Research paper

Alkoxysilane production from silica and dimethylcarbonate catalyzed by alkali bases: A quantum chemical investigation of the reaction mechanism

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ABSTRACT

Density functional theory (DFT) calculations were carried out to investigate mechanistic details of the reaction between silica and dimethylcarbonate (DMC) catalyzed by an alkali base. Various experimental studies have reported that several silicon dioxide sources can react with DMC in the presence of alkali base catalysts to produce tetramethoxysilane (TMOS), but details of the reaction mechanism are still elusive. Our DFT calculations suggest that the reaction can be characterized by four mechanistic steps. The first two steps include the activation of Si−O bonds by the alkali base catalyst, and the cleavage of the Si−O bond forming $-Si^+$ and $-O^-$. In the third step, the O^- moiety reacts with the methyl group of DMC to form the $-O-CH_3$ moiety; this is the rate-determining step of the overall reaction. Finally, transfer of a methoxy group from DMC to the silicon occurs to produce a compound in which two Si−O bonds in silica are replaced by two $Si-OCH_3$: i.e., dimethoxylsilyloxide. DFT calculations reveal that the rate-determining step of the reaction depends strongly on the nature of the cationic part of the alkali base catalysts. The order of barrier height of the rate-determining step was computed to be LiOH > KOH > CsOH, and this trend is in agreement with previous experimental studies. The Li cation was found to interact with DMC to form a very stable intermediate compound that causes the barrier height of the reaction between the O^- moiety of the activated SiO_2 and DMC to be higher than that of the reaction catalyzed by other cations.

1. Introduction

Polysiloxanes, known as silicones, are polymers widely used for many industrial applications [1]. An industrial process for the synthesis of monomeric compounds for silicones such as dimethyldichlorosilane (Me_2SiCl_2) includes the production of elemental silicon, which is prepared by the carbothermal reduction of silica (SiO_2) at very high temperatures. Obviously, such a reduction process is very energy demanding. It is thus desirable to develop low-cost alternative preparation methods that do not require the production of elemental silicon. Therefore, because of the importance for industry, several studies have been conducted to investigate the direct conversion of silica to organosilicon compounds [2–7].

Laine et al. [2] have reported on the reaction of silica and diols catalyzed by bases to form spirocyclic alkoxysilanes and $Si(OEt)_4$. This method is an attractive one from a practical point of view because it allows separation of the desired products by distillation.

Ono et al. [3] reported that silica gel reacts with gaseous dimethylcarbonate (DMC) in the presence of a base catalyst supported on the silica at 500–600 K to yield tetramethoxysilane (TMOS). The catalysts employed were alkali hydroxides, MOH, where M was Na, K, Rb, Cs, and metal halides (CsF, KF, KCl, NaCl). They also reported that impure silica from rice hull ash yields TMOS through a reaction with DMC. Later, Lewis et al. [4] investigated the same reaction using different low-cost silicon sources and found that amorphous material gave the best results in terms of the formation of TMOS. Besides the already cited rice hull ash, diatomaceous earth and opal tailings are other available low-cost sources of silicon. However, crystalline samples were found to be less reactive towards TMOS formation.

In recent studies, some of the authors of the present paper proposed an efficient new method of synthesizing TMOS directly from SiO_2 and methanol using a base catalyst and 2,2-dimethoxypropane as an organic dehydrating reagent [5]. This method avoids the direct use of DMC, which is a relatively expensive industrial raw material. Here, DMC is formed in situ as a result of the reaction between CO_2 and methanol, using 2,2-dimethoxypropane as a recyclable organic dehydrating

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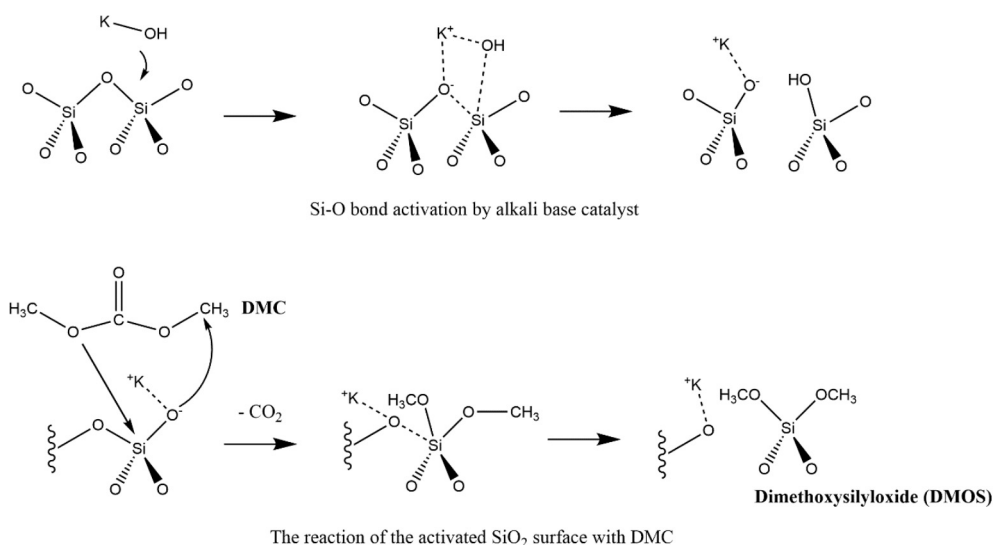
Scheme 1. Plausible mechanism for the reaction between SiO_2 and DMC catalyzed by an alkali base [3,4].

reagent. All the above experimental studies employed alkali bases as the catalyst. It was also reported that organic amines could be used for a similar purpose [7].

Previous studies clearly indicate that some sort of base catalyst is required to activate inert Si—O bonds of silica. Ono et al. have suggested that the base catalyst activates the Si—O bond of silica as described in Scheme 1 [3]. According to the mechanism, the cationic part of the catalyst interacts with the oxygen atom of the Si—O bond and the hydroxide part interacts with the silicon atom, resulting in the cleavage of the Si—O bond. As is evident in Scheme 1, the oxygen atom, which is separated from the neighboring silicon atom by the catalyst, bears an anionic character. A plausible reaction mechanism for the reaction between SiO_2 and DMC after Si—O bond activation has been suggested by Lewis et al. (see Scheme 1) [4]. This mechanism indicates that the anionic oxygen atom attacks the methyl group of DMC while the methoxy group of DMC is simultaneously detached from the carbonyl moiety of DMC to form Si—OCH_3. CO_2 was detected in this experiment, consistent with the proposed mechanism. Hence, this reaction converts two Si—O bonds of tetrahedral SiO_2 into two Si—OCH_3. If the same process (i.e., SiO_2 activation by the base catalyst followed by the reaction with DMC) is applied to the remaining two Si—O bonds of silica, TMOS is finally obtained.

Some mechanistic aspects have been proposed in the literature [3,4], but details of this reaction mechanism are still elusive, such as information on the rate-determining step. Furthermore, previous experimental studies indicate that the activity order of the base catalyst depends on the nature of the alkali metal and its anion moiety. For example, Ono et al. reported that the activity of alkali base catalysts is CsOH > KOH [3]. A study conducted by some of us also shows that the yield of TMOS depends on the catalysts used (CsOH ≫ LiOH) [5]. However, the molecular-level origin of such a trend is currently unknown.

In this context, computational explorations can shed light on the mechanistic details involved in each step of the catalytic reaction, providing important information about the nature of the key intermediates that most often cannot be isolated experimentally because of their very short lifetime. In this paper, we present a detailed study of the reaction mechanism between crystalline SiO_2 and DMC catalyzed by different alkali hydroxides to yield dimethoxylsilyloxide (DMOS). Three different alkali hydroxides based on Li, K, and Cs alkali metals were studied in an effort to understand the cation size effect on the reaction.

2. Method

2.1. Computational protocol

Geometry optimizations and frequency calculations for all reactants, intermediates, products, and transition states (TSs), were performed using density functional theory (DFT), as implemented in the Gaussian 09 quantum chemistry package [8]. We selected the BLYP functional [9], which combines Becke's 1988 [9a] exchange functional with the correlation functional by Lee, Yang, and Parr [9b]. BLYP functional has been reported to perform satisfactorily on modeling chemical reactions in comparison with hydrid or *meta*-GGA functionals [10].

As for the basis sets, we choose the DZP–DKH all-electron basis set for the Cs atom and the full-electron basis set 6-31G* [11] for O, H, C, Si, H, Li, and K atoms. The density fitting approximation was used for the BLYP calculations. For the confirmation of transition states, the vibrational mode associated with the imaginary frequency was carefully checked for correspondence to the correct movement of the involved atoms.

2.2. Cluster description

As mentioned earlier, experimental studies have shown that crystalline SiO_2 samples are less reactive towards the TMOS formation reaction than amorphous SiO_2. However, the amorphous natural Celite has a significant crystalline component. On the basis of this important evidence and considering the more difficult challenge in simulating the amorphous material, we decided to commence our theoretical investigation using a cluster model of SiO_2 carved out from its crystallographic structure, the size of which was chosen on the basis of a previous computational modeling study describing a different reaction on a crystalline SiO_2 surface in which an identical cluster size was used [12]. In our cluster model, the Si atoms of the first and second layers were saturated by adding H atoms, whereas the Si atoms belonging to the third layer were saturated by OH groups (see Fig. 1). During the geometry optimization, the lower two layers were fixed in their bulk positions. Such a modeling strategy is widely used in DFT modeling studies on chemical reactions on surface [12,13].

3. Results and discussion

First, we present results of DMOS formation catalyzed by LiOH to discuss mechanistic aspects of the reaction. Fig. 2 shows energy profiles