Impact of Thermal Activation Conditions on Physicochemical Properties of Nanosheet-derived Mg-Al Mixed Oxides

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Mg-Al mixed oxides were synthesized by anion-exchange of carbonates in Mg-Al layered double hydroxides (MgAl-LDHs) with isethionates and subsequent thermal treatment. Anion-exchange causes stacking disorder in MgAl-LDHs as reported in the literature and allows their delamination in water. Despite highly disordered structure of dried materials, thermal treatment of them in air yielded Mg-Al mixed oxides with low surface area and CO_2 adsorption capacity. In contrast, thermal treatment in N_2 or N_2 followed by air resulted in marked increase in CO_2 adsorption capacity up to ≈800%. Moreover, their surface areas and CO_2 adsorption capacity exceeded those derived from the original MgAl-LDHs.

Keywords: layered double hydroxides, CO_2 separation, nanosheet

1. Introduction

Mg-Al mixed oxides derived from MgAl-LDHs have been investigated as acid-base catalysts [1,2], catalyst supports, and high-temperature CO_2 adsorbents like those used in sorption-enhanced steam reforming of methane (SE-SRM) [3]. Previous work demonstrated a prospective performance of Mg-Al mixed oxides in SE-SRM, but indicates that further improvement in CO_2 adsorption capacity is required to realize industrial application. In the course of our investigation on water-dispersible Mg-Al double hydroxide nanosheets reported in the literature [4] to aim at synthesizing Mg-Al oxides with a high concentration of accessible basic sites, we observed that thermal activation has significant influence on their physicochemical properties. Here, we report these new findings to demonstrate a prospective route for the synthesis of Mg-Al mixed oxides with a high concentration of accessible basic sites.

2. Experimental

MgAl-LDHs bearing isethionates (MgAl-Ise) were prepared by the literature method [4] by anion-exchanging synthetic hydrotalcites ($Mg_3Al(OH)_8(CO_3)0.5\cdot mH_2O$, MgAl-$CO_3$, Kyowa Kagaku Kogyo Co.) with isethionic acid ammonium salt (Sigma-Aldrich, 99%) in ethanol. The solids were separated, dried and subsequently heated at 300−1000 ºC in flowing air or nitrogen for 3 h. Some of the resultant materials were subject to the second heat treatment in air or N_2. A part of MgAl-Ise was delaminated in water and subjected to the same heat treatments as MgAl-Ise. Samples were characterized by elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD) technique, N_2 adsorption at –196 ºC and CO_2 adsorption at 25 ºC as well as elevated temperatures, thermogravimetric (TG) analysis, and transmission electron microscopy.

3. Results and discussion

Characterization of MgAl-Ise by IR spectroscopy, elemental analysis, and PXRD indicates near complete exchange of carbonates with isethionates (Ise). The PXRD data show that the anion-exchange with Ise expanded the interlayer distance of Mg-Al LDHs and caused turbostratic disordering in the lamellar structure. MgAl-Ise was delaminated by simply slurrying its powder in water at a high dilution under a N_2 flow, and yielded a suspension that exhibited Tyndall effect. These results are in line with those reported in the literature [4], confirming successful anion-exchange and delamination.

Thermal treatments of Ise-containing MgAl-LDHs yielded Mg-Al mixed oxides characterized as periclase phase at ca. 300–700 ºC and $MgAl_2O_4$ spinel phase at higher temperatures. Although thermal activation in air and N_2 formed the same phase, N_2 and CO_2 adsorption data show substantially different properties for samples heated in air and N_2. MgAl-Ise treated in N_2 at 500 ºC or N_2 followed by air both at 500 ºC showed BET surface areas ≈400% higher than MgAl-Ise heated in air and ≈160% higher than Mg-Al mixed oxides derived from the original $MgAl\text{-}CO_3$ (Figure 1). The CO_2 adsorption data for MgAl-Ise heated in N_2 at various temperatures exhibited significantly higher CO_2 adsorption capacity (up to ≈800% higher) than MgAl-Ise heated in air.

Analysis of the effects of thermal activation conditions by TG, elemental analysis and IR spectroscopy indicates that thermal activation in N_2 enables the removal of sulfur species formed from Ise at ~400 ºC. On the other hand, the removal of sulfur species in air required temperatures as high as ~900 ºC as indicated by the step weight loss in the TG data (Figure 2). Because the literature data [5] indicate that thermal activation of MgAl-LDHs bearing sulfates (SO_4^{2-}) in the interlayer region results in grafting of sulfates on brucite layers at ~250 ºC and removal of these species requires temperatures higher than 900 ºC, we infer that the thermal activation of MgAl-Ise in N_2 prevents the oxidative decomposition of Ise to sulfates and limits bridging of sulfur species between Mg-Al double hydroxide nanosheets, and enables the formation of micropores between them upon their transformation into Mg-Al mixed oxides.

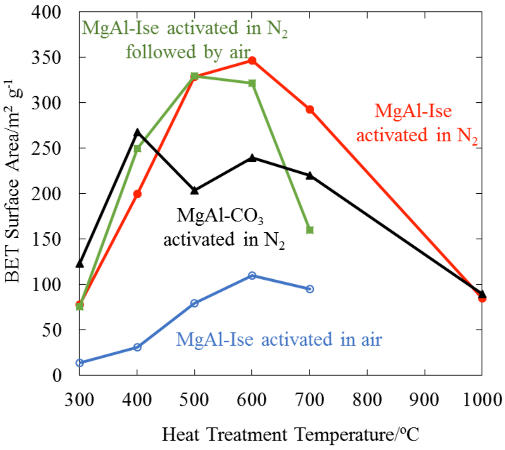

Figure 1. BET surface area characterizing MgAl-Ise and $MgAl\text{-}CO_3$ thermally activated at various temperatures.

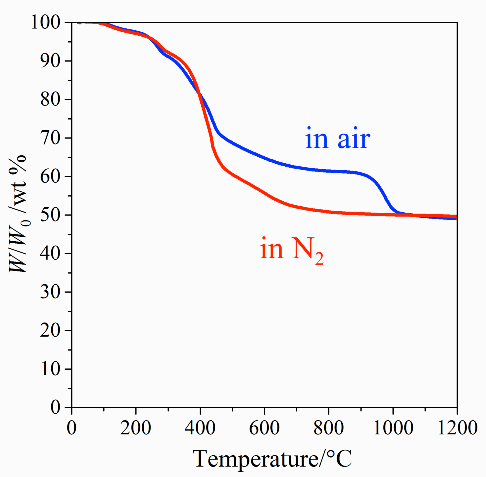

Figure 2. TGA curves characterizing MgAl-Ise in air or N_2.

4. Conclusions

Anion-exchange of carbonates in $MgAl\text{-}CO_3$ with Ise proceeded successfully and formed disordered MgAl-LDHs, which were readily delaminated in water. Although the materials possessed highly disordered structure, thermal activation in air yielded Mg-Al mixed oxides possessing low surface areas and CO_2 adsorption capacity. In contrast, thermal activation in N_2 or a sequence of N_2 followed by air resulted in marked increases in surface area and CO_2 adsorption capacity. Investigation on the impact of thermal activation conditions indicates that activation in N_2 enables removal of sulfur species at low temperature and limits bridging of them between nanosheets. The results show that the proper activation conditions in addition to structural disordering caused by anion-exchange and delamination yielded Mg-Al mixed oxides possessing higher surface areas and CO_2 adsorption capacity than those derived from the original $MgAl\text{-}CO_3$. Our results also suggest a general strategy to synthesize Mg-Al mixed oxides with a high concentration of accessible basic sites by tuning the nature of interlayer anions and their reactivity in thermal activation steps.

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References

1. F. Cavani, F. Trifirò, A. Vaccari, Catal. Today, 11 (1991) 173.
2. A. Corma, V. Fornés, R.M. Martín-Aranda, F. Rey, J. Catal., 134 (1992) 58.
3. D.P. Harrison, Ind. Eng. Chem. Res., 47 (2008) 6486.
4. Nobuo Iyi, Yasuo Ebina, and Takayoshi Sasaki, J. Mater. Chem, 21 (2011) 8085.
5. V.R.L. Constantino, T.J. Pinnavaia, Inorg. Chem., 34 (1995) 883.