

Natural and synthetic clay minerals for tailoring preparation of nanostructured functional materials

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Clay minerals and their synthetic analogs possess specific properties, such as intercalation, ion exchange and swelling, as a result of the various facets of their layered structure (Bergaya and Lagaly, 2006; Zhang et al., 2010). In particular, the interlayer space introduces steric effects which promote the selectivity of catalysis and adsorption (Zhou et al., 2004; Tong et al., 2009). In the context, the interlayer space of clay minerals can be regarded as a type of space-confined nanoreactors, which can be used for the preparation of nanostructured materials. For instance, self-supporting 2-D graphite films have been prepared using phosphate-treated montmorillonite (mmt) as a template (Isayama et al., 1996) and metallic nanoparticles have been fabricated in the interlayer space of smectite minerals (Zhou et al., 2006). The interlayer space of natural clay minerals can host guest species either by adsorption or by ion exchange. Moreover, the synthetic clay minerals can well be tuned for promoting a certain specific feature (Zhou, 2010), for example cation exchange capacity (CEC), delamination (Zhou et al., 2005; Lagaly et al., 1999) and the chemical composition of each layer (Tong et al., 2010), thereby providing more choice for space-confined nanoreactors to meet the needs for preparing a specific functional material. Here we show the size-controllable preparation of graphitic carbon nitride nanosheets by using the interlayer space of smectitic clays, namely mmt and synthetic saponite (spt) as a confined nanoreactor. Also, we describe that the structure of “card-of-house” from delaminated platelets of synthetic hectorite (hect) can be used as space-confined reactors for tailoring the formation and growth of zeolitic titanosilicate-1 materials.

Carbon nitrides, a class of covalent carbon-nitrogen compound, exhibit unique properties such as extreme hardness, catalysis and biocompatibility. As for catalysis, however, bulk carbon nitride remains inactive mainly because there are no defects in the graphitic layers (Goettmann et al., 2006). One solution is to prepare nanostructured graphitic carbon nitride (g-CN). Indeed, nanoporous g-CN shows excellent catalysis in Frieda-Crafts acieration. Nevertheless, such nanostructured carbon nitrides were usually obtained by so-called hard-template technique by using cost-intensive synthetic microporous zeolite, mesoporous SBA-15, SBA-16 and nano-silica. So far the preparation of carbon nitride nanosheet has not been reported yet. Here we prepared a type of g-CN nanosheets by using the confined interlayer nanospace of layered clays. The preparation was realized by intercalation of mmt and synthetic spt with cyanamide, following by condensation of cyanamide and then removal of the clay template. The controllability over the particle size of a g-CN nanosheet via different smectite

clays was also investigated. The prepared solids were characterized by X-ray diffraction, FTIR, SEM and TEM. The resultant g-CN nanosheet has a crystal size of ca. 4.2 nm, and particle size of 50-100 nm when NH⁴⁺-spt was used (Fig. 1A), while in the case of mmt, the particle size is about 100-150 nm with crystal size of 6.0nm (Fig. 1B, Fig. 2). The reason for such difference is that mmt and spt provide different available interlayer space as a result of the difference of CEC and basal spacing. This work shows that the preparation of g-CN can be tailored by judicious choice of layered clay as a nanosheet template.

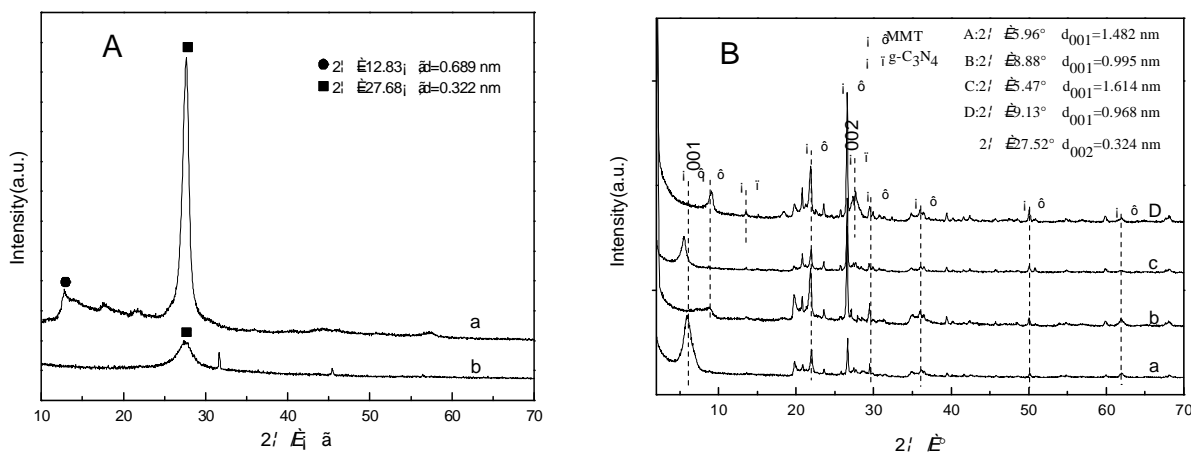


Fig. 1. Powder XRD patterns of samples. (A): (a) g-CN (condensation of cyanamide at 550°C); (b) g-CN-S nanosheet (prepared in the interlayer of NH⁴⁺-saponite) (B): (a) mmt; (b) mmt after calcination at 550°C for 4 h; (c) mmt after adsorption of cyanamide; (d) composites from calcined cyanamide-mmt at 550°C for 4 h.

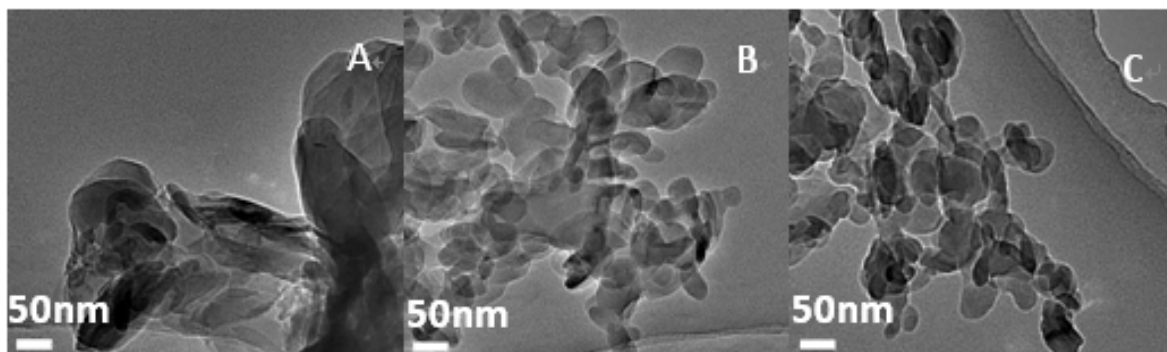


Fig. 2. TEM images of (A) g-CN, (B) g-CN-spt nanosheet and (C) g-CN-mmt nanosheet.

Zeolitic titanosilicate-1 materials (TS-1) with well-defined micropore structures are of great interest due to their potential applications as sensors, catalysts, adsorbents and ion exchangers (Li et al., 2006; Anson et al., 2010). Their performances can be significantly improved when nano-sized TS-1 crystallites was used because it resulted in a remarkable increase of the specific surface area with a simultaneous decrease in the pore diffusion resistance (Xie et al., 2008). In this context, we developed a route to tune the formation and orient the growth by using the space-confined structure of delaminated clay minerals. The clay-TS-1 composites were prepared by hydrothermal nucleation and

crystallization of TS-1 in an aqueous dispersion of clay minerals. For comparison, mmt, hect and fluorohectorite were used. The catalytic properties of the typical composites as catalysts were evaluated in the epoxidation of allyl chloride (AC) to epichlorohydrin (ECH) (Zhou et al., 2009).

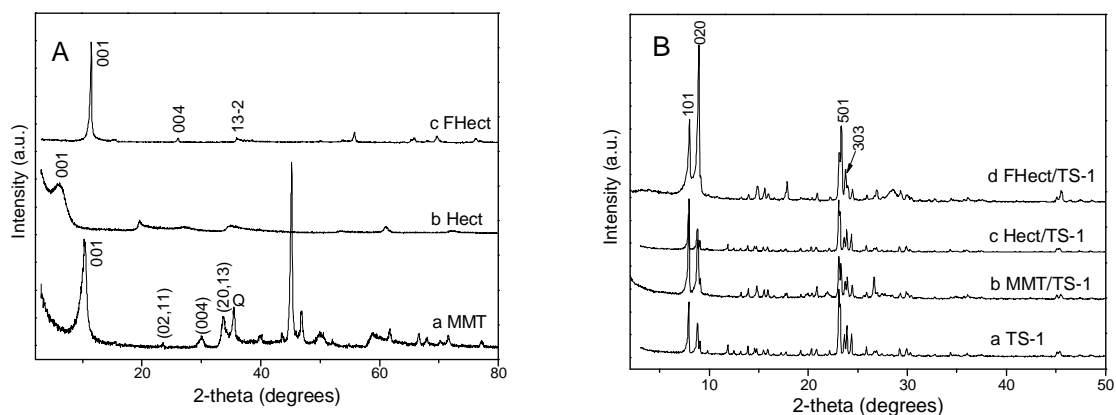


Fig. 3. PXRD patterns of samples. A: a) montmorillonite (mmt), b) hectorite (hect), c) fluorohectorite (FHect) B: a) TS-1 and the Clay-TS composites prepared with addition of b) mmt, c) hect, d) FHect.

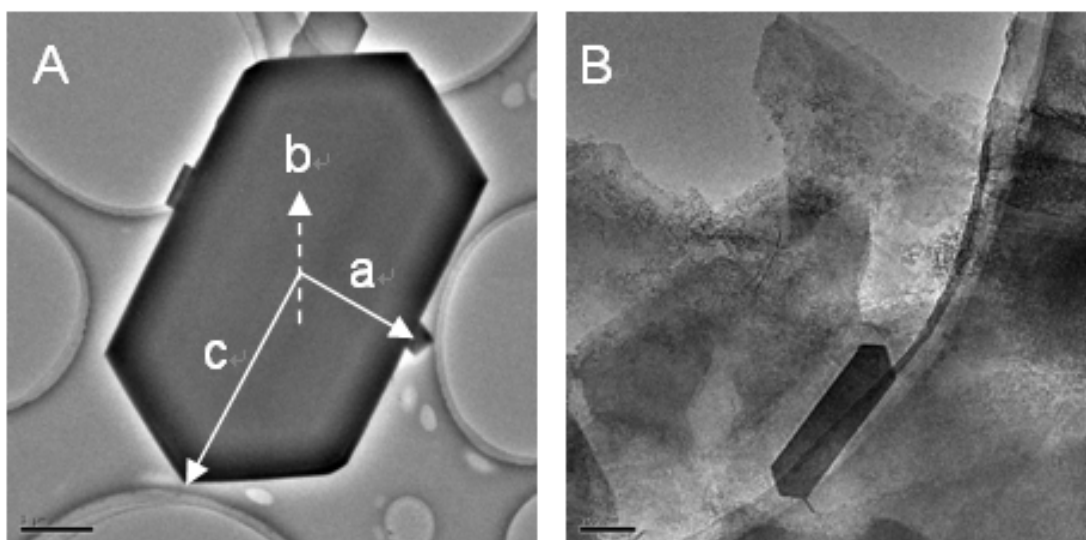


Fig. 4. TEM Images of A) TS-1 and B) fluorohectorite/TS-1 composite (Purified FHect/TS-1)

As observed from XRD and TEM (Fig. 3, Fig. 4), the oriented growth and size of TS-1 can be tuned by using a clay mineral. Moreover, the results showed that the existence of impurities of excess metallic ions such as Na^+ and Li^+ in the synthetic clay plays a negative role in the catalytic performances of the resultant composite. Nevertheless, the clay-TS-1 composite made from using purified fluorohectorite shows similar catalytic properties to those of pure TS-1. The conversion of AC was 68.4% and the selectivity to ECH was 97.3% with a 95.2% utilization efficiency of H_2O_2 .

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