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Asymmetrical coexistence of associatively and dissociatively adsorbed alcohol species over α-Fe2O3 iron oxide nanoparticles

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A B S T R A C T

The interaction of three gas phase short chain alcohols (methanol, ethanol, and 2-propanol) with α-Fe2O3 (hematite) nanopowder was examined using a combination of temperature programmed desorption (TPD), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and density functional theory (DFT) calculations using a model ferric oxyhydroxide cluster. TPD analysis and FTIR spectra clearly indicated the asymmetric coexistence of associatively and dissociatively adsorbed alcohol species and different degree of surface coverages which are not only dependent of temperature but also dependent of the chemical identity of the alcohol molecule. The comprehensive analysis of IR spectra and the calculated vibrational frequencies for adsorbed alcohols obtained through DFT modeling suggest that the mechanistic pathway for alcohol chemisorption over α-Fe2O3 surfaces is regulated by the presence of accessible coordinately unsaturated Fe sites. A linear correlation between the Brønsted acidity of the alcohol and the ratio of associatively/dissociatively adsorbed species on the α-Fe2O3 surface is reported.

1. Introduction

Iron-bearing oxide minerals differ in composition, oxidation state and crystalline structure [1]. This diversity in chemical structure, provides iron oxide species with a wide range of properties which play a fundamental role in soil and groundwater chemistry [2]. For this reason, iron bearing materials have been investigated for a wide range of environmental applications. Among iron oxide/hydroxides, hematite (α-Fe2O3) is the most stable phase for iron oxide, formed in nature by spontaneous aging of maghemite and magnetite [3]. This material has been extensively evaluated for applications in adsorption of gas phase and aqueous inorganic and organic contaminants [4–7] and used for the environmental remediation of soil and groundwater in industrial sites [8,9]. In these applications, contaminant adsorption by hematite-bearing iron oxide has been identified as a key mechanism [10,11]. The mechanisms for these process are still under debate [10]; with studies involving gas phase organic molecules acting as probe for hematite surfaces providing detailed information about the distribution and strength of the different adsorption sites present in these surfaces [12]. For instance, adsorption of NO, SO2, CO and CO2 have demonstrated the existence of active Lewis acid sites on iron oxides surfaces [12–14]. Experiments on adsorption and desorption of organic compounds have revealed the crucial role of surface hydroxyls present in iron oxides/

hydroxide surfaces in the adsorption process [15]. However, a complete description of the adsorption mechanisms of organic molecules on hematite is not complete since obtaining a quantitative description of the distribution of adsorbed species is quite challenging due to the heterogeneity and complexity of hematite surfaces. Some of these challenges can be overcome by synthesizing for iron oxide nanocrystals with controlled facets [16,17]. Regardless of the synthesis method, the surface of hematite is covered with chemisorbed water, surface hydroxyls (potential Brønsted acid sites), and coordinately unsaturated Fe cations (potential Lewis acid sites). In this contribution, the study of the adsorption for a series of C1, C2 and C3 alcohols over hematite was chosen as a proxy to investigate the interaction of polar organic gas phase molecules with hematite surfaces using surface sensitive spectroscopy techniques and thermal desorption analysis. Additionally, adsorption of these alcohols over an iron oxide cluster model (oxyhydroxide (Fe2(OH)6(H2O)4)) was calculated using Density Functional Theory to verify the vibrational assignments observed in the spectroscopic analysis and to provide a quantitative description for each type of adsorbed species present in the system.

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2. Experimental

2.1. Material preparation

Nanosized maghemite (γ-Fe$_2$O$_3$) was purchased from Sigma Aldrich (particle size < 50 nm and surface area between 50 – 254 m^2 g^{-1} as per manufacturer specifications) and used without further purification. Hematite (α-Fe$_2$O$_3$) was prepared by thermal phase transformation of γ-Fe$_2$O$_3$, in a quartz glass tubular reactor (1.27 mm O.D.) with a porous bed quartz frit heated in flowing helium (Praxair, UHP, 10 cm^3 min^{-1}) at 500 °C for 5 h.

2.2. Iron oxide characterization

The specific surface areas of the obtained materials were measured by seven points Brunauer-Emmett-Teller (BET) method using N$_2$ adsorption-desorption isotherms at 77 K (Micromeritics TriStar II 3020 Physisorption Analyzer) previous degassing at 90 °C for 1 h and 200 °C for 4 h under N$_2$ atmosphere. Raman spectra of samples were collected using a Raman instrument (Jovin Yvon-Horiba LabRam 800) equipped with air-cooled charge coupled device (CCD). The 514 nm excitation line from a 1 W diode-pumped solid-state (DPSS) laser was used. The laser power at the sample position ranged from 1.0 to 2.0 mW. Raman spectra were then taken at ambient temperature, data collection was set 30 sec for the spectral window ($-50 – 1500$ cm^{-1}). The Raman shift was calibrated by interpolation of the Rayleigh line and a silicon wafer signal (520 cm^{-1}). The crystalline structure of the obtained samples was evaluated by X-ray diffraction (XRD) conducted on Rigaku rotating-anode X-ray diffractometer using CoKα radiation (λ = 1.54059 Å), operated at 45 kV and 160 mA with a scan rate of 0.02° over 2θ range of 10–60°.

The number of accessible OH groups (potential Brønsted acid sties, H_B^+) and coordinately unsaturated Fe sites (potential Lewis acid sites, H_L^+) present initially over α-Fe$_2$O$_3$ was determined by a combination of pyridine titration at 200 °C and analysis of the pyridine adsorption using IR spectroscopy (bands at 1548 cm^{-1} for Brønsted and 1435 cm^{-1} for Lewis sites). The total acid site density was quantified by isothermal chemical titration with pyridine. A small amount of sample (150 mg) was loaded into a quartz micro reactor (9.5 mm inner diameter), supported on a coarse quartz frit. The solid powder was treated *in situ* under flowing air (zero grade, Linde, 5.0, 0.83 cm^3 s^{-1}) at a constant heating rate of 0.083 °C·s^{-1} – 200 °C for 1 h. As the reactor temperature reached and was maintained isothermally at 200 °C, the air flow was switched to helium (Linde, grade 5.0, 0.83 cm^3 s^{-1}). This was carried without exposing the sample to the atmosphere. Thirty minutes after He flow started, pyridine (Sigma-Aldrich, > 99.9%, CAS #110-86-1) was introduced at $3.42 \times 10 - 8$ mol s^{-1} through a gastight syringe (SGE, Model 006230, 0.25 mL) into a vaporization zone maintained at 120 °C and located at the upstream of the reactor, within which pyridine was evaporated and mixed with the flowing He stream. The amount of pyridine in the effluent stream was quantified using a flame ionization detector (FID) in a gas chromatograph (Agilent, 7890A). Pyridine adsorption was completed when the analysis of the molar flow rate of pyridine in the effluent stream became indicated it had become identical with that of the feed stream, at which point the isothermal chemical titration step was completed. The number of total accessible H$^+$ sites was determined by counting the pyridine uptake (denoted as mol H$^+$) based on the assumption that a pyridine-to-H$^+$ molar ratio is equal to unity. After pyridine titration, the sample was carefully transferred to IR spectroscopy (Bruker, vertex 70) to avoid the exposure to moisture then the pyridine adsorption IR spectra was acquired.

2.3. In situ FTIR experiments

In situ FTIR experiments were carried to probe the surface interaction of the alcohol molecules with α-Fe$_2$O$_3$. Experiments were carried on a FTIR vertex 70 Bruker, equipped with a liquid nitrogen cooled MCT detector and external globar IR source. A diffuse reflectance cell (Harrick Scientific) with ZnSe windows, water cooling and electric heating system was used. Spectra were preliminarily obtained using ZnSe powder (Sigma, 99.99%) as spectral baseline before and sample pretreatment. Alpha-Fe$_2$O$_3$ were pretreated to desorb moisture and remove impurities by heating it to 300 °C under a He flow (Praxair, UHP, 45 cm^3 min^{-1}) for 1 h at a rate of 10 °C min^{-1}. Once the pretreatment step was completed, the clean surface was utilized as a spectroscopic background throughout the experiment. Following this step, either methanol (Caledon Lab., 99.8%), absolute ethanol (distilled, Brampton, Ontario), or 2-propanol (Sigma, HPLC grade) was slowly introduced to reaction cell at 0.0167 mL min^{-1} (liquid phase, equivalent to 2.09 kPa of methanol, 1.45 kPa of ethanol and 0.94 kPa of 2-propanol in the gas phase.) via a gas tight syringe mounted on a syringe infusion pump (Model KDS100, KDS scientific) attached to vaporizing zone, in which the alcohol was evaporated and mixed with a He stream (Praxair, UHP, 45 mL min^{-1}) at 120 °C for 30 min until the sample was saturated with gas phase alcohol. The injection port and transfer lines were heated to 120 °C to prevent condensation. IR spectra were continuously obtained right after the injection at intervals of 5 min at a spectral resolution of 4 cm^{-1} averaging 256 scans in the 4000–600 cm^{-1} range. This step was followed by purging of the gas phase alcohols inside the IR reaction chamber using He stream of 45 cm^3 min^{-1} for 1 h to remove the gas phase in the reaction chamber, after gas phase alcohol removal the IR spectra was acquired under isothermal conditions.

2.4. Temperature programmed desorption

Temperature programmed desorption (TPD) was used to obtain the desorption profiles of alcohols. This was carried using a flame ionization detector (FID, SRI instrument). TPD experiments were carried out in a continuous flowing system under atmospheric pressure. Before starting the experiments, samples were first pretreated at 300 °C under He flow (Praxair, UHP, 50 cm^3 min^{-1}) for 2 h. Then, the sample was cooled down to the adsorption temperatures (50, 100, 125 and 150 °C) while flowing in He of 50 cm^3 min^{-1}. Following this step the sample was saturated with one of the alcohols (methanol, ethanol, or 2-propanol, 0.2 kPa in He flow) for 1 h. To get rid of the condensed molecules in the stream, samples were evacuated for 4 h under He flow. In the flushing process, FID signal was continuously monitored until it turned back to the initial baseline value indicating absence of alcohol in the gas stream. The effluent gases, generated during desorption experiments were monitored using an Agilent GC7890A attached to a mass spectrometer (Agilent MSD model 5975C).

2.5. Computational details

The DFT calculations were carried out using the Gaussian 09 package of computer codes for geometry optimization and IR frequencies, running on SHARCNET. Density functional theory calculations were performed on Fe (III) hydroxide cluster models with alcohols attached in various configurations to evaluate the configuration of possible surface species. The geometries of the cluster models were previously optimized at the UB3LYP unrestricted hybrid exchange-correlation functional level with the 6–311 G (d,p) basis set.

3. Results and discussion

3.1. Material characterization

Fig. 1 shows the Raman spectrum and X-ray diffraction pattern of α-Fe$_2$O$_3$ (hematite) obtained by calcining γ-Fe$_2$O$_3$ at 500 °C for 5 h in flowing dry air. The Raman spectrum (Fig. 1a) displays five characteristic bands at 219 (A1g), 284 (E$_g$), 398 (E$_g$), 488 (A$_{1g}$), and