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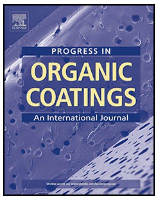

Synthesis of cyclohexanone-formaldehyde resin catalyzed by rehydrated Mg–Al hydrotalcite

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ABSTRACT

Cyclohexanone-formaldehyde resin (CFR) was synthesized over rehydrated Mg–Al hydrotalcite (HT). Therein, Mg–Al HT was rehydrated from Mg–Al HT of good crystallinity using a liquid method. Rehydrated Mg–Al HT (HT-r) shows certain catalytic activity for aldol condensation and catalytic activity is dramatically improved in the presence of hexadecyl trimethyl ammonium bromide (CTAB) because CTAB as a phase transfer catalyst is helpful to enhance the mass transfer among three phases. Both higher temperature and longer reaction time are preferable to increase the molecular weight of CFR. Though the catalytic activity of HT-r decreases as the reutilization cycle increases, the deactivated HT-r can be easily regenerated upon calcining and rehydrating.

1. Introduction

Ketone aldehyde resins are one kind of thermoplastic resins through aldol condensation between ketones and aldehydes. Therein, cyclohexanone-formaldehyde resin (CFR) with low molecular weight is produced though aldol condensation between cyclohexanones and formaldehyde and widely applied in coating and ink industry due to its excellent dissolution in polar and apolar solvent. Because of unique compatibility with a variety of polymers, CFR is used as a multifunctional additive to improve weathering resistance and filler dispersion in polymer matrix [1,2]. Traditionally, aldol condensation is catalyzed by aqueous alkaline, which involves corrosion of equipment, tedious separation and harm to the environment.

In recent years, various solid base catalysts have attracted much more attention during the development of green chemical engineering. Among various solid base catalysts, hydrotalcite-like compounds ($[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot mH_2O$) and their derivatives such as double metal oxides have been focused because their basicity can be tuned based on the diversity of cations and anions [3–6]. The tuning methods include changing cations during the synthesis and post anion exchange [7–11]. By now, hydrotalcite-like compounds and their derivatives have been used to catalyze aldol condensations, etherification reaction and transetherificaion reaction [12–15].

In our previous research, Li–Al hydrotalcite with strong basicity is synthesized through replacing Mg^{2+} with Li^{+} and their corresponding double metal oxide is used to catalyze transesterificaion between ethylene glycol and soybean oil [16]. Herein, Mg–Al hydrotalcite (HT) with stronger basicity are synthesized through exchanging $CO_3{}^{2-}$ with OH^- and are used to catalyze aldol condensations in the preparation of CFR. To obtain high crystallinity, Mg–Al HT was synthesized by a urea method in which pH of the solution can be kept at a homogeneous level and agglomeration can be avoided [17,18]. The exchanging $CO_3{}^{2-}$ with OH^- was realized through the liquid rehydration of Mg–Al HT [19]. Considering liquid–liquid–solid multi-phase reaction, the phase transfer catalyst CTAB was introduced to enhance the mass transfer. The effect of reaction temperature, reaction time and catalyst loading on catalytic activity were studied. Furthermore, the reutilization and regeneration of the catalyst were investigated, too.

2. Experimental

2.1. Synthesis of HT

$Mg(NO_3)_2\cdot 6H_2O$ (15.38 g), $Al(NO_3)_3\cdot 9H_2O$ (7.50 g) and urea (21.62 g) ($n_{Mg^{2+}} : n_{Al^{3+}} = 3$; $n_{urea} : n_{NO^{3+}} = 2 : 1$) was dissolved in deionized water (150 ml) and the solution was fed into a 250 ml flask equipped with a condenser and a mechanical stirrer. The solution was agitated at 100 ± 5 °C under 400 rpm for 10 h and then aged

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statically without agitation at the same temperature for another 20 h. The resulting slurry was filtrated and washed with deionized water until the pH value was equal to 7. The solid was dried for 24 h at 90 °C and named as “HT”.

2.2. Rehydration of HT

HT was calcinated at 500 °C under N$_2$ for 8 h in the furnace. The obtained Mg–Al mixed oxide was named as “HT-c”. Deionized water (400 ml) was heated to 40 °C in a 500 ml flask equipped with a mechanical stirrer and bubbled with N$_2$ for 30 min. Then HT-c (4.00 g) was dispersed into it and the vigorous stirring continued for 8 h under N$_2$. The suspension was filtrated to obtain solid rehydrated HT. After drying at 40 °C in vacuum for 24 h, the product was named as “HT-r”.

2.3. Synthesis of CFR

Formaldehyde aqueous solution (37%, 10.97 g), cyclohexanone (10 ml), CTAB (0.50 g) and HT-r were fed into a three-necked 100 ml flask equipped with a reflux condenser and a mechanical stirrer. The mixture was stirred at certain temperature under N$_2$ to avoid carbonation of HT-r for a period of time. After the reaction ended, HT-r was collected by centrifugation. The product was extracted with methylbenzene and then precipitated in ligarine. The solid product was dried overnight in vacuum at 25 °C.

2.4. Characterization

X-ray powdered diffraction patterns (XRD) were recorded with a Shimadzu XRD-6000 powder diffractometer using Cu Kα ($\lambda = 0.1542$ nm) radiation (40 kV and 30 mA). Transmission electron microscopy (TEM) was performed using JEOL-JEM 1200 equipment operating at 100KV. FT-IR spectra were recorded from 400 to 4000 cm^{-1} on a Thermo Nicolet IR 200 spectrometer. The rotational viscosity of CFR solution was determined by Rotating cylinder viscometer LVDV-2 (Shanghai Jingtian Co.).

3. Results and discussion

3.1. Synthesis and rehydration of HT

According to Javier, Mg–Al HT with Mg–Al molar ratio of 3:1 has proved to have higher catalytic activity [20]. Therefore, Mg–Al HT of same composition was synthesized by a urea method. The XRD pattern of synthesized HT is shown in Fig. 1a. The sharp and symmetric characteristic peaks indicate that HT has good crystallinity. Upon calcinations, the disappearance of the characteristic peaks corresponding to the layered structure indicates that the layered structure of HT is destroyed and Mg–Al double mixed oxide forms (Fig. 1b). However, the layered structure is recovered after the rehydration (Fig. 1c). The microstructure of HT, HT-c and HT-r was characterized with TEM and their images are shown in Fig. 2. As shown in Fig. 2a, HT has a well-developed layered structure. Upon calcination at 500 °C for 8 h, a porous platelet structure forms which indicate that HT is transformed to Mg–Al mixed oxide due to dehydration (Fig. 2b). When HT-c is rehydrated by a liquid method, the layered structure is recovered (Fig. 2c). This is in agreement with the results of XRD.

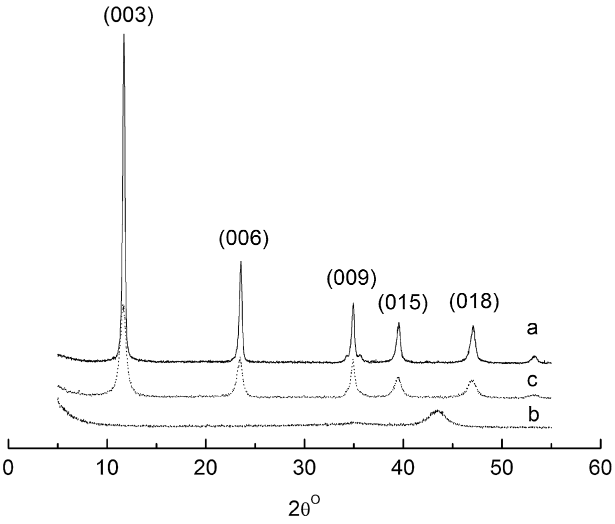

Fig. 1. XRD patterns of HT (a), HT-c (b) and HT-r (c).

3.2. Aldol condensation catalyzed by HT-r

Due to easy volatility of formaldehyde, excess formaldehyde was added in the reaction and the mole ratio between formaldehyde and cyclohexanone ratio was set as 1.4. Preparation of CFR is different from simple aldol condensation because molecular weight increases as aldol condensation proceeds. Herein, except that the yield, CFR viscosity of toluene solution (30 wt%) was determined to indirectly characterize molecular weight of CFR. When the reaction was catalyzed by HT-r, there existed liquid–liquid–solid three phases in the reaction system. To enhance mass transfer, CTAB as a phase transfer catalyst was added. As shown in Table 1, HT-r can catalyze the aldol condensation between formaldehyde and cyclohexanone with low yield and the yield of CFR with the aid of CTAB increases dramatically. CTAB itself has no catalytic activity and just enhance the mass transfer among phases. FT-IR spectrum of synthesized CFR is shown in the Fig. 3. The strong band at about 1711 cm^{-1} is ascribed to $C{=}O$ absorption peak. The band at around 3449 cm^{-1} is the absorption peak of OH. The band at 1448 cm^{-1}

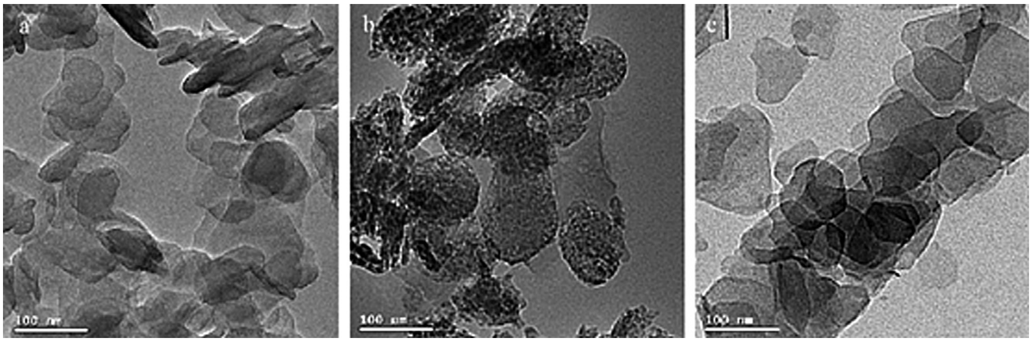

Fig. 2. TEM images of HT (a), HT-c (b) and HT-r (c).

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