INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 11131–11140

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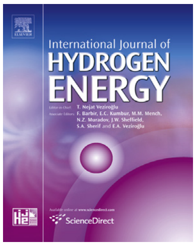

Borohydride salts as high efficiency reducing reagents for carbon dioxide transformation to methanol: Theoretical approach

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ARTICLE INFO

Article history:
Received 13 February 2016
Received in revised form
27 April 2016
Accepted 8 May 2016
Available online 28 May 2016

Keywords:
Carbon dioxide
Methanol
Borohydride salts
Borane
Reduction

ABSTRACT

In this work, the mechanism of CO_2 reduction to methanol using the borohydride salts of M $[RBH_3]$ ($M = Li^+$, Na^+ and R = Ph, CH_3, CN and H) as the reduction reagents, has been investigated, theoretically. In spite of expensive and less reactive boranes such as pinacolborane, borohydride salts have unique properties such as simplicity of use, low cost, and high chemoselectivity. Previously, the production of Methoxyborane $(MeOBO)_3$ by using the boron molecule, carbon dioxide and sodium borohydride was reported, experimentally. But, in addition to sodium borohydride, we investigated the effects of three other types of borohydride salts. The studied steps of the overall reaction have been divided into three phases, and the effects of the substituted groups (R = Ph, CH_3, CN and H) on the kinetics have been fully investigated. Two considered phases have been affected by R group which their effects have been justified by the electronic interactions of the substituted groups and electron density of boron atom. Finally, it has been concluded that $Li[MeBH_3]$ and $Li[PhBH_3]$ are the best reduction reagents for the reaction, thermodynamically and kinetically.

Introduction

The conversion of carbon dioxide as a very plentiful, nontoxic, nonflammable and easily available C1 source to the valuable compounds such as methane [1], methanol [2], carbon monoxide [3], and sugar [4] is one of the most interesting issues in chemical industries and carbon recycling in the nature. Up to now, the large majority of the carbon sources are based on the crude oil, natural gas and coal but, CO_2 introduces a renewable carbon source [5]. Naturally, the capture and transformation of CO_2 is performed by metalloenzymes in photosynthetic organisms such as plants, algae and cyanobacteria [4]. However, the activation and application of CO_2 is difficult because, it is thermodynamically stable [6]. On the other hand, in the most of the investigations, using the potent substrates and vigorous reaction conditions are necessary for CO_2 activation which limit the application of such procedures [7]. Therefore, in order to overcome the thermodynamic and kinetic barrier, an effective catalyst is

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http://dx.doi.org/10.1016/j.ijhydene.2016.05.050
0360-3199/

vital for converting CO_2 to the valuable compounds. A key issue for transformation of CO_2 to valuable chemical intermediates and products is the application of the efficient catalysts [8]. Recently, the application of metal-free organocatalysts, such as frustrated Lewis pairs (FLPs) [9], carbenes [10], bicyclic amidines [11], and ionic liquids [12] as chemicals for the activation of CO_2 at the room temperature have been reported. For example, FLPs were used to catalyze the CO_2 reduction to methanol and methane [13]. Nanocatalysts are also the other compounds which have been used for absorption or transformation of CO_2 to valuable material. Cu_xO [14] and Ni nanocatalysts [15], have been applied for reduction of carbon dioxide while, nano thin films of α-Fe_2O_3 has been used for carbon dioxide adsorption [16]. Chemical compounds such as organometallic reagents, three-member heterocyclic compounds, reductive reagents and oxygen or nitrogen containing materials react with CO_2 and produce useful materials [17].

The reduction of carbon dioxide to methanol as a hydrogen storage material has attracted more attention with an estimated global demand of around 48 million metric tons in 2010 [18]. Several catalytic systems which reduce carbon dioxide to methanol are known, and some of these procedures are now commercialized [19]. However, the investigation of the novel catalysts is still ongoing. Recently, the designing of the new systems for the reduction of carbon dioxide has been developed. For example, aluminum [20] and silylium cations [21] have been used to reduce carbon dioxide to methane and methanol. Homogeneous reduction of CO_2 with hydrogen [17,21–23], hydrosilane [24] and hydroborane [25] as reducing agents are one of the interesting issues in the last decade. Among the reductive reagents, hydroboranes are classified as the efficient reagents for the catalytic reduction of carbon dioxide to methanol [7,26]. Boron derivatives are able to activate CO_2 in various ways. The formation of the strong B–O bond is the driving force in the reaction of the borane compounds. Nevertheless, the hydride transfer as the first step of the reduction needs a catalyst which can be a metal hydride complex, an ambiphilic compound, a strong Lewis base or a hydroborate compound [27].

Mizuta and coworkers reported the transformation of carbon dioxide to methoxyborane in the presence of the borane molecules and sodium borohydride as a reductive reagent [28]. Sodium borohydride is a moderate and chemoselective reducing agent for the carbonyl functional group. The simplicity of using, low cost, and high chemoselectivity and availability makes it one of the best reduction reagents which does not require any complex additives such as transition-metal catalysts or organocatalysts [29]. A worthwhile investigation has been reported for the reaction of sodium borohydride and carbon dioxide in aqueous solution by Kyle A. Grice and coworkers [30]. They showed that formate ion competes with H_2 molecule as the final products. Therefore, the hydride transfer reactions to CO_2 are very favorable and competitive with hydrogen formation mechanism, yielding the formate which may also be increased under the higher pressure [30]. Another valuable theoretical investigation has been presented for the mechanism aspects of the NaBH4 hydrolysis in aqueous solvent which shows that the solvent has significant role in the hydrolysis reaction [31]. Recently, by spectroscopic and crystallographic characterization, Cummins and coworkers introduced triformatoborohydride, $Na[HB(OCHO)_3]$ through the reaction of CO_2 with $NaBH_4$ [32]. In this procedure, monoformatoborohydride, $Na[H_3B(OCHO)]$ and diformatoborohydride, $Na[H_2B(OCHO)_2]$, are the intermediates. Fig. 1 shows the reduction of carbon dioxide to $(MeOBO)_3$ which is converted to methanol and boric acid in the presence of water.

Although, Mizuta and coworkers reported a reduction reaction only by sodium borohydride, but unique properties of this reagent leads to the discovery of the numerous derivatives of sodium borohydride which have been investigated in various reduction reactions [29]. Therefore, the investigation of the effects of the other derivatives of borohydride, Fig. 2, which have already been synthesized [33,34] is mechanistically of our interest.

In this work, the role of these salts on the mechanism of carbon dioxide conversion to methanol has been studied, theoretically. The studied reagents have been indicated by $M[RBH_3]$ which $M = Li^+$ and Na^+ and $R = Ph, CH_3$, CN and H. Because of the different electronic behaviors of the R group, various outcomes have been obtained in CO_2 reduction. In order to have a knowledge of the correlation between the electronic effects of the R group in the reagents and the reduction mechanism, natural bond orbital (NBO) and topological analyses have been carried out.

Computational details

The structures of the reactants, transition states (TSs) and products of the reaction were optimized, using the Gaussian09 computational package [35] with the density functional method as implemented in the computational package. The geometry optimization of the stationary points on the potential energy diagrams was performed using the B3LYP/6-311++G(d,p) level of the theory. The synchronous transit-guided quasi Newton (STQN) [36] and the intrinsic reaction coordinate (IRC) method [37] were used to locate the TSs, respectively. In order to determine the natural charges on the boron atom, NBO analysis was done [38,39]. The electron density of the atoms at the bond critical points (BCPs) has been obtained by using the Bader's quantum theory of atoms in molecules (QTAIM) [40] in AIM2000 package [41] with the wave functions generated at the B3LYP/6-311++G(d,p) level. Since the solvent–solute interactions are more considerable in the solution, the conductor like polarizable continuum model (CPCM), was applied for the calculation of the Gibbs free energy of solvation [42].

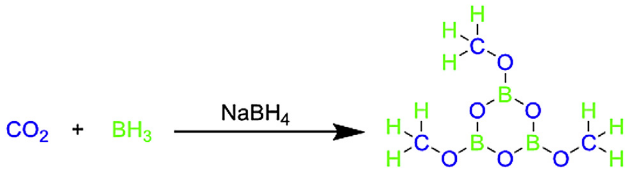

Fig. 1 – Reduction reaction of CO_2 to methoxyborane $(MeOBO)_3$ by borane and sodium borohydride as the reductive reagents.