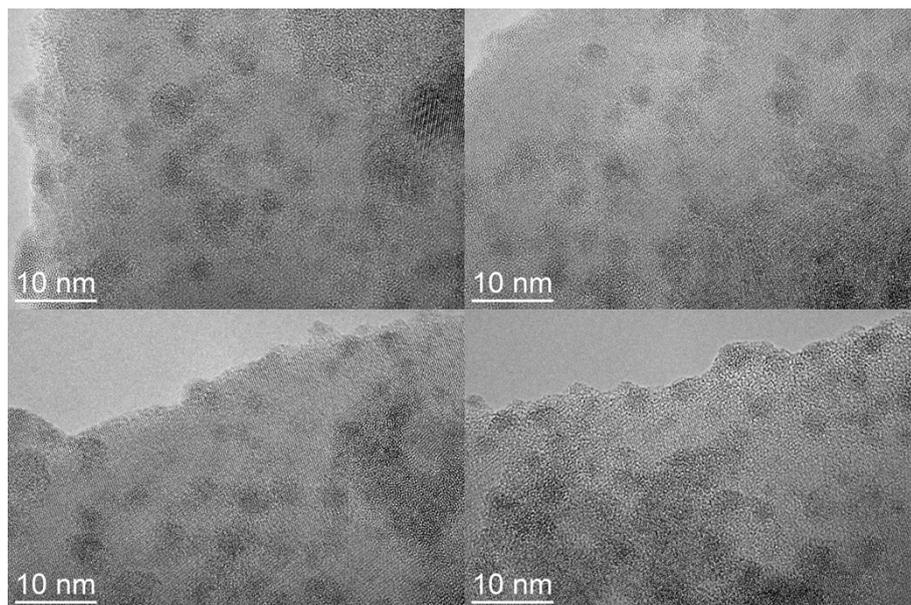Fig. S1 UV-vis DRS spectra of SiN support and xB_2O_3-$1FeO_x$/SiN samples.

Fig. S2 TEM images of the $1FeO_x$/SiN sample.
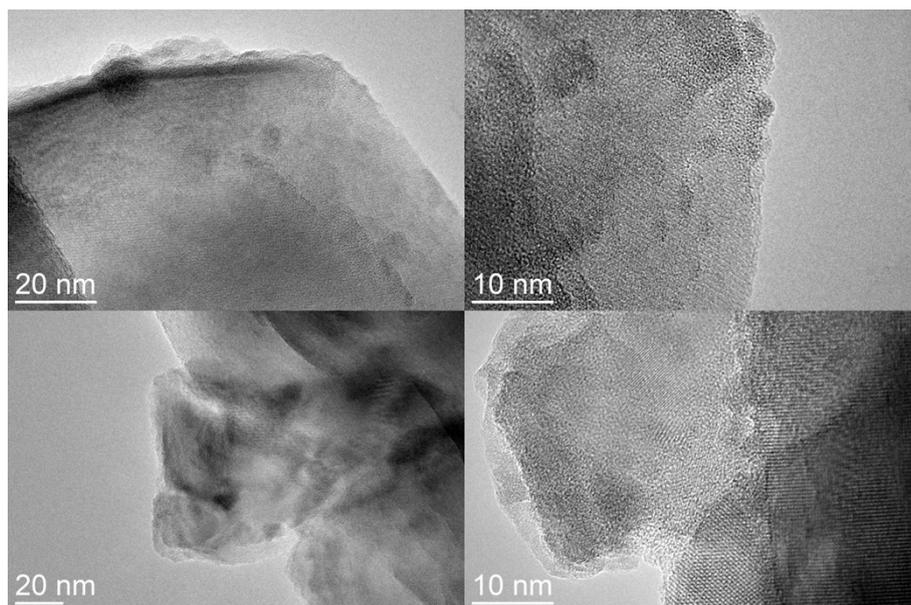
Fig. S3 TEM images of the $0.2B_2O_3$-$1FeO_x$/SiN sample.
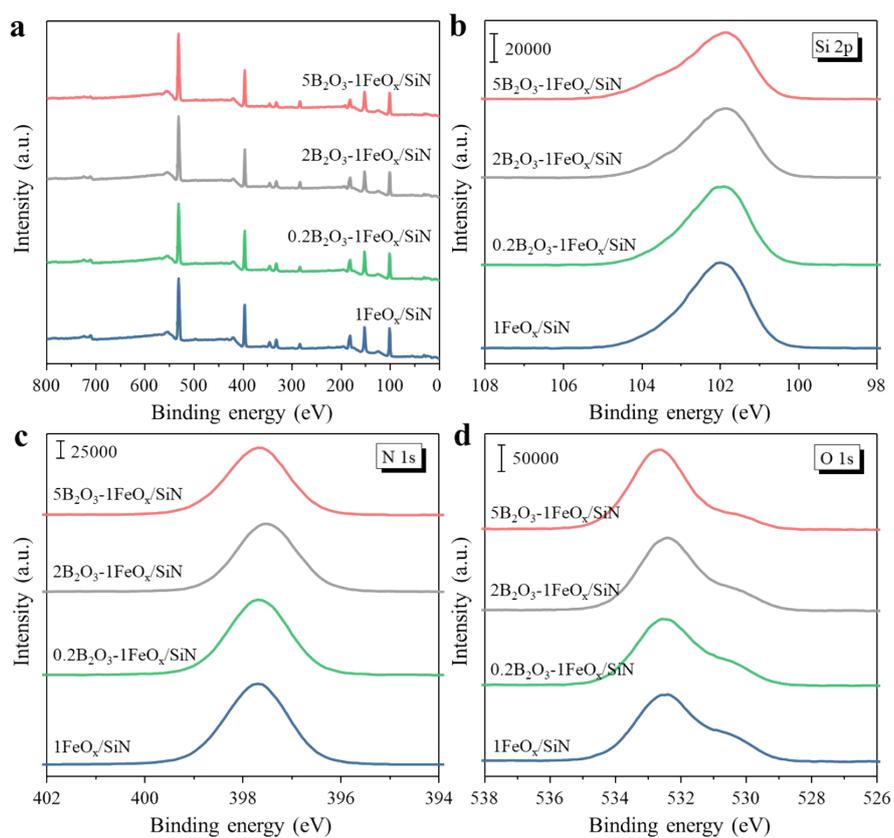
Fig. S4 XPS spectra for $1FeO_x$/SiN, $0.2B_2O_3$-$1FeO_x$/SiN, $2B_2O_3$-$1FeO_x$/SiN, and

$5B_2O_3$-$1FeO_x$/SiN samples: (a) Survey; (b) Si 2p; (c) N 1s; (d) O 1s.