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Calcium carbide and its recent advances in biomass conversion

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ABSTRACT

Calcium carbide (CaC_2) is a sustainable source of acetylene which plays an important role in organic synthesis due to its active triple bonds and terminal protons. Solid CaC_2 has several advantages over acetylene gas such as easy handling, convenient storage and transportation. The CaC_2 is considered as a safer and more convenient source of acetylene. The chemistry of the CaC_2 is not confined to its use as a source of acetylene and its applications are not limited to the known reactions of acetylene. With the CaC_2 chemistry being actively developing recently, it may eventually lead to the development of new transformations of alkyne chemistry. Herein, this mini review is focused on the synthesis and application of the CaC_2 in biomass transformations.

1. Introduction

In the middle of the last century, calcium carbide (CaC_2) had played an important role in acetylene chemistry which served as the primary feedstock for a wide variety of commodity and specialty chemicals (Galkin and Ananikov, 2016; Wu et al., 2018). The advances in petroleum refining technology have since minimized the importance of acetylene. However, as the natural reserves of petroleum is diminishing, the CaC_2 can potentially act as a sustainable resource for the chemical industry. Indeed, the CaC_2 is recently re-emerging as a viable feedstock for organic synthesis (Rodygin et al., 2019).

The CaC_2 is a source of acetylene which plays an important role in organic synthesis due to its active triple bonds and terminal protons (Galkin and Ananikov, 2016). Importantly, utilizing CaC_2 has great advantages over acetylene gas (Rodygin et al., 2016b; Ledovskaya et al., 2018). Neither oil nor natural gas is required for the CaC_2 synthesis. The storage and handling of acetylene gas is a costly and dangerous procedure. On the other hand, transportation of the solid CaC_2 does not require complicated equipment and has no similar risks like acetylene. Therefore, the CaC_2 is considered as a safer and more convenient source of acetylene. The chemistry of the CaC_2 is not confined to its use as a source of acetylene and its applications are not limited to the known reactions of acetylene. With the CaC_2 chemistry being actively developing recently, it may eventually lead to the development of new transformations of alkyne chemistry. Herein, this mini review is focused on the synthesis and application of the CaC_2 in biomass transformations.

2. Sustainability of calcium carbide

The CaC_2 is traditionally synthesized from coal/coke in an electric furnace at 2000–2200 °C (Wilson, 1895). Recently, it was demonstrated that utilizing renewable biochars instead of granular coke as a carbon source allows a shorter reaction time (below 5 min) and lower reaction temperature (by 500 °C) for CaC_2 synthesis will greatly increase the thermal efficiency and decrease the cost (Fig. 1) (Kim et al., 1979; Li et al., 2010; 2018). The detailed transformation of this process was further studied by performing experiments at different C/CaO ratios and particle sizes. The biochars were synthesized from lignocellulosic biomass via pyrolysis (Lehmann, 2007). This process represents a new route for sustainable biomass conversion to commodity chemicals. The low production

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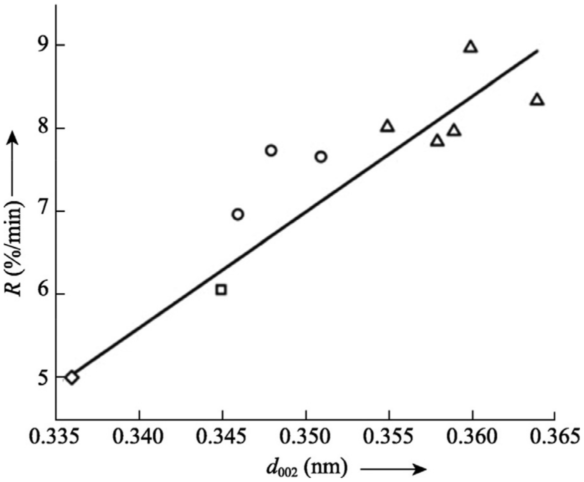

Fig. 1. Conversion rates of CaO (*R*) at 1650 °C for reaction of CaO with chars. *R* is conversion rate of CaO. The d_{002} values are the interplanar distances from XRD analysis of the chars treated at 1650 °C. Δ: biochars (from apricot shell, willow wood, bamboo, corncob, and pine wood, in the order of increasing d_{002}); ○: coal chars (from anthracite, bituminous coal, and lignite, in the order of increasing d_{002}); □: petroleum coke; ◊: graphite (Li et al., 2010).

costs and high sustainability of this new method have put CaC_2 in a better position to serve as a sustainable resource for the chemical industry.

3. Calcium carbide related reactions with biomass and derivatives

3.1. Calcium carbide as catalyst in biomass conversions

Before the use of the CaC_2 in chemical reactions is gaining popularity, it was reported to play a role in biomass conversion by acting as a catalyst in catalytic pyrolysis of waste inner tube rubber (Mabood et al., 2010a) and low-density polyethylene (Mabood et al., 2010b) to fuel oil. Its role as a catalyst is essential to the waste rubber degradation. With 20% of the CaC_2 as catalyst, 28% of liquid oil and 36.5% of gas were produced under optimized conditions which is higher than a 20% total conversion of liquid and gas products without catalyst. For the degradation of low-density polyethylene, liquid oil fraction increased from 10% yield without catalyst to 70% yield with 20% of the CaC_2 as catalyst. However, the detailed mechanism of these catalytic processes has not been reported.

Upgrading bioethanol to value-added chemicals is an important topic. The CaC_2 is known as an efficient catalyst for the aldol condensation of acetone to various value-added platform chemicals (Li et al., 2016; Xu et al., 2018). Recently, the CaC_2 demonstrated catalytic activity in condensation of ethanol to C_4–C_9 alcohols at 27−300 °C (Wang et al., 2019a). With the CaC_2 as the catalyst (about 10%), up to 39%–56% total product yield was obtained with ethanol conversion of 46%–64% at 275 °C. It was reported that the CaC_2 is effective in catalyzing aldol-condensation reactions of various aliphatic alcohols including ethanol, through adsorption and activation of alcohols, followed by condensation of its aldehyde species with alcohols over CaC_2 (Fig. 2). This finding may potentially open up new catalytic applications of the CaC_2 in organic transformations.

Additives of high-density fuels such as methyl-substituted benzenes and naphthalenes can also be obtained from the CaC_2 and acetone in one pot at 200–350 °C (Wang et al., 2019b). The CaC_2 plays two different roles in this transformation: it catalyzes acetone condensation, while its alkynyl moiety also directly participates in aromatization reaction to form methyl-substituted naphthalenes.

3.2. Calcium carbide and vinylation of biomass derivatives

Biomass feedstocks are abundant source of carbon, oxygen and hydrogen. Vinylation of biomass feedstocks using CaC_2 as acetylene source are seen as new insights toward biomass-related degradation to useful products. Earlier, the CaC_2 was mainly focused in transition metal-catalyzed reactions such as Sonogashira coupling (Zhang et al., 2006; Chuentragool et al., 2011; Thavornsin et al., 2014; Matake et al., 2015; Hosseini et al., 2017) and alkyne-amine-aldehyde (AAA) or alkyne-haloalkane- amine (AHA) coupling (Lin et al., 2012; Yu et al., 2013; Matake et al., 2015; Turberg et al., 2018). Alkynylation of aldehydes and ketones (Sum et al., 2013; Hosseini et al., 2015) and tertiary amines (Teong et al., 2016) using CaC_2 have also been reported. In recent years, utilization of the CaC_2 in transition-metal free catalyzed reactions was gaining attention with the main focus on vinylation reactions. Examples include vinyl sulfides (Rodygin et al., 2015; Rodygin and Ananikov, 2016a; Rodygin et al., 2017), N-vinyl indoles (Rattanangkool et al., 2016; Rodygin et al., 2018a) or N-vinyl heterocyclic compounds (Rodygin et al., 2018a), and vinyl ethers (Matake et al., 2016; Rattanangkool et al., 2016; Teong et al., 2017a; 2017b; Werner et al., 2017; Rodygin et al., 2018b; Parshina et al., 2019). More recently, an interesting trideuterovinylation was reported from alcohols, thiols and NH-compounds with CaC_2 (Ledovskaya et al.,

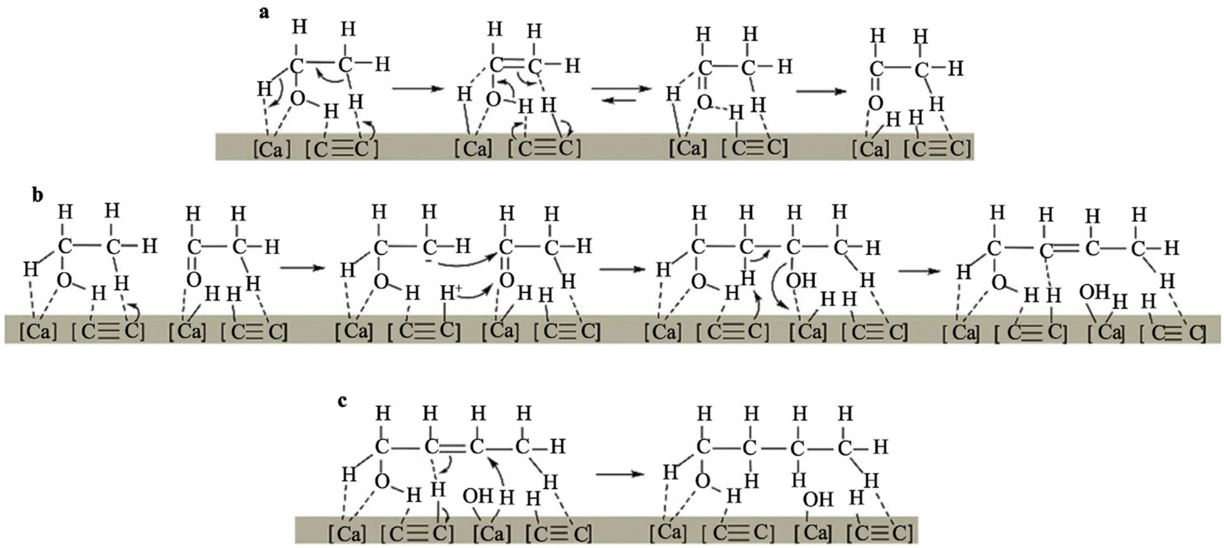

Fig. 2. A proposed pathway of CaC_2-catalyzed aldol-condensation of ethanol to 1-butanol. (a) dehydrogenation of ethanol; (b) aldol condensation; (c) hydrogenation (Wang et al., 2019a).

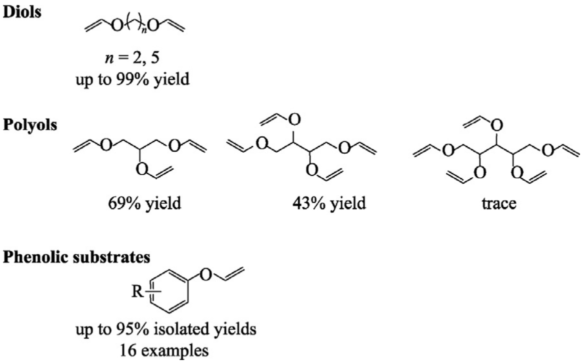

Fig. 3. Vinylation of natural alcohols and derivatives with CaC_2.

2019), and ^{13}C-labeled O, S, N-functionalized vinyl derivatives with $Ca^{13}C_2$ was also demonstrated for efficient labeling of organic molecules (Ledovskaya et al., 2020).

Vinyl ethers are particularly interesting due to the oxygen atom involved, which is abundant in many biomass feedstock, such as polyols, lignin and cellulose. This reaction is a modification of the well-known process as the Favorskii-Reppe reaction, a direct vinylation of alcohols with acetylene gas in the presence of base catalyst, which has been used as the industrial process for vinyl ethers since 1960s (Favorskii, 1905; 1907; Reppe, 1956).

With the CaC_2 now rated as a renewable source (Li et al., 2018; Pääkkönen et al., 2019), the possible technology for vinylation directly with the CaC_2 has no doubt attracted attention where its preliminary transformation to acetylene gas, a procedure requiring special equipment, handling and safety precautions is avoided.

As early as 1964, Trofimov and Atavin (1964) successfully vinylated a series of alcohols including methanol with CaC_2 in water using potassium hydroxide (KOH) as a catalyst. Its scalability and applicability for producing methyl vinyl ether (MVE), have been recently demonstrated and realized on a 10 g scale in the presence of K_2CO_3 or Na_2CO_3 (140–150 °C, 1 L steel rotating autoclave, maximum autogenic pressure 1.82×10^6–3.04×10^6 Pa) (Parshina et al., 2019). Up to 73% of methanol conversion was achieved in this system.

On a laboratory scale basis, while various reports demonstrated the vinylation of aliphatic (Matake et al., 2016) and aromatic alcohols (Matake et al., 2016; Rattanangkool et al., 2016) (up to 91% excellent yields) with CaC_2 in dimethyl sulfoxide (DMSO)/H_2O using superbasic system, vinylation of phenol remains to be a challenge. Larger alcohols like glycerol also reportedly did not undergo vinylation with CaC_2 under the studied conditions (Rodygin and Ananikov, 2016a). Our research group then reported direct vinylation of diols (up to 99% yield), polyols (up to 69% yield) and phenolic substrates (up to 95% isolated yield, 16 examples) with CaC_2 in the superbasic DMSO/Cs_2CO_3 system (Teong et al., 2017a) (Fig. 3). Apparently, the amount of water and the CaC_2 plays an important role and has to be adjusted carefully for the reaction to proceed.

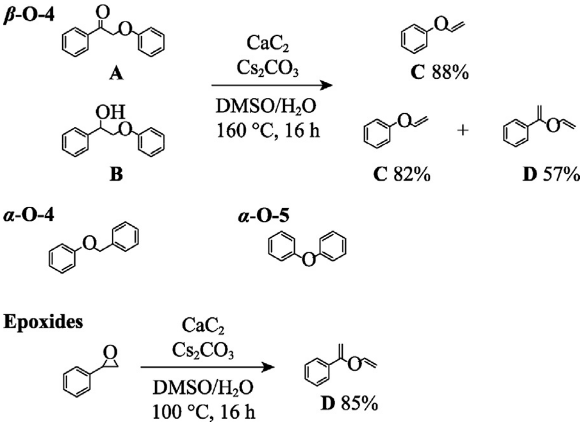

Fig. 4. Vinylation of lignin model compounds (LMCs) and epoxides with CaC_2.

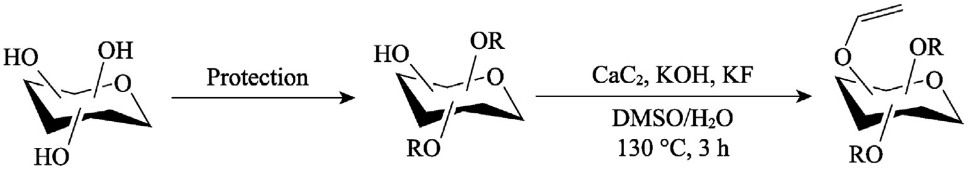

Fig. 5. Vinylation of protected carbohydrates with CaC_2.

This inspired further work to be carried out in the vinylation of other biomass-derived materials with CaC_2. From the study, the system was found to be able to activate stable C—O bond. It was then demonstrated to produce vinyl ethers from lignin β-O-4 linkage model compounds and epoxides through C—O bond cleavage (Teong et al., 2017b). Lignin model compounds (LMCs) A and B were used to represent the β-O-4 linkage in the study with > 80% yield obtained from both LMCs (Fig. 4). The LMCs representing α-O-4 and α-O-5 linkages did not show promising results.

Werner et al. (2017) obtained vinylated products in high yields from aliphatic alcohols and phenols (up to 97%, 17 examples) as well as vinylation of functionalized biologically active molecules such as cholesterol and estradiol with yields up to 91%. Additive potassium fluoride (KF) is shown to improve the vinylation in this DMSO/K_2CO_3 system via the etching of the CaC_2 surface by the fluoride ions and the fluoride-mediated activation of alcohols for the nucleophilic transformations.

Protected carbohydrates are also vinylated under similar system (Fig. 5), using KOH as the base and KF as additive, with yields up to 95% (11 examples) (Rodygin et al., 2018b). Tetravinylation was performed with methyl a-d-glucopyranoside using the KF as additive and 75% yield was obtained. Similarly, the ratio of water and CaC_2 is noted to be crucial for the reaction to work efficiently.

Summary and perspective

In general, using CaC_2 directly as an alternative acetylene source or catalysts for various transformations is an attractive area worth exploring, particularly in the green chemistry perspective. The synthesis of vinyl ethers has been gaining strength and using biomass-derived materials as feedstock helps to provide new visions toward biomass-related degradation to useful products. To the best of our knowledge, currently there is no study on degradation of raw biomass such as lignin or cellulose using CaC_2. It is worthwhile to investigate further to extend the application of CaC_2 for a more efficient degradation of raw biomass materials.

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