Adsorption of trimethyl phosphate and triethyl phosphate on dry and water pre-covered hematite, maghemite, and goethite nanoparticles

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ABSTRACT

Adsorption of trimethyl phosphate (TMP) and triethyl phosphate (TEP) on well-characterized nanoparticles of hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), and goethite (α-FeOOH) has been studied by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), 2D correlation DRIFTS analysis, and X-ray photoelectron spectroscopy (XPS) on dry and water pre-covered surfaces. It is shown that, at room temperature and low coverage, both TMP and TEP coordinate to Lewis acid Fe sites through the O phosphoryl atom on hematite and maghemite, while hydrogen bonding to Brønstedt acid surface OH groups dominates on goethite. At room temperature, slow dissociation of TMP occurs on the iron (hydr)oxide nanoparticles, whereby a methoxy group is displaced to form surface methoxy, leaving adsorbed dimethyl phosphate (DMP). Methoxy is further decomposed to formate, suggesting an oxidative degradation pathway in synthetic air on the oxide particles. Relatively, larger amounts of DMP and surface methoxy form on maghemite, while more formate is produced on hematite. Upon TMP adsorption on dry goethite nanoparticles, no oxidation surface products were detected. Instead, a slow TMP hydrolysis pathway is observed, yielding orthophosphate. It is found that pre-adsorbed water stimulates the hydrolysis of TMP. In contrast to TMP, TEP adsorbs molecularly on all iron hydr(oxide) nanoparticles. This is attributed to the longer aliphatic chain, which stabilizes the loss of charge on the methoxy C—O bonds by charge redistribution upon phosphoryl O coordination to Fe surface atoms. The presented results implicate different reactivity depending on specific molecular structure of the organophosphorus compound (larger functional groups can compensate loss of charge due to surface coordination) and iron (hydr)oxide surface structure (exposing Lewis acid or Brønstedt acid sites).

1. Introduction

Interactions of organophosphorus (OP) compounds with iron and its (hydr)oxides are important in a number of applications, including remediation technologies, catalysis, and environmental fate analysis [1–4]. To date, very few detailed studies have, however, been reported on the interactions of organophosphorus (OP) compounds with iron (hydr)oxides [5,6], which may be related to the relative complexity of these systems. Further, there are only a limited number of studies of other OP/oxide systems. Nanostructured hematite (α-Fe$_2$O$_3$) catalyzes the decomposition of pesticides and chemical warfare agents, in particular when stimulated with light [7,8]. It is proposed that clays and iron oxide minerals may be used as catalysts of Fenton-like reactions for the decontamination of soils, groundwater, sediments, and industrial effluents [9]. In environmental sciences, the interaction of OP compounds with iron (hydr)oxides is important for understanding the bioavailability and degradation of industrial and domestic wastes, pesticides, etc. [8,10–14]. Overload of OP in nature strongly contributes to high levels of anthropogenic phosphate causing eutrophication in soil and water. As a consequence of the high content of iron (hydr)oxides in the earth's crust, and the high reactivity of phosphates toward solid iron-containing particles in terrestrial and aquatic environments [15], iron minerals constitute an important part of the anthropogenic phosphorus cycle. Iron oxides may promote decomposition of OP and can also act as a sink for OP [10]. Furthermore, OP may promote mineral dissolution, regulate available sorption sites, and control sorption of other compounds [16].

An important step toward a comprehensive understanding of OP interactions with iron (hydr)oxides is to devise and study simplified model systems, conducted under idealized conditions, for example, under vacuum or in controlled gas atmosphere, to scrutinize possible elementary steps in the surface chemistry of these systems. Previous studies of such systems include trimethyl phosphate (TMP) adsorption on TiO$_2$ [17,18], WO$_3$ [18–20], MgO [21], and α-Fe$_2$O$_3$ [22], respectively, and triethyl phosphate (TEP)

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adsorption on TiO_2 [17] and MgO [21], respectively. In addition, there are several studies on model phosphonates, such as di-methyl–methyl phosphonate (DMMP), on well-defined metal oxide systems, in particular TiO_2 [23,24], and also on iron oxides [8]. Similar model studies of OP interactions with iron (hydr)oxides are hitherto by and large lacking [6].

In the present study, we employ three distinct, well-characterized forms of iron (hydr)oxide colloidal particles [6]: hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and goethite (α-FeOOH), respectively, as model systems for OP interaction with iron (hydr)oxide in synthetic air. We use two simple OP compounds, TMP and TEP, which differ only by the length of the aliphatic chain. These OP constitute the basic structures of many pesticides [10]. We employ in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS) to study the gas-phase OP adsorption on iron oxide nanoparticles, with and without pre-adsorbed water in synthetic air. The inclusion of water vapor aims to simulate an intermittent situation between adsorption at the gas–solid and liquid–solid interfaces.

2. Experimental

2.1. Materials

The preparation of oxide and hydroxide nanoparticles and their physical properties have been reported in a previous publication [6]. The samples were pre-treated prior to experiments to remove organic residues as determined by DRIFT spectroscopy as follows: Maghemite samples were calcined at 300 °C for 80 min and washed in 4 mM NaOH and milliQ-water to remove organic residues [25]. The hematite and goethite samples were in addition annealed in situ in the reaction cell at 400 and 200 °C, respectively, for 20 min in synthetic air and then cooled to 20 °C. The lower annealing temperatures for maghemite and goethite were necessary to ensure phase purity. Phase purity (determined by Raman spectroscopy) and spectroscopic purity of the samples (determined by in situ DRIFT during pre-treatment) were confirmed prior to measurements. The physical properties of the nanoparticles are summarized in Table 1 [6]. The OP compounds trimethyl phosphate (liquid TMP; $C_3H_9O_4P$) (98% GC purity, Merck Germany) and triethyl phosphate (liquid TEP; $C_6H_{15}O_4P$) (98% GC purity, Sigma–Aldrich, USA) were used without further purification.

2.2. Diffuse reflectance infrared Fourier transform spectroscopy

In situ Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS), measurements were performed in a modified reaction cell using a Bruker IFS-66v/S spectrometer equipped with

liquid nitrogen-cooled broad-band MCT detector. Spectra were acquired at 4 cm^{-1} resolution, and each spectrum was the average of 128 scans. Repeated in situ DRIFT spectra were acquired as a function of dosing time with background spectra acquired in synthetic air $\sim$6 min before introduction of TMP and TEP. The reported spectra are raw spectra without any smoothing or baseline corrections. The DRIFT reaction cell was connected to a gas generator system, which allows controlled dosing of reaction gas in the reaction cell as described elsewhere [25]. Briefly, the reaction gas was generated by evaporation of OP liquids into a carrier gas stream (synthetic air, 100 ml min^{-1}) from a diffusion tube connected to a temperature controlled reservoir held at $T = 62 \pm 0.2$ °C, yielding a gas injection rate of 6.08 and 2.56 μg min^{-1} into the feed gas for TMP and TEP, respectively (equivalent to 19 ppbv and 6 ppbv, respectively). This low dose rate was chosen to be able to explore sub-monolayer adsorption with sufficient time-resolution in the in situ experiments. In experiments with pre-adsorbed water, the samples were exposed to humidified air (relative humidity, RH 17%) for 20 min, followed by 20 min of dry synthetic air (purging). This corresponds roughly to an initial water coverage on the surfaces of ca. 4 monolayers (MLs), assuming that the water desorption energy is equal to the sublimation energy. Here, 1ML of water is defined to be 10^{19}-molecules m^{-2}. To ensure reproducibility, the water exposure was simultaneously measured by in situ DRIFTS. A rough estimate assuming zero order desorption showed that 0.5% of the water coverage desorbs during the purging period (20 min). OP dosing was then performed in the same manner as in the dry experiments. Liquid reference spectra of OP liquids were acquired using a DuraSamplIRII ATR accessory equipped with a nine internal reflection diamond element and collected at 2 cm^{-1} resolution. Each spectrum was averaged over 300 scans and corrected for the wavelength dependent intensity [26].

2.3. 2D correlation analysis

DRIFT spectra were analyzed with 2-dimensional (2D) correlation analysis using the 2Dshige program [27] following the general procedures described by Noda and Ozaki [28]. Spectral 2D correlation was analyzed as a function of OP dosing time (external perturbation). The analysis was performed in the methyl stretching region between 3050 and 2790 cm^{-1} and in the finger print region between 1600 and 1000 cm^{-1}. The spectra were baseline corrected by fitting straight lines between the endpoints of each region. From the 2D correlation analysis, correlated and uncorrelated spectral variations were identified, as well as the time-sequences of absorbance variations. This facilitated assignments of vibrational bands associated with uncorrelated species, and their temporal evolution as a function of OP dosing time, which were used to construct kinetic models of OP reactions on the (hydr)oxide particles. Detailed description of the 2D correlation analysis is provided in the Supporting information.

2.4. Kinetic modelling

Kinetic models were constructed based on the temporal evolution of the concentrations of uncorrelated surface species obtained from DRIFTS and 2D correlation analysis. Parameter fitting of the kinetic models was performed using iterative numerical integration over the time interval $0 \leqslant t \leqslant 42$ min, defined by the discrete time step, t_i, using the Matlab ODE Runge–Kutta solver, ode45. For each DRIFT spectrum, the root means square, rms, function, $rms\sum_i \sqrt{\sum_i (\theta_i(t_i) - \hat{\theta}_j(t_i))^2}$, was minimized over the parameter space defined by the uncorrelated species, where j is the OP rate constants for adsorption and reactions, θ_j is the surface coverage of specie j at time t_i obtained from numerical integration, and $\hat{\theta}_j$

Table 1
Physical properties of iron oxide and hydroxide nanoparticles.

Material	d (nm) (TEM)	d (nm) (XRD)	Fe/O ratio (XPS)	BET surface area ($m^2 g^{-1}$)	BJH average pore width (nm)
Hematite	$\sim$30	30.74[d]	2:3.031	28.98	22.2
Maghemite	$\sim$20 ($\sim$35)[a]	16[e]	2:2.931	90.03	7.9
Goethite	$\sim$11[b] $\sim$62[c]	8.06[f] 31.83[g]	1:981	100.06	13.6

[a] Value in parenthesis shows the average d determined for the (sedimented) large particles.
[b] Average calculated as an average of height and width.
[c] Average calculated from length of long-axis.
[d] Average calculated from the $\langle 012 \rangle$, $\langle 104 \rangle$, $\langle 110 \rangle$, $\langle 116 \rangle$ reflections.
[e] Average calculated from the $\langle 220 \rangle$, $\langle 311 \rangle$, $\langle 400 \rangle$ reflections.
[f] Average calculated from the $\langle 110 \rangle$ reflection.
[g] Average calculated from the $\langle 002 \rangle$ reflection.