

Development of Highly Selective Inorganic Anion-Exchange Materials for Efficient Removal of Nitrate Ions

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[Abstract]

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The imbalance in nitrogen circulation is global environmental concern, in association with contamination of harmful nitrate ion in agricultural runoff arising from the overuse of nitrogen-rich fertilizers. Separation in commonly used technologies (such as adsorption-based and membrane-based processes) for ionic species is driven based on host–guest interactions (size exclusion, coulombic interaction, and chemical binding affinity). The binding energies of ions are also affected by guest–guest interactions in nanoporous materials, such as clays, zeolites, and metal oxides, which in turn changes selectivity and ion-storage capacity. The importance of this mechanism is particularly profound for low nucleophilic nitrate ions owing to weak host–guest interactions. However, the key design criteria for materials that control guest–guest interactions remain unclear because anionic compound classes are limited. Herein, through layered double hydroxides (LDHs), a class of anionic clay, with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, A^{n-} is the charge-compensating anion, and x is the molar fraction of the trivalent cation [$M^{3+}/(M^{2+} + M^{3+}) = 0.166\text{--}0.33$], we demonstrate that the guest–guest interactions (i.e., steric interaction and hydrogen-bond) considerably influence the ion separation of a low-nucleophilicity nitrate ions, which can be precisely controlled by the modulated chemical composition of anionic site (OH) and metal cationic site (M^{3+} , M^{2+}) in the metal hydroxide layers. Especially, the specific hexagonal cation ordering improves the nitrate ion adsorption capacity up to ~250% of that of a conventional LDHs (prepared by co-precipitation) with trivalent metal ratio of 0.25–0.28 (e.g., Mg/Al, Mg/Ga, and Co/Fe). In addition, using two LDHs, having different interlayer filling density were prepared with modulated host charge density, we showed that 24% decrease in the filling density increase the storage capacity by 300%. Furthermore, quartz crystal microbalance with dissipation monitoring (QCM-D) was studied to prove the dynamic structural change of LDHs upon nitrate storage. The results were combined with multimodal *ex situ* experimental results and theoretical calculations, and clarified that the low filling density effectively facilitates the 2D hydrogen-bond networking structure in the interlayer water around nitrate ions retaining the original layered structure, which leads to the high storage capacity while the high filling density requires the 3D networking structure and destabilize the LDHs.