Greatly enhanced reactivity of CaC$_2$ with perchloro- hydrocarbons in a stirring ball mill for the manufacture of alkynyl carbon materials

Qing-nan Liu[a,b], Liang Cheng[a,b], Xue-bing Xu[a,b], Hong Meng[b], Ying-zhou Lu[b], Chun-xi Li[a,b,c,*]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[c] Beijing Key Laboratory of Energy Environmental Catalysis, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

Calcium carbide (CaC$_2$) is a potential feedstock for various alkynyl chemicals, but its actual activity is very low due to its high lattice energy and insolubility. A stirring ball mill was used here to intensify its reaction with perchloro-hydrocarbons (PCHCs), namely hexachlorobenzene (HCB), hexachloroethane (HCE), tetra-chloroethene (TCE) and tetrachloromethane (TCM), forming corresponding alkynyl carbon materials (ACMs), viz. ACM$_{HCB}$, ACM$_{HCE}$, ACM$_{TCE}$ and ACM$_{TCM}$, respectively. The reaction intensification may be ascribed to the activation of CaC$_2$ and its effective collision with PCHCs by the intensive impingement of the milling balls. The as-prepared ACMs were characterized by XRD, Raman, elemental analysis, XPS, SEM and BET analysis, and their adsorption performance was evaluated. These ACMs are mesoporous materials with over 70% carbon content, varying amount of acetylenic groups, rich micro-pores and high specific areas ranging from 270 to 970 m^2 g^{-1}. ACM$_{HCB}$ is found to be a promising sorbent with adsorption capacity of 514.7 mg-Hg g^{-1} for HgCl$_2$ aqueous solution and 24.4 mg-S g^{-1} for DBT oil, which is much superior to most of carbonaceous sorbents due to its rich micro-porosity and abundant acetylenic groups.

1. Introduction

Carbon materials(CMs) have attracted great attention in recent years due to their unique physicochemical properties and wide applications as battery materials [1,2], sorbents [3–5], catalysts [6,7] etc., being one of the research frontiers of advanced materials. The most important and representative carbon allotropes, e.g. fullerenes, carbon nanotubes (CNTs) and graphene, are prepared via CVD or catalytic pyrolysis of organic molecules under high temperature. These methods played an important role in the development of CMs, but their commercial use is heavily hindered by the high capital investment and production cost. In order to develop new CMs with unique structure, rational cost, and milder preparation conditions, it is necessary to explore new method and/or novel feedstock. In this regard, we proposed a new preparation method of CMs through mechanochemical reaction of calcium carbide and perchlorohydrocarbons (PCHCs).

Calcium carbide is an important industrial chemical. Its production capacity in China is 3.8 × 10^7 t.y^{-1} in 2016, which accounts for 90% of the global production capacity [8]. Calcium carbide has been widely used for producing vinyl chloride, vinyl acetylate, 1,4-butadiol, and carbon black through acetylene route. But, it is rarely used directly as feedstock for chemical synthesis, because of its very low reactivity to many chemicals except to water [9,10].

The stone-like inertness of calcium carbide contrasts sharply to its high intrinsic reactivity, which may be attributed to its high lattice energy and insolubility that greatly lowers its accessibility to other reactants. In this regard, the intrinsic reactivity of CaC$_2$ may be ignited if massive acetylenic anions can be produced dynamically and exposed instantly to the reactants. Moreover, explosive reaction was found accidently in our laboratory between CaC$_2$ and CCl$_4$ in a vibrating miller at ambient conditions. This finding arose our interest for mechanochemistry study of calcium carbide, and preparation of acetylenic carbon materials (ACMs) is one of these endeavors [11,12].

Recently, some calcium carbide derived carbon materials (CCDCs) with rich porosity and high specific area have been prepared via thermal reaction of CaC$_2$ with other reactants [13–20]. Xie et al. [13] firstly reported the thermal reaction between calcium carbide and chlorohydrocarbons in an autoclave at high temperature after an explosive ultrafast reaction as manifested by a sudden surge of pressure. Dai et al. [14] prepared a carbon material by reacting calcium carbide with fresh chlorine at atmospheric pressure and 120 °C. The thermal synthesis method seems not viable for commercial production of CCDCs

since the reactions are too intensive to be controllable at high temperature. To conduct a controllable reaction at mild conditions, Li et al. [12] studied the mechanochemical reaction of calcium carbide with PCHCs in a planetary ball mill, whereby ACMs with varying structure and characteristics were obtained. However, its feasibility needs to be justified further since the mechanical energy intensity(MEI) of the planetary ball mill used therein is much higher than that of industrial ball mills. In this regard, a stirring ball mill was used here for studying the similar reactions, so as to elucidate the effect of MEI, the mechanism of the mechanochemical reactions, and its feasibility for the commercial production of ACMs. Meanwhile, the resulting ACMs were characterized by various techniques, their adsorptive performance for Hg^{2+} in water and dibenzothiophene (DBT) in oil was tested.

2. Experimental

2.1. Chemicals and equipment

The chemicals used here are all analytical grade reagents unless otherwise specified. They were purchased from varying suppliers, and used as received without further purification. Specifically, CaC_2 (68 wt %) was purchased from Tianjin Fuchen Com. and ground into 100 mesh particles before use. Tetrachloroethylene (TCE) and hexachloroethane (HCE) were obtained from Tianjin Guangfu Chem. Works (China). Hexachlorobenzene(HCB) and dibenzothiophene(DBT) were purchased from Aladdin Ind. Corp. (China). Tetrachloride methane(TCM), nitric acid, hydrochloride acid, anhydrous ethanol, *n*-octane, and KOH were bought from Beijing Chem. Works (China). $Hg(NO_3)_2$ was prepared by the nitrolysis of elemental mercury.

The main equipment used include stirring ball mill (JM-1L, Tianchuang, China), small crusher (2N-02, Beijing Xingshi Lihe Com. China), electronic balance (AR2130, Ohaus, USA), sulfur-nitrogen analyzer (KY-3000SN, Jiangyan Keyuan Co. Ltd., China), and UV–vis spectrometer (Labtech A, China).

2.2. Synthesis of ACMs

The bulk calcium carbide was firstly ground with a crusher, followed by sieving with 100 mesh thieve (Beijing Qiandingjin Com. China), whereby CaC_2 fine powder was obtained and stored in a sealed bottle. For the synthesis of ACMs, specific amount of CaC_2 powder was added to the ball mill, evacuated, and pre-milled 6 h at 1200 rpm. Then definite amount of PCHCs was added, and milled for a period of time at specific speed with alternate direction every 10 min followed by 5 min stop. The reaction temperature was controlled by the flowing cooling water outside the miller. When the reaction finished and cooled to room temperature, the solid mixture was treated with dilute nitric acid, washed repeatedly with water and ethanol, respectively, and the filter cake was vacuum dried for 12 h at 100 °C. The as-prepared ACMs by reacting CaC_2 with C_6Cl_6, C_2Cl_6, C_2Cl_4 and CCl_4 were noted as ACM_{HCB}, ACM_{HCE}, ACM_{TCE} and ACM_{TCM}, respectively. Typical experimental conditions are as follows unless otherwise specified: 1500 g stainless steel ball with 2 mm in diameter, milling 12 h at 1200 rpm for a mixture of 10 g CaC_2 and definite amount of PCHC with their stoichiometric mole ratio being 1.5.

2.3. Adsorption of ACMs for DBT in oil

The model oil used here is a mixture of DBT and *n*-octane with sulfur content of 1000 μg g^{-1}(ppm). For the adsorption experiment, 10 g of oil (w_{oil}) and 0.2 g of carbon sorbent (w_s) were added to a 25 mL glass vial, which was fixed in a thermostatic bath and stirred magnetically for 4 h. The adsorption amount of the sorbent q (mg-S g^{-1}) was calculated by Eq. (1) with the S-concentration before and after adsorption (C_0 and C_e in ppm), whereby the best ACMs sorbent can be selected.

$$q = \frac{w_{oil}(C_0 - C_e) \times 10^{-3}}{w_s} \tag{1}$$

To determine the adsorption isotherm, the adsorption experiment was repeated by using different model oils with varying initial S-concentration of 100–1000 ppm. Sulfur concentration of oil samples was determined by sulfur-nitrogen analyzer with detection limit of about 0.2 ppm and reproducibility of 1–2% [21].

2.4. Adsorption of ACMs for Hg^{2+} in water

A stock solution of Hg^{2+} (250 ppm, pH = 5) was prepared in advance, and the working solutions of (40–200) ppm were prepared instantly via dilution method. The adsorption amount (q in mg-Hg g^{-1}) was determined following similar procedure and equation as described above. In a typical adsorption experiment, 50 g aqueous solution of $HgCl_2$ and 0.025 g of carbon sorbent were added to a 25 mL glass vial, being immersed in a thermostatic water bath, stirred magnetically for 3 h, and then took sample for analysis. The Hg^{2+} concentration of the samples was determined by spectrometer using the method as described elsewhere [22] with detecting limit of mercury of 0.2–1.0 ppm, and the average absolute relative deviation (AARD) of the experimental data is within 3.3% [23]. The adsorption isotherm was made by repeating the experiments at different initial concentrations of Hg^{2+} in the range of 40–200 ppm.

3. Results and discussion

3.1. Effect of MEI on the reactivity of CaC_2

Theoretically, the stoichiometric reaction between $CaC_2$and PCHCs may be expressed by Eq. (2), and the resultant ACMs (C_mC_n) are composed of carbons with different hybridization types.

$$C_mCl_n + \frac{n}{2}CaC_2 = C_mC_n + \frac{n}{2}CaCl_2 \tag{2}$$
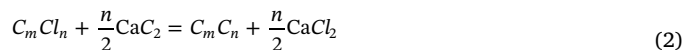
The reaction mechanism is assumed to be a nucleophilic substitution reaction between the exposed carbide anions(Ca−C≡C)− and C−Cl bonds, forming $CaCl_2$ and carbon materials with alternating acetylenic carbons and the carbons from the chlorinated hydrocarbons [12]. For the heterogeneous reaction, mechanical energy is crucial, whereby the lattice structure of CaC_2 is destroyed dynamically, and acetylenic anions are exposed instantly, which greatly enhance their accessibility and reactivity under intensive collisions of the milling balls [24–26]. In fact, some Cl atoms may be remained in the final product of ACMs due to their incomplete substitution by the acetylenic anions. Further, structure rearrangement may occur in the as-formed ACMs due to the higher reactivity of the C≡C triple bonds and the intensive mechanical energy of the milling balls.

As analyzed above, the milling balls are mainly used to (1) mix the reactants as uniform as possible; (2) mill the reactants into ultrafine powders with high specific surface area and least crystallinity; (3) activate calcium carbide by eliminating the restriction of the high lattice energy to its intrinsic reactivity, which may be one of the most important roles; and (4) provide intensive mechanical energy for the effective collision and reaction, which may be comparable to the function of temperature(i.e. thermal energy RT in J mol^{-1}) for thermal chemical reactions. For the stirring ball mill, MEI (in W mol^{-1}) may be roughly estimated by the input mechanical energy (w in J s^{-1}) and the amount of reactants involved (n_t in mole) via Eq. (3). The mechanical energy can be calculated by deducting the friction heat from the input shaft energy. In this paper, the friction heat is not measured, and the mechanical energy is approximated by the input shaft energy. Therefore, MEI here is only a rough indicator instead of a quantitative parameter.

$$MEI = \frac{Input\ of\ mechanical\ energy\ (J.\ s^{-1})}{total\ amount\ of\ substance\ (mol)} = \frac{w}{n_t}$$