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Supplement of

The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite

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Section S1 XRD patterns of the synthesized and humid samples

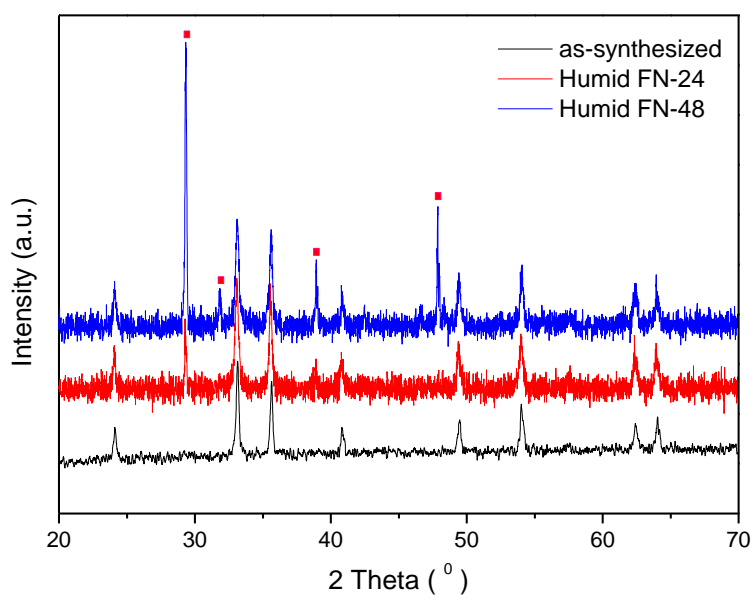


Fig. S1. XRD patterns of the synthesized sample, humid FN-24 and FN-48.

The synthesized sample presented some diffraction peaks in the wide angle X-ray diffraction region. These characteristic peaks that emerged can be indexed according to the hematite crystalline phase, and no other crystalline phase was found in the peaks, indicating that the synthesized sample was a fairly pure α -Fe₂O₃ sample.

The crystalline peaks at 29.65°, 31.9°, 39.0° and 47.9° can be identified as the characteristic reflections of NaNO₃. No amorphous sodium nitrate was present because there was no broad amorphous peak in the 20° - 40° range. In addition, except for the crystalline peaks of hematite and nitrate, no other crystalline phases were formed, which indicated that no secondary processes occurred on the hematite surface during the sample preparation and the subsequent sample equilibration.

Section S2 Schematic diagrams of DRIFTS and White Cell-FTIR apparatus

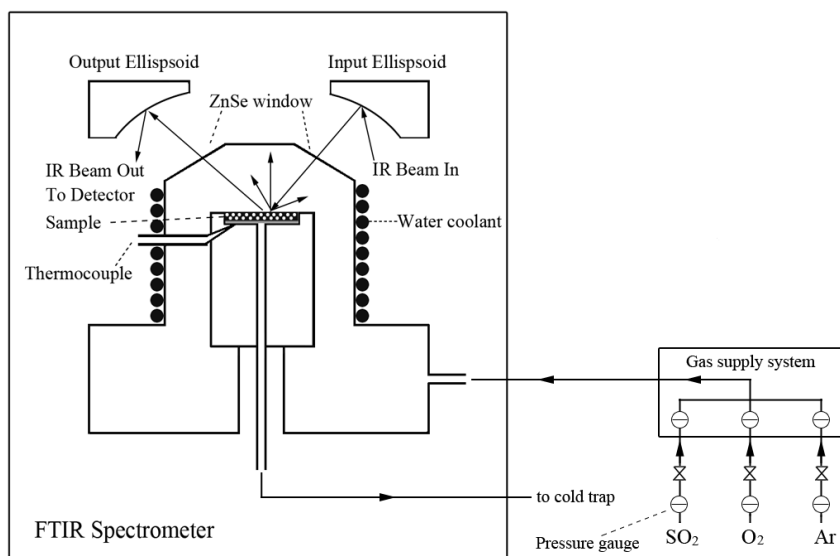


Fig. S2. Schematic diagram of DRIFTS apparatus

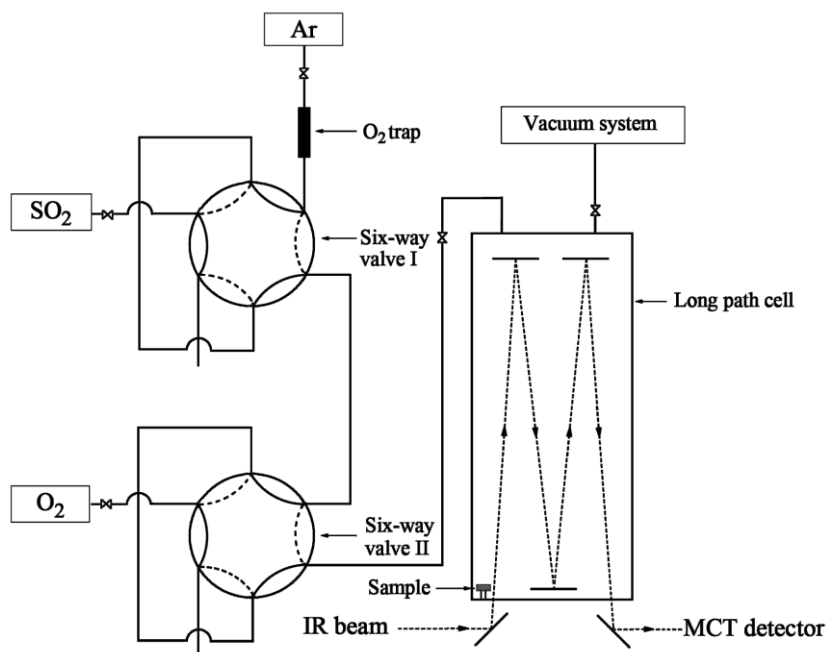


Fig. S3. Schematic diagram of White Cell-FTIR apparatus

Section S3 The variations of the fitting peak areas with reaction time

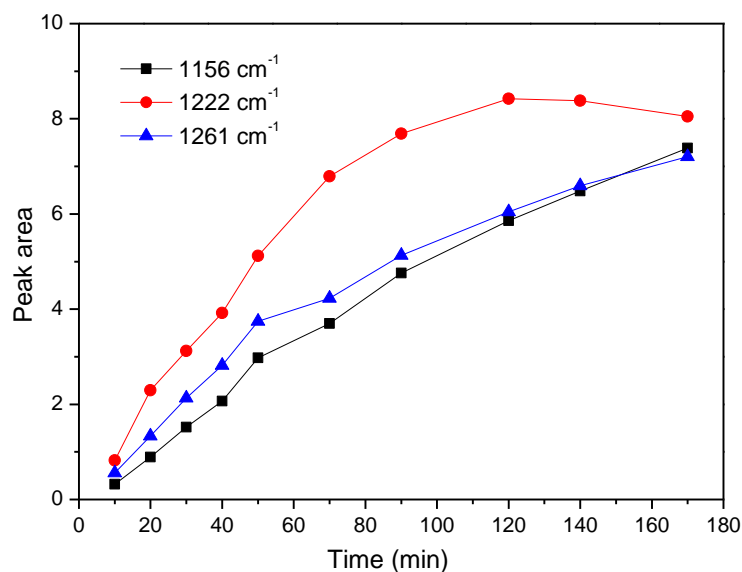


Fig. S4. The variations of peak areas at 1261, 1222 and 1156 cm⁻¹ with reaction time

Upon exposure of SO₂, the surface-adsorbed H₂O was gradually consumed and the surface acidity of pure hematite sample was gradually enhanced. The transformation of the adsorption mode of the surface-formed sulfate would occur with the increase of the surface acidity, and then the peak at 1219 cm⁻¹ appeared (Yamaguchi et al., 1986; Persson and Lovgren, 1996; Faguy and Marinković, 1996; Hug, 1997). The slight decrease in intensity of the peak at 1219 cm⁻¹ after it reaches the maximum may be due to partial dissolution of hematite along with consumption of surface acidic species, which would lead to the formation of Fe³⁺ ions and some other surface species on the water-containing surface (Chun and Quon, 1973; Shi et al., 2011).

In addition, it should be pointed that peak fitting can produce bias, and hence the fitting band at 1222 cm⁻¹ corresponds to the band at 1219 cm⁻¹ in Fig. 1.

Section S4 Peak heights of the main peaks observed on FN-24

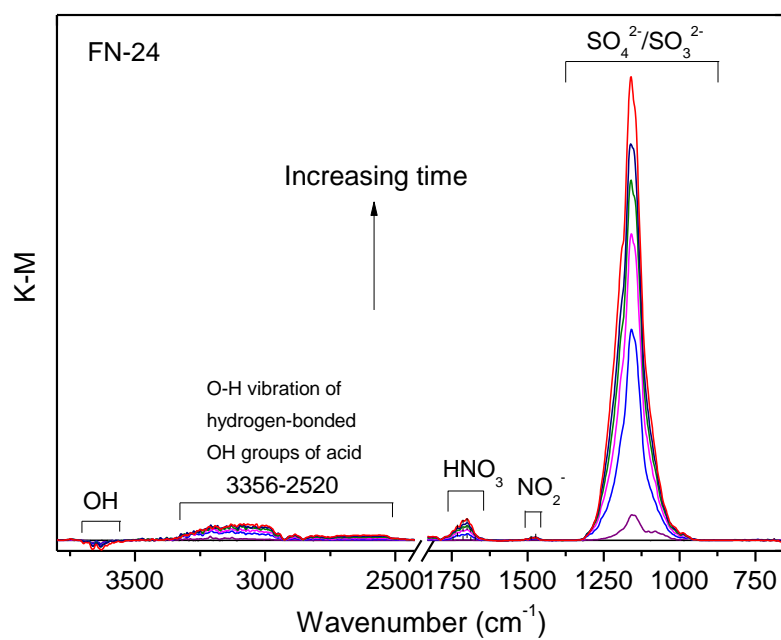


Fig. S5. Peak heights of the main peaks in different infrared spectral regions.

Section S5 Chromatogram and EI mass spectrum of N₂O

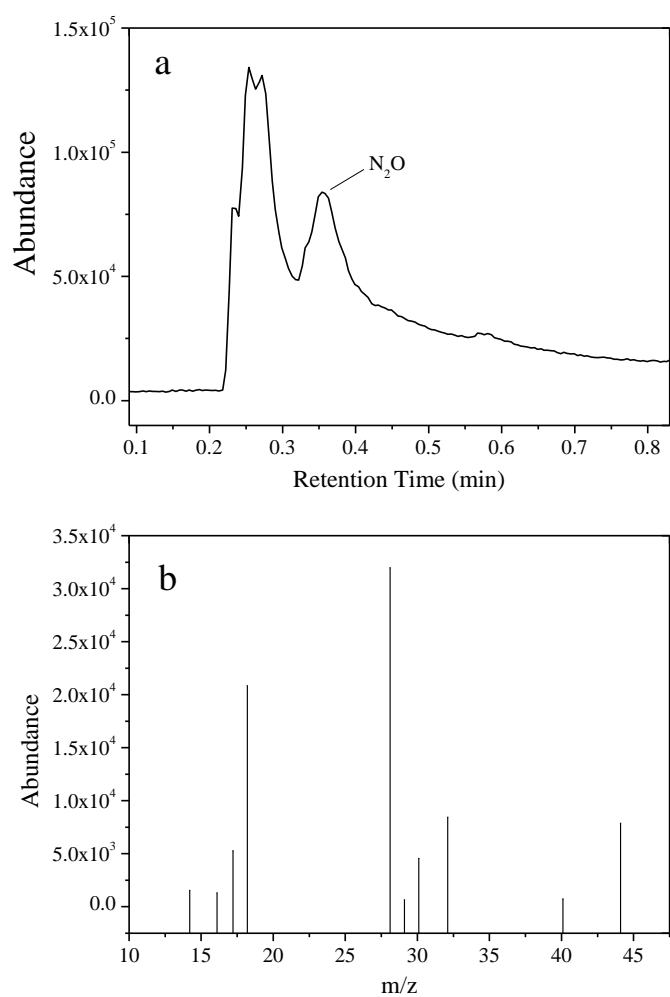


Fig. S6. Chromatogram (0.1-0.8 min) of the gas-phase sample collected from the heterogeneous reaction of SO₂ on FN-24 in a closed glass bottle in the dark (a) and corresponding EI mass spectrum of N₂O (b).

Section S6 Assignments of the broad peak in the region between 1100 and 900 cm^{-1} observed on pure hematite

A broad peak containing several weak peaks, especially at the beginning of the reaction, is also observed between 1100 and 900 cm^{-1} . Several peaks in this region can be assigned to the stretching motion of adsorbed sulfite and/or bisulfite based on previous studies on SO_2 adsorption on different metal oxide surfaces (Zhang et al., 2006; Wu et al., 2011; Nanayakkara, et al., 2012). These peaks can be overlapped by the symmetric stretching of sulfate in this region (Nanayakkara et al., 2012; Zhang et al., 2006), and it is difficult to distinguish these absorption peaks in this region because of the increase of surface sulfate species and the decrease of surface sulfite species during the reaction. These results indicate that surface S (IV) species such as adsorbed or surface-coordinated H_2SO_3 , HSO_3^- and SO_3^{2-} species were converted to sulfate in the reaction process and some S (IV) species have not been completely oxidized to sulfate on the pure hematite surface after the experiment.

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