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Enhancement of diatomite solid acidity by Al incorporation, as evaluated by the catalytic effects on the thermal decomposition of 12-aminolauric acid

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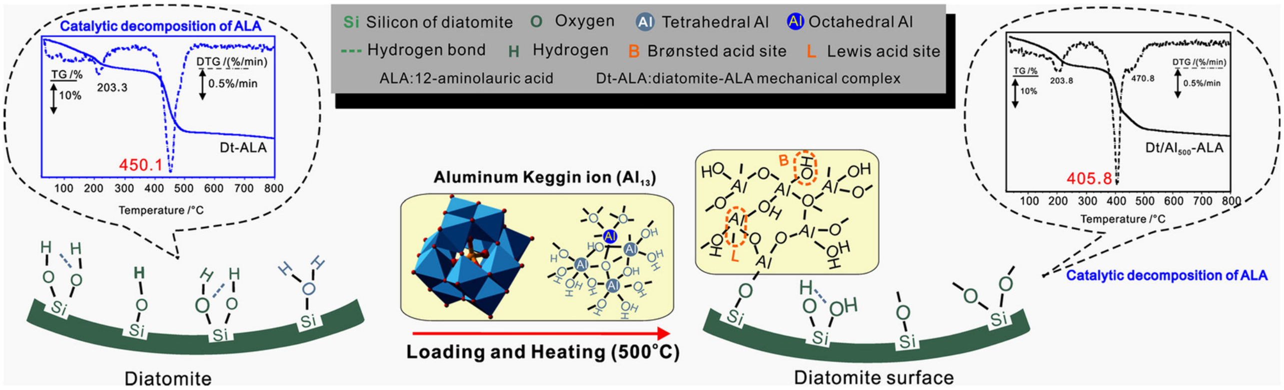
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Tridecameric aluminium polymer-incorporated diatomite has high solid acidity.
- Lewis acidity of Al-incorporated diatomite is stronger than Brønsted acidity.
- Al-incorporated diatomite decreases the ALA degradation temperature by catalysis.

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ABSTRACT

In this study, Al was incorporated into the structure of diatomite by loading tridecameric aluminium polymer and subsequently heating to improve the solid acidity of diatomite. The results show that Al incorporation increased the number of Brønsted (B) and Lewis (L) acid sites of diatomite by implanting Al-OHs and unsaturated Al^{3+} ions, respectively. L acid sites increased with the increment of preparation temperatures of Al-incorporated diatomite, whereas the B acid sites decreased. Moreover, L acid sites

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have stronger acidity than B acid sites. Al-incorporated diatomite exhibits high catalytic activity and considerably decreases the degradation temperature of 12-aminolauric acid (ALA). Large quantities of NH_3 and CO_2 were generated, which was sourced from ALA decomposition with the catalysis of B and L acid sites, respectively; and CO_2 was obtained at a lower temperature than NH_3. The manufactured Al_{13}-diatomite composite shows promise as a solid acid catalyst.

1. Introduction

Diatomite, which is a natural biogenetic mineral, is sourced from the assemblage of the mineralized exoskeletons of diatoms [1,2]. Diatomite is primarily composed of amorphous hydrated silica ($SiO_2{\cdot}nH_2O$), which is categorized as non-crystalline opal-A, according to the mineralogical classification [3–5]. Because diatomite has macroporous structures with pore sizes that range from the nanometric to the micrometric domains [2,6], it has been widely used as adsorbents [7–11], supports [12–18], and templates of macroporous materials [2,6] [19–22].

Diatomite contains Brønsted (B) acid sites, which originate from diatomaceous silanols (Si-OHs) and exhibit weak catalytic activity [3–5]. In our previous study [20–23], the inherent solid acidity of diatomite was utilized to catalyze the decomposition of furfuryl alcohol to prepare diatomite-templated carbon with a unique macroporous structure. However, the catalytic activity of diatomite is ordinary because of the small number and weak acidity of these solid acid sites and because of the lack of Lewis (L) acid sites in the structure of diatomaceous silica. This disadvantage of the solid acidity of diatomite generally restricts the application of diatomite as a catalyst.

In our recent study [24], hydroxyl aluminium polymer (tridecameric aluminium polymer, abbreviated to Al_{13}) was incorporated into the structure of diatomite via a condensation reaction to investigate the possible mechanism of its incorporation. The solid acidity of diatomite markedly increased, and L acid sites appeared after the Al incorporation, as investigated using Fourier transform infrared (FTIR) spectroscopy. Moreover, the Al-incorporated diatomite exhibited various solid acidity values when prepared at various temperatures, which implies that it is a promising catalyst. However, until now, the properties of these new acid sites, such as their acid strength and catalytic effect, were unclear, even though such information would aid the practical application and industrial production of diatomite products.

In the present work, Al-incorporated diatomite was prepared by loading Al_{13} onto the surface of diatomite and subsequently heating the resulting composite at various temperatures. The acidity of the obtained diatomite products was investigated using temperature programmed desorption (TPD). 12-aminolauric acid (ALA; $NH_2(CH_2)_{11}COOH$) was selected as the model for evaluating the catalytic activity of the Al-incorporated diatomite. ALA contains amino and carboxyl groups and can provide simultaneous estimates of the B and L acidity of the catalyst during thermal decomposition, as previously reported [25–27].

2. Materials and methods

2.1. Diatomite

Diatomite was purchased from Sigma-Aldrich, Inc. (CAS number: 6179053-2). The dominant diatoms in diatomite were of the genus *Coscinodiscus* Ehrenberg (Centrales) and were disk-shaped, with a highly developed macroporous structure. The diatomite samples are denoted as Dt.

2.2. Preparation of Al-incorporated diatomite

Al-incorporated diatomite was prepared as follows. Al_{13} was loaded onto the surface of the diatomite, and the obtained diatomite-Al_{13} composite was subsequently heated. Heating was performed in a programmable temperature-controlled muffle oven at 250, 350 or 500 °C for 3 h. The obtained samples were ground into powder in an agate mortar; they are denoted hereafter as Dt/Al_{250}, Dt/Al_{350} and Dt/Al_{500}, respectively.

The structure, morphology and macroporosity of the diatomite before and after the Al incorporation are described in our previous report [24].

2.3. Measurement of the solid acidity of diatomite and its Al-incorporated products

The acidity of diatomite and its derivative was investigated using the NH_3-TPD method. The TPD analysis was performed using a TP 5000-II multiple adsorption apparatus (Tianjin Xianquan Corporation of Scientific Instruments, China). Approximately 100 mg of diatomite and its Al-incorporated products were pretreated under an argon atmosphere at 60 °C for 1 h. When the mass baseline was stable, the argon flow was stopped and NH_3 was introduced until the adsorption of the samples was saturated. The sample chamber was then purged with argon to remove residual NH_3 from samples' surfaces. The samples were then heated under flowing argon to 600 °C at a rate of 10 °C/min for NH_3 desorption. The desorbed gas was monitored using a mass spectrometer (Hiden QIC-20) by tracking the $m/z = 15$ mass-to-charge signal with subsequent numerical integration.

2.4. Evaluation of the catalytic activity of diatomite and its Al-incorporated products

The catalytic activity was evaluated on the basis of the thermal behaviors of ALA in the presence of diatomite and its derivatives using a thermogravimetry (TG) instrument. First, 10 g of diatomite and its derivatives were mixed with 2.5 g of ALA; they were then ground by ball milling for 20 min using a Pulverisette-6 planetary mill. These ALA-diatomite complexes are denoted as Dt-ALA, Dt/Al_{250}-ALA, Dt/Al_{350}-ALA, and Dt/Al_{500}-ALA according to the Dt and Al-incorporated products.

The TG analysis of the samples was performed on a Netzsch 449C instrument. Approximately 20 mg of finely powdered samples was heated from 30 to 1000 °C at a heating rate of 10 °C/min under a high-purity N_2 atmosphere (60 cm^3/min).

Gaseous products such as CO_2 and NH_3 from —COOH and —NH_2 groups of ALA were formed from the thermal degradation of ALA when ALA was catalyzed by solid acid sites, as previously reported [26]. The gaseous products were estimated using red litmus test papers and $CaCl_2$ for NH_3 and CO_2, respectively. The mixed indicator contained 1% bromocresol green ethanol solution and 2% methyl red ethanol solution with a volume ratio of 3:1; the color of the indicator changed from red to green when the pH value of the solution was greater than 5.1 [28–30].