Supplementary Information

Bromination of Aromatic Compounds Using an Fe_2O_3/Zeolite Catalyst

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1. Methods

1-1. SEM measurements SEM measurements were performed on SEM (JEOL JSM-6700FE). Sample powder was coated with evaporated platinum.

1-2. EDX measurements EDX measurements were performed on an SEM (JEOL JSM-6700FE) equipped with an energy-dispersive X-ray analyser (JEOL JED-2200F). The atomic ratio of Fe:Al:Si (at%) was determined.

1-3. XRD measurements X-ray diffraction patterns were obtained on an X-ray powder diffractometer (Rigaku RINT-2000) using Cu Kα radiation.

1-4. NMR measurements NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are relative to solvent peaks [chloroform: 7.27 (^{1}H), 77.00 (^{13}C)]. The NMR spectra of products showed complete agreement with the known data.

1-5. GC measurements GC analysis was carried out with Shimadzu GC-2014 equipped with FID detector . The chemical yields were determined using dodecane as an internal standard. Calibration curves were prepared using commercially available standard samples.

2. **Experimental Details**

2-1. Preparation of Catalyst $FeCl_3{\cdot}6H_2O$ (1 mmol) and zeolite (1 g) were stirred in MeOH (1 mL) for 1 h. Solvent was removed by rotary evaporator. The recovered solid material was calcined at 300 °C for 1 h.

Other catalysts were prepared with the same procedure.

2-2. Bromination of aromatic compounds The Fe_2O_3/zeolite was heated with heating gun (HAKKO, No.881, 1000W) for 10 min in a vacuum prior to use to remove adsorbed H_2O. All reactions were performed in argon atmosphere using dehydrated benzene (Table 1, Figure 4, and Scheme 2) or dehydrated CH_2Cl_2 (Table 2) in screw-capped test tube.. After the reaction, the mixtures were treated with aq. $Na_2S_2O_3$ to remove unreacted Br_2.

2-3. Catalyst recycling method A After the reaction, the reactor was connected to a vacuum pump with cold trap. After removal of solvent, starting materials, and product(s), the reactor was filled with argon and used for the next reaction.

2-4. Catalyst recycling method B After the reaction, the reaction mixture was filtered with Millipore membrane filter (0.2 μm). The collected pale brown solid ($FeBr_3$/zeolite) was placed into a muffle furnace and heated at 300 °C for 1 h in air to give orange solid (α-Fe_2O_3/zeolite) (Figure S1). The calcined catalyst was used for the next reaction.

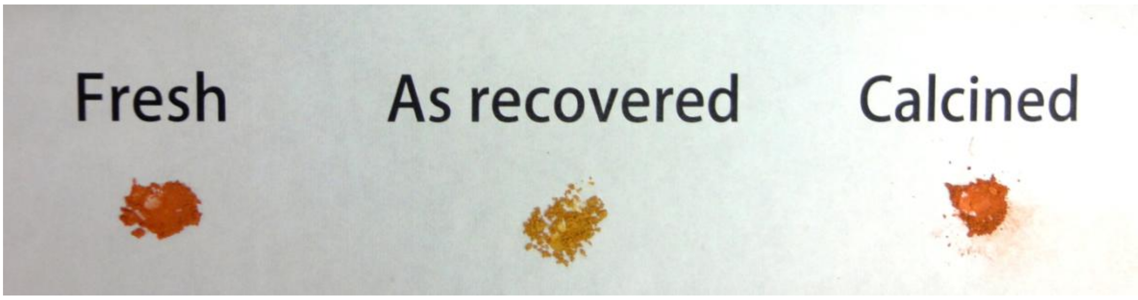

Figure S1 Fresh Fe2O3/zeolite (left), as recovered catalyst (middle), and recovered and calcined catalyst (right).