Nitrate Photochemistry in Zeolite NaY: Product Formation and Product Stability under Different Environmental Conditions

Abstract

In the atmosphere, mineral dust particles are often associated with adsorbed nitrate from heterogeneous reactions with nitrogen oxides. Nitrate ions associated with mineral dust particles can undergo further reaction including those initiated by solar radiation. Although nitrate photochemistry in aqueous media is fairly well studied, much less is known about the photochemistry of nitrate adsorbed on mineral dust particles. In this study, the photochemistry of nitrate from HNO$_3$ adsorption in NaY zeolite under different environmental conditions has been investigated using transmission FTIR spectroscopy. NaY zeolite is used as a model zeolite for studying reactions that can occur in confined space such as those found in porous materials. Upon nitrate photolysis under dry conditions (relative humidity < 1%), surface nitrite is formed as the major adsorbed product. Although nitrite has been proposed as a product in the photochemistry of nitrate adsorbed on metal oxide particle surfaces, such as on alumina, it has not been previously detected. The stability of nitrite in NaY is attributed to the confined three-dimensional structure of the porous zeolite which contains a charge compensating cation that can stabilize the nitrite ion product. Besides adsorbed nitrite, small amounts of gas phase products are observed as well including NO$_2$, NO and N$_2$O at long irradiation times. The amount of nitrite formed via nitrate photochemistry decreases with increasing relative humidity whereas gas phase NO and N$_2$O become the only detectable products. Gas-phase NO$_2$ does not form at RH > 1%. In the presence of gas phase ammonia, ammonium nitrate is formed in NaY zeolite. Photochemistry of ammonium nitrate yields gas phase N$_2$O as the sole gas phase product. Evidence for an NH$_2$ intermediate in the formation of N$_2$O is identified with FTIR spectroscopy for HNO$_3$ adsorption and photochemistry in NH$_4$Y zeolite.