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A Highly Efficient Cu/Al$(OH)_3$ Catalyst for the Hydration of Acrylonitrile to Acrylamide

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A highly efficient, easily filterable Cu/Al$(OH)_3$ catalyst for the hydration of acrylonitrile to acrylamide has been synthesized by reducing a particle-size-controlled malachite phase-free Cu/Al hydrotalcite. The stability of the Cu/Al$(OH)_3$ catalyst under aqueous reaction conditions was further improved by treatment with H_3PO_4.

Acrylamide is an industrially important compound and currently produced at an annual rate of 5×10^5 t y^{-1}.[1] Notably, it is employed as a monomer for the synthesis of polyacrylamide, which is used in flocculants for waste water treatment, fillers in pulp for paper production, water-soluble thickeners, adhesive agents, soil improvement agents, and materials for enhanced oil recovery.[2] In addition, some acrylamide is used in the manufacture of dyes and in the manufacture of other monomers.

In industry, acrylamide is produced by the selective hydration of acrylonitrile, which is, however, often accompanied by undesired side reactions such as the hydration of the C=C bond and further reaction of acrylamide product with H_2O to give the corresponding carboxylic acids. Thus, effort has been focused on increasing product selectivity as well as improving catalytic activity. A number of catalysts have been developed for the reaction under mono- or multiphase conditions, involving metal complexes,[3] metal or metal oxide solid catalysts,[4] and enzyme catalysts.[5] From a practical point of view, heterogeneous catalytic liquid-phase hydration is preferable in terms of the simpler work-up after reaction and its utility in continuous-flow processes for large-scale production. Thus, various kinds of Cu-based heterogeneous catalysts have been employed for the industrial production of acrylamide.[6] Raney copper, for example, is a representative heterogeneous catalyst, but it exhibits low catalytic activity.

We herein report that a Cu/Al hydrotalcite-derived Cu/Al$(OH)_3$ catalyst prepared using coprecipitation serves as an easily filterable, highly efficient heterogeneous catalyst for the liquid-phase hydration of acrylonitrile to acrylamide. The key to this catalyst preparation was to grow the precursor particles of the Cu/Al hydrotalcite [$Cu_7Al_3(OH)_{20}(CO_3)_{1.5} \cdot mH_2O$ classically referred to as a Cu/Al "hydrotalcite-like" compound] without producing the malachite [$Cu_2(OH)_2CO_3$] phase, because the malachite phase is transformed to larger Cu particles with less active sites during the subsequent reduction step to Cu/Al$(OH)_3$. Literature is currently available on the synthesis of the binary Cu/Al hydrotalcite particles.[7,8] It is well-known that the malachite phase cogenerates during the crystallization to Cu/Al hydrotalcite because of the Jahn–Teller effect on the Cu^{2+} ion.

We first examined the aging conditions of the amorphous precipitate, which had been prepared by a simultaneous addition of the aqueous $Cu(NO_3)_2 \cdot 3H_2O$–$Al(NO_3)_3 \cdot 9H_2O$ mixed solution and the aqueous Na_2CO_3 solution. The crystal structure and mean diameter of the Cu/Al hydrotalcite particles were found to be dramatically influenced by the aging conditions. When the amorphous precipitate (denoted as **AP-1**) was aged in water at 90 °C for 1 h under air bubbling, a malachite phase-free Cu/Al hydrotalcite (denoted as **HT-1**) formed as shown in Figure 1a. On the other hand, the aging without air bubbling at 90 °C for 4 h yielded a low-quality Cu/Al hydrotalcite bearing a significant content of the malachite phase (**HT-2**), as shown in Figure 1b. It is assumed that the threefold molar excess of carbonate ions (CO_3^{2-}) contained in the amorphous precipitate[9] retarded the crystallization of Cu/Al hydrotalcite during the aging, while they accelerated the formation of the undesired malachite phase. The concentration of carbonate ions, however, could be reduced by performing the aging under the bubbling of air, which removed the carbonate ions as gaseous CO_2, leading to the smoother crystallization of Cu/Al hydrotalcite without the formation of the malachite phase.[10]

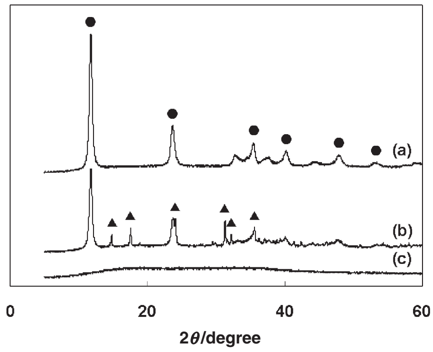
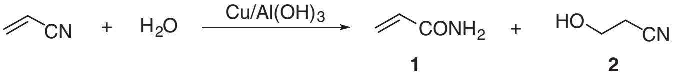


Figure 1. XRD profiles of the precursor Cu/Al hydrotalcites prepared from the amorphous precipitate (a) by aging at 90 °C for 1 h with air bubbling (**HT-1**), and (b) by aging at 90 °C for 4 h without air bubbling (**HT-2**). (c) Parent amorphous precipitate (**AP-1**). Symbols indicate the presence of Cu/Al hydrotalcite (●) and malachite (▲).

Figure 2 shows the scanning electron microscopic (SEM) images of various Cu/Al hydrotalcite particles prepared under different conditions. Average diameter of the particles of **HT-1** was ca. 3 µm (Figure 2a), whereas the particle size could further be enlarged to 15 µm by adding the amorphous precipitate slurry continuously (**HT-3**, Figures 2b and 2c). Based on the morphology of the particles, it is conjectured that some coagulation was involved in the particle growth process. Reduction of the Cu/Al hydrotalcites with molecular hydrogen at 200 °C did not alter the parent size and morphology of the particles, regardless of the preparation conditions. However, the crystal structure was drastically changed to yield the Cu nanocrystallite-dispersed amorphous Al$(OH)_3$ [denoted as Cu/Al$(OH)_3$], as revealed by X-ray diffraction (XRD) analysis.

Table 1 compares the behavior of various copper catalysts for the hydration of acrylonitrile to acrylamide performed in a

Table 1. Catalytic behavior of the copper catalysts for the hydration of acrylonitrile to acrylamide[a]



Catalysts	Precipitant	Precursor structures	Surface area[h] /m^2 g^{-1}	Cu(111) crystal size[i]/nm	Conv./%	Select./%	
						1	**2**
Cu/Al$(OH)_3$[b]	Na_2CO_3	Hydrotalcite (**HT-3**)	138	7.6	72.8	99.3	0.6
Cu/Al$(OH)_3$[b]	Na_2CO_3	Hydrotalcite (**HT-1**)	145	7.2	72.2	99.2	0.5
Cu/Al$(OH)_3$[b]	Na_2CO_3	Amorphous (**AP-1**)	125	7.4	73.2	99.3	0.5
Cu/Al$(OH)_3$[b]	Na_2CO_3	Hydrotalcite + malachite (**HT-2**)	83	32.1	40.1	99.2	0.5
Cu/Al$(OH)_3$[c]	NaOH/Na_2CO_3	Hydrotalcite (**HT-4**)	—[j]	—[j]	66.2	99.2	0.6
Cu/Al$(OH)_3$/H_3PO_4[b,d]	Na_2CO_3	Hydrotalcite (**HT-3**)	139	8.5	55.6	99.3	0.5
Cu/Al$(OH)_3$/H_3PO_4[b,e]	Na_2CO_3	Hydrotalcite (**HT-3**)	151	7.9	11.4	99.1	0.7
Raney Cu[f]	—	—	10	65.2	38.1	99.4	0.5
0.5%Cr/Cu[g]	HCHO	—	13	24.9	45.6	99.4	0.5

[a]Acrylonitrile 0.19 mol, H_2O 3.05 mol, catalyst 3 g, 70 °C, 2 h. [b]Cu/Al molar ratio = 7/3. [c]Cu/Al molar ratio = 2/1. [d]H_3PO_4 3 mol % for Al. [e]H_3PO_4 6 mol % for Al. [f]Purchased from Kawaken Fine Chemicals. [g]The catalyst was obtained by reducing a mixture of $CuCl_2$/$Cr(NO_3)_3$ in aqueous NaOH solution with HCHO described in ref. 6e. [h]Determined by BET method. [i]The sizes were determined by XRD analysis using the Scherrer equation. [j]Not measured.

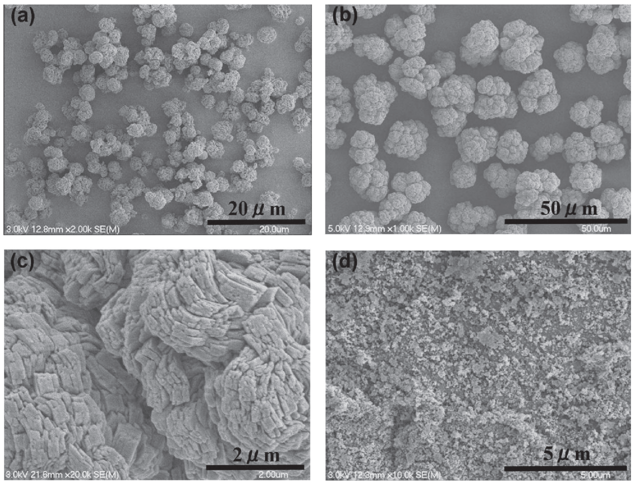


Figure 2. SEM images of the precursor Cu/Al hydrotalcites prepared from the amorphous precipitate by aging at 90 °C for 1 h with air bubbling. (a) Prepared batch-wise (**HT-1**). (b) Prepared by a continuous method (**HT-3**). (c) Magnified photograph of (b). (d) Parent amorphous precipitate (**AP-1**).

batch reactor at 70 °C for 2 h. All the catalysts gave acrylamide in >99% selectivity, but they were strikingly different in activity. The conventional hydration catalysts such as the Raney copper catalyst and the 0.5% Cr/Cu catalyst afforded rather low conversions of 38.1 and 45.6%, respectively. In contrast, the use of the Cu/Al$(OH)_3$ catalyst prepared from **HT-3** resulted in a much higher conversion (72.8%). This conversion was equal to that given by the Cu/Al$(OH)_3$ catalyst prepared from **HT-1** or amorphous precipitate (**AP-1**) with much smaller particles, indicating that the difference in particle size was not a crucial factor for determining the hydration activity. Note, however, that the catalyst obtained from **HT-3** with larger particle size is superior to those from **HT-1** and **AP-1** with smaller particle sizes in terms of easier filtration. When the Cu/Al hydrotalcite containing the malachite phase (**HT-2**) was used as a precursor, the corresponding Cu/Al$(OH)_3$ catalyst showed much lower activity (40.1% conversion). A powder XRD analysis revealed that the crystallite size of Cu(111) on the **HT-2**-derived catalyst was 32.1 nm, which was much larger than that of the **HT-3**-derived catalyst (7.6 nm).[11] It is assumed that the malachite phase in **HT-2** was converted to the larger Cu particles with smaller numbers of active sites, thereby leading to lower activity.

Velu and Swamy reported that a pure Cu/Al hydrotalcite could be synthesized even when the aging as well as precipitation was carried out at room temperature using a mixed base, NaOH–Na_2CO_3.[12] We also employed this method, and successfully obtained a malachite phase-free Cu/Al hydrotalcite (**HT-4**), after aging the amorphous precipitate at 26 °C for 20 h. However, the Cu/Al$(OH)_3$ catalyst obtained from the **HT-4** was composed of much smaller particles than those of the **HT-3**-derived catalyst (Figure S1),[16] which resulted in inferior filterable property. In addition, a slightly lower activity was observed for the **HT-4**-derived catalyst.

Although the **HT-3**-derived Cu/Al$(OH)_3$ was thus composed of easily filterable large particles and afforded a satisfactory reaction, a problem still remained concerning the lack of stability with the amorphous Al$(OH)_3$ support due to its inherent water-solubility. This problem is non-negligible particularly when the catalyst suspension is employed for a liquid-phase continuous reaction, because some small particles that are composed mainly of aluminum particles gradually come away and clog the filter placed at the end of the reactor, leading to the retardation and ultimately complete stop of the reactant/product feeds.

We found that the surface modification of the Cu/Al$(OH)_3$ catalyst with H_3PO_4 could improve its stability under aqueous conditions. Thus, treatment of the **HT-3**-derived Cu/Al$(OH)_3$ with a deoxidized aqueous solution of H_3PO_4 (3 mol % for Al) at room temperature, followed by aging of the mixture at 90 °C for 8 h, afforded a slightly less active (Table 1), but much more water-tolerant catalyst. There was an optimal amount of H_3PO_4 for the surface modification, as can be seen in a drastic decrease in activity when the amount was increased to 6 mol % for Al.

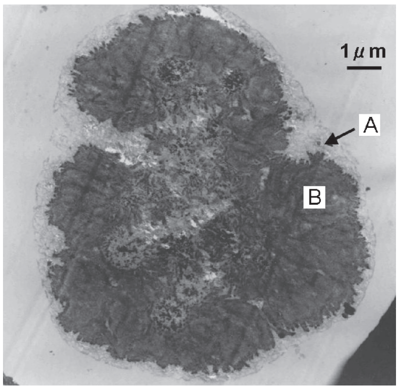


Figure 3. Cross-sectional TEM image of the Cu/Al(OH)$_3$ catalyst after treating with H_3PO_4 (3 mol % for Al) in deoxidized water at 90 °C for 8 h.

The surface morphology was also changed drastically after the treatment with H_3PO_4. Figures 3 and S2[16] compare the TEM images of the Cu/Al(OH)$_3$ and the H_3PO_4-treated Cu/Al(OH)$_3$ aged in the deoxidized water at 90 °C for 8 h. On the outer surface of the Cu/Al(OH)$_3$ catalyst, thin needle-like crystals composed of boehmite, γ-AlOOH, could be seen, while thick fibrous boehmite crystals were observed for the H_3PO_4-treated Cu/Al(OH)$_3$ particles, as can also be seen in the cross-sectional TEM image of the particle. Due to the high solubility of amorphous Al(OH)$_3$ in the aqueous solution, the transformation of the support structure from amorphous Al(OH)$_3$ to γ-AlOOH took place probably through dissolution–recrystallization of the aluminum species. Selected-area diffraction and energy-dispersive X-ray spectrometry (EDX) analysis revealed that the inside of the particles of the H_3PO_4-treated Cu/Al(OH)$_3$ catalyst consisted of the metal copper particles dispersed on the amorphous aluminum species (Table S1).[13,16]

Table S2[16] shows the results of a catalyst reuse study with the H_3PO_4-treated Cu/Al(OH)$_3$ for the hydration of acrylonitrile to acrylamide conducted in a batch reactor at 70 °C for 2 h. These results clearly show that the catalysts could be reused with only a slight loss of catalytic activity probably due to the oxidation of the Cu metal surface by air contamination during handling.

In summary, we have successfully developed a highly efficient Cu/Al(OH)$_3$ catalyst, which exhibits a high activity for the hydration of acrylonitrile to acrylamide and shows good filterability. The stability of the catalyst under aqueous reaction conditions was successfully improved by the surface modification with H_3PO_4. A survey of the potential and limitations of both the Cu/Al hydrotalcite[8,12,14] and the Cu/Al(OH)$_3$ catalysts[15] for other copper-catalyzed reactions is now in progress.

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9 The amount of evolved CO_2 gas was measured when the amorphous precipitate was dissolved in 0.5 M aqueous H_2SO_4 solution.

10 The crystallization of the amorphous precipitate to the hydrotalcite phase quickly proceeded with the pH lowering in the aging solution from 7.8 to 7 when the amount of carbonate ion decreased twofold to form hydrotalcite under air bubbling with 15 min.

11 Samples for XRD analysis were made in a N_2 glove box. The catalysts were suspended in the clear lacquer solution containing acrylic resin. Then organic solvent was dried off with N_2 flow. The coherent catalysts were mounted on an XRD glass cell to prevent the oxidation of Cu metal catalysts when the samples were exposed to air.

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.