Study on the coating of nano-scale SiO₂ film on the surface of nanocrystalline Mg-Al layered double hydroxides

ZHANG Zejiang¹,²,³, MEI Xiujuan², XU Chenghua¹ & QIU Fali¹

1. Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China;
2. Sichuan Fire Research Institute of Public Security Ministry, Chengdu 611830, China;
3. Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Correspondence should be addressed to Zhang Zejiang (email: zzjzzjzz@mail.sc.cninfo.net)

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Abstract  The coating process of a nano-scale SiO₂ film on the nanocrystalline Mg-Al layered double hydroxides via a sol-gel process was investigated. The uniform and dense SiO₂ film with a thickness of about 5 nm on the nano-LDHs particles was characterized by the solubility test in the dilute HNO₃ or HCl acid, TEM and FT-IR, XRD, TG and DSC. The chemical shifts of binding energies of Al 2p, Mg 2p, Si 2s and O 1s on the coated particles indicate that the coating of the SiO₂ nano-film on the surface of the nano-LDHs proceeds through the formation of Mg-O-Si and Al-O-Si bonds. The thermal analysis shows that both the SiO₂-coated nano-LDHs and the nano-LDHs have a similar mass loss process, in which there are three obvious stages of mass loss in the temperature range of 40—700°C. Furthermore, the more the coated amount of SiO₂ on the surface of the nano-LDHs is, the less the mass loss of the samples is at 700°C. The nano-LDHs have two obvious endothermic peaks at 244.67°C and 430.13°C, whose corresponding heat absorption capacities are 412.28 J/g and 336.30 J/g, respectively. In contrast, the coated nano-LDHs have only one endothermic peak at 243.60°C with a heat absorption capacity of 221.25 J/g.

Keywords: layered double hydroxides, nanocrystalline, silica, coating.

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Since the layered double hydroxides (abbreviated as LDHs) were firstly reported to be used as precursors of new catalytic materials by S. Miyata¹ in 1971, their preparations, ion-exchanges with the balancing interlayer anions, structure characteristics and the other potential applications have attracted more and more interests. It should be noticed that the nanocrystalline layered double hydroxides² (abbreviated as nano-LDHs) could play a quite important and unsurpassable role in its applications. It was a kind of composite metal hydroxide with a well-defined layered structure, wherein contained important functional groups such as crystal water and hydroxyl groups, which made the nano-LDHs have an excellent fire-retardant and smoke-restrained performance³. However, the nano-LDHs’ hydrophilicity and oleophobicity⁴ gave rise to a poor affinity between inorganic and organic phases, leading to its mal distribu-
tion in polymer matrices and an interphase disfigure-
ment between two phases. On the other hand, the in-
terlayer OH- groups in the nano-LDHs could react
with CO₂ in air, leading to saltingout phenomena.
These were very disadvantageous to their applications
in the fire-retardant products. In order to solve this
problem, researchers usually adopted the surfactant
or coupling agent to modify the surface of the nano-
LDHs. In this work, we firstly used a sol-gel method
to coat a SiO₂ nano-film on the surface of the
nano-LDHs so as to modify the nano-LDHs. The
coated nano-LDHs were characterized by TEM images
and FT-IR, XRD and XPS curves. And their thermal
behaviors of the coated nano-LDHs were investigated
and analyzed by TG and DSC curves.

1 Experimental

1.1 Materials

The nano-LDHs, Mg₆.₄₁A₁₁.₇₀(OH)₁₅.₉₂CO₃·₄.₂₆
H₂O synthesized according to the literature[6], pos-
sessed a particle size of 10—40 nm. Its XRD pattern
showed an apparent intense peak of the (003) crystal
surface for the double layered compounds at 2θ =
11.2° and the corresponding interlayer distance (d)
was 0.792 nm. Another apparent peak at 2θ = 60.₄₉°
was attributed to the (110) crystal surface of the dou-
bble layered compounds and the d value was 0.15 nm.
The intensities of peaks were strong and acute, exhib-
it ing that the well-crystallized nano-LDHs had a
unique and ordered crystal structure.

The other reagents were of analytical reagent
grade and used without further purification.

1.2 Synthesis of the coated nano-LDHs

0.₀₅ g of sodium hexametaphosphate dispersant
was added to 70 mL deionized water and stirred for 10
min so as to ensure a complete dissolution of the ma-
terial. Then, 2 g of the nano-LDHs was added into the
above solution and dispersed for 30 min under the su-
personic vibration in order to make the nano-LDHs
become a single-grain disperse state by and large. The
 suspension was heated up to 90°C and then its pH
value was adjusted and monitored at 9.₅ with a solu-
tion of NaOH (0.₅ mol/L). Then, 11 mL sodium sil-
cate solution and 2% HNO₃ solution were simultane-
ously added dropwise to the above suspension with
continuous stirring. During the addition, the pH of the
 suspension was held at 9.₅ through carefully control-
ing the addition rate of both solutions. Subsequently,
the solution was stirred continuously for additional 5
min and then aged at 90°C for 120 min. The obtained
solid products were filtrated and washed free of excess
hexametaphosphate ions by 100 mL deionized water at
40°C, then dried at 105°C for 2₄ h and ground to ob-
tain sample A, B, C, D and E.

1.3 Characterization

Powder X-ray diffraction (XRD) patterns were
recorded on an X'Pert Pro MPD X-ray diffraction in-
strument (Philips), using a CuKα (λ = 0.15405 nm)
radiation with Ni filtered at 20 mA and 40 kV, 2q an-
gel ranging from 3° to 85° and a scanning rate of
2°/min. FT-IR spectra of KBr disks were recorded on a
NICOLET 200SXV FT-IR spectrophotometer (Am-
erica). TEM images were recorded on a Hitachi H-800
transmission electron microscope (Hitachi). The XPS
data were tested by a JSE-5900LV V4105X energy
spectrometer. TG was carried out on the samples
weighing 1—2 mg at 10°C/min in N₂ atmosphere (80
cm³/min) using a Perkin-Elmer TGA7 thermal analy-
sis instrument. DSC was performed on the samples
weighing 1—2 mg sealed in Al pan, the estimated er-
ror of the peak temperature was 2°C and the enthalpy
calculated was ±6% at 10°C/min in N₂ atmosphere
(80 cm³/min) using a Perkin-Elmer DSC7 thermal
analysis instrument.

2 Results and discussion

2.1 Composition and acid-solubility of the samples

Comparing the quantity of the coated products
with that of the raw nano-LDHs (see table 1), we can
clearly see that the coated products are 0.₁₅—₀.₈₁ g
more than the raw nano-LDHs, indicating that SiO₂ or
its hydrate has been formed on the surface of the
nano-LDHs. The excess amounts are attributed to SiO₂