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COMMUNICATION

Fabrication of solid strong bases with a molecular-level dispersion of lithium sites and high basic catalytic activity†

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New solid strong bases were fabricated at room temperature by grafting lithium-containing molecular precursor onto β-cyclodextrin. The solid bases show strong basicity with a molecular-level dispersion of lithium sites, which is highly active in transesterification reactions and impossible to realize through the traditional high-temperature method.

For the need of sustainable development and green chemistry, extensive attention has been paid to the replacement of traditional homogeneous catalysts by heterogeneous ones.[1] Among heterogeneous catalysts, solid strong bases are highly fascinating for applications in environmentally friendly and economic catalytic processes, due to some evident merits such as no corrosion, easy separation, and neglectable waste production.[2] So far many attempts have been made to construct materials with strong basicity. By doping nitrogen or grafting amino groups onto porous oxide supports, some interesting solid bases can be prepared.[3] Nevertheless, the basicity of these materials is relatively weak. Aiming to enhance the base strength, inorganic base precursors were introduced to porous supports, and strong basicity can be generated from the decomposition of precursors through calcination. However, there are two shortcomings existed in such a well-known method for the preparation of solid strong bases. First, high temperatures are required for the decomposition of base precursors. For instance, the decomposition of precursor KNO_3 to basic species K_2O on silica proceeds at about 700 ℃.[4] In addition to the high energy consumption, high temperature calcination may cause the shrinkage of support structure and in some cases, the complete collapse of pore symmetries.[5] This leads to the formation of materials with quite small surface areas and low catalytic activity. Second, aggregation of resultant active species is almost unavoidable at high temperatures. It is known that the catalytic efficiency is strongly dependent on the dispersion degree of active species, since only basic species accessible by reactant molecules can act as catalytically active sites. Apparently, the dispersion degree of active species resulted from this conventional method is rather limited, which compromises the catalytic performance of solid bases. Industrial advances place greater demands on new, efficient catalysts, while the conventional high-temperature method for the preparation of solid strong base is far from being satisfactory. It is therefore extremely desirable to develop a facile method to fabricate solid strong bases with highly dispersed active sites under mild conditions.
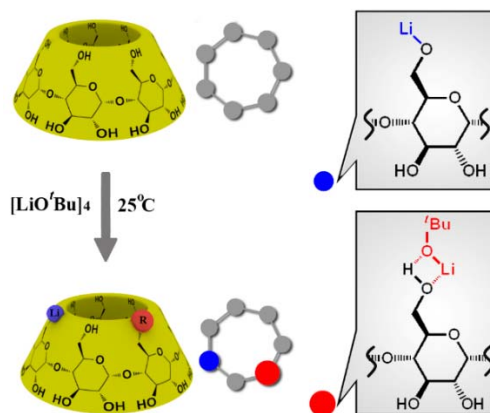
Scheme 1 Fabrication of isolated lithium sites on CD by the molecular-precursor-grafting strategy.

Herein, we report a facile strategy to fabricate strong basicity by a molecular-precursor-grafting method (Scheme 1). β-cyclodextrin (CD) was employed as the support due to the abundant hydroxyl groups dispersed on the rims. Isolated lithium sites can be grafted onto CD through the reaction of metal alkoxide (i.e. lithium *tert*-butoxide, LTB) with hydroxyl groups at room temperature. A new kind of solid base with strong basicity was thus successfully produced. Noteworthily, the obtained materials show a molecular-level dispersion of basic sites, which are extremely desirable for catalysis but impossible to achieve through traditional methods. Besides avoiding the aggregation of active species that happens in traditional high-temperature processes, the molecular-precursor-grafting strategy that proceeds at room temperature can save lots of energy. Our results also demonstrate that the obtained new solid strong bases are highly active in heterogeneous catalytic synthesis of diethyl carbonate (DEC), and the activity is obviously superior to the materials prepared by traditional methods and typical strongly basic catalysts.

The solid bases were prepared by grafting LTB onto the hydroxyl groups of CD at 25 ℃ (see ESI for experimental details). The resultant materials were denoted as Li-CD-1, Li-CD-2, and Li-CD-3, corresponding to a lithium content of 0.8, 1.8, and 2.5 mmol g^{-1}, respectively.
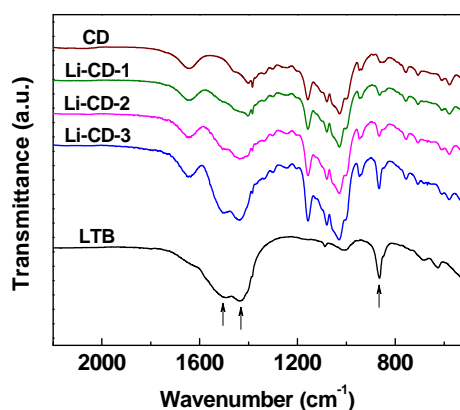
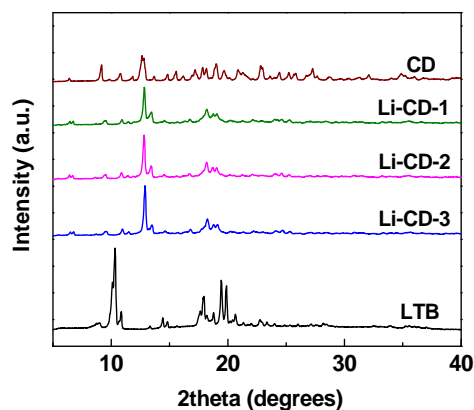**Fig. 1** IR spectra of pristine CD, LTB, and LTB-grafted CD samples.

Fig. 2 XRD patterns of pristine CD, LTB, and LTB-grafted CD samples.

Fig. 3 ^{1}H NMR spectra of CD before and LTB grafting recorded in *d*-DMSO.

Infrared (IR) spectra were first employed to characterize the obtained materials. As shown in Fig. 1, the spectra of pristine CD presents an intense band at 1028 cm^{-1}, which originates from carbon-hydroxyl group (CR$_3$−CH$_2$−OH). The bands at 1080 and 1150 cm^{-1} can be attributed to C−O−H and C−O−C groups, respectively. These IR characteristics indicate the barrel-shaped structure of CD molecule. After grafting LTB, these bands can still be clearly identified, implying that the introduction of basic sites does not result in the damage of CD structure. What's more, three new bands at 1503, 1434, and 866 cm^{-1} appear on the samples grafted with LTB, which derive from the ligand −O(CH$_3$)$_3$. Also, the intensity of these three bands increases with the increase of lithium content in the samples. This suggests that some lithium are still linked with *tert*-butoxy groups in the final materials.

Fig. 2 depicts X-ray diffraction (XRD) patterns of different samples. It is worth noting that the grafted samples present totally different diffraction peaks as compared with both pristine CD and LTB. This demonstrates that the grafted samples are not simple physical mixtures of CD and LTB. By comparing the patterns of grafted samples with the reported ones,[6] we find that the diffraction peaks between 10-20° are quite analogous to glucosylated β-cyclodextrin (JCPDS No. 53-1903), in which CD molecule is anchored with a glycosylated group through hydroxyl group. This reflects that the appearance of new diffraction peaks are due to the grafting of lithium species. Moreover, the diffraction peak at 2θ of 12.8° becomes intense with the increase of lithium content in the samples. That means, such a peak is related to the amount of lithium species grated on CD.
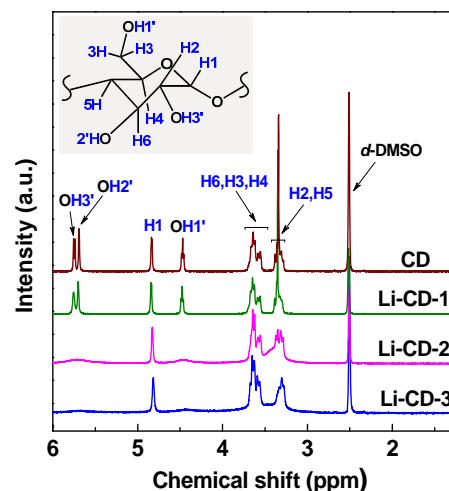
Further information on the structure of grafted samples can be obtained from ^{1}H nuclear magnetic resonance (NMR) spectra. The pristine CD shows nine kinds of protons as displayed in Fig. 3. The hydroxyl protons (denoted as OH1', OH2', and OH3') locate at chemical shift of 4.410-4.333, 5.646-5.662, and 5.686-5.708 ppm, respectively. Interestingly, the grafting of lithium species results in the decline of hydroxyl protons, whereas the amount of non-hydroxyl protons keeps constant. For the sample Li-CD-3 with a lithium content of 2.5 mmol·g^{-1}, the peaks of hydroxyl protons almost disappear. On the basis of these results, it is evident that lithium species are grafted on the hydroxyl groups of CD. The maximum amount of lithium species that can be introduced to CD should be around 2.5 mmol·g^{-1}, since almost all of the hydroxyl groups were consumed in Li-CD-3.

Thermogravimetric (TG) analysis of different samples were conducted and the results are shown in Figs. S1-S3. The decomposition of pristine CD occurs in three regions, corresponding to water desorption, CD degradation, and soot combustion, respectively. The degradation of CD gives rise to a sharp weight loss centered at about 290 °C. In the meanwhile, the thermal decomposition of pure LTB shows one main weight loss centered at 294 °C. For the grafted samples, the shape of TG curves is generally similar to pristine CD, while the weight losses of LTB and CD are combined. The grafted samples give a predominant weight loss centered at about 310 °C, which is different from both pristine CD and LTB. Moreover, the temperature for soot decomposition increases with the rise of lithium content in the grafted samples. Apparently, the existence of lithium species improves the thermal stability of CD. These data thus confirm the results of IR, XRD, and NMR, pointing out the successful grafting of lithium species onto CD.

The basic property of different samples were characterized by the amount of basic sites. The amount of basic sites is 0 mmol·g^{-1} for pristine CD, indicating that CD is not basic at all. The introduction of lithium species leads to obvious enhancement of basic sites, and the amount of basic sites for Li-CD-1 is 0.9 mmol·g^{-1}. With the increase of lithium content, the amount of basic sites rise accordingly. In the case of Li-CD-3, the amount of basic sites reaches 2.6 mmol·g^{-1}. It is noticeable that the amount of basic sites is almost equal to the content of lithium in the samples (Fig. S4). This mirrors that all of the lithium species in the grafted samples function as basic sites.

Due to the basicity and high dispersion degree of basic sites, the present materials are supposed to catalyze some reactions efficiently. They were applied to catalyze the synthesis of DEC via the transesterification of ethylene carbonate and ethanol. DEC is a

versatile chemical due to its excellent physical and chemical properties.[7] DEC is also considered a promising fuel additive, since its oxygen content is higher than that of methyl *tert*-butyl ether and it has more favorable gasoline/water distribution coefficients than dimethyl carbonate and ethanol.[8] Traditionally, DEC is synthesized in the presence of homogeneous strong bases, while increasing attention has been paid to the development of heterogeneous catalysts recently. Fig. 4 presents the heterogeneous catalytic performance of different materials on the synthesis of DEC. No DEC is produced at all even after reaction for 4 h over pristine CD. The introduction of a small number of lithium to CD leads to the evident enhancement of catalytic activity, and the yield of DEC becomes 22.7% on Li-CD-1. With increasing lithium content, the yield of DEC continues to rise. It is worthy of note that the yield of DEC can reach as high as 30.6% under the catalysis of Li-CD-3. To deeply understand the catalytic performance, several typical solid bases were employed for comparison. The catalysis of classic solid base MgO produces only 4.0% of DEC under the same conditions. Lithium species were also introduced to typical supports Al_2O_3 and SiO_2 by the conventional high-temperature method, leading to the formation of Li/Al_2O_3 and Li/SiO_2 with an identical lithium content to Li-CD-3. The activity of Li/SiO_2 is negligible (1.1%) because of the reaction of basic species with the support SiO_2 at high temperatures.[4b] The solid strong base Li/Al_2O_3 exhibits considerable activity and the yield of DEC is 15.7%, which is still much lower as contrast to Li-CD-3 (30.6%). These results clearly show that the present materials are highly active in the synthesis of DEC. The recyclability of the obtained catalysts was examined as well. After three cycles, the yield of DEC becomes 29.1%, which is slightly lower as compared with that on the fresh catalyst (30.6%). That means, the present catalysts can maintain most of the activity during recycling.

The obtained materials were also applied to catalyze typical reactions including Knoevenagel condensation and Michael addition (Tables S1-S3). In Knoevenagel reactions, two reactants, namely malononitrile and ethyl cyanoacetate, were used to react with benzaldehyde (Schemes S1 and S2), while the latter is more difficult. Under the catalysis of Li-CD-3, the Knoevenagel condensation of benzaldehyde with malononitrile can proceed smoothly with a yield of 100%. Similarly, a high yield of 97% can be obtained for the reaction of benzaldehyde with ethyl cyanoacetate. Michael addition reaction is known to require stronger basic sites than Knoevenagel condensation. By use of Li-CD-3 as catalyst, the yield is 88% from Michael addition of 1,3-diphenyl-2-propenone with nitromethane (Scheme S3). Although the reactions reported in literature were carried out under different conditions, it is possible to approximately compare the catalytic activity based on the results of Knoevenagel condensation and Michael addition as well as transesterification reaction. The catalytic activity of Li-CD-3 should be higher than nitrogen-incorporated and amines-grafted mesoporous silicas, MgO, and zeolite CsX, while lower than $Ba(OH)_2$ and KF/Al_2O_3.
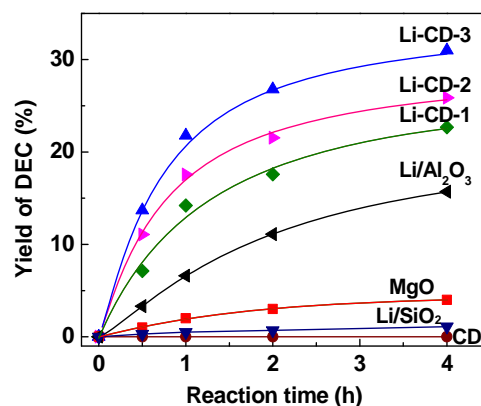

Fig. 4 The yield of DEC under the catalysis of different samples.

On the basis of aforementioned results, the grafting mechanism can be proposed. Anchoring lithium on CD may be realized through two modes as illustrated in Scheme 1. The reactions of LTB with hydroxyl groups on CD result in the formation of Li−O−CD along with the liberation of *tert*-butanol, which has been detected by gas chromatography in the solutions after grafting reactions. Alternatively, lithium can also be linked with *tert*-butoxy groups in the final materials, as demonstrated by the above IR spectra as well as previous reports.[9] Despite the anchoring modes, the maximum amount of lithium that can be accommodated by CD should be around 2.6 $mmol·g^{-1}$, as can be seen from the above results. We also tried to enhance the lithium content by raising the amount of precursor LTB in grafting reactions. However, the obtained materials exhibit quite similar lithium contents and catalytic performance to Li-CD-3. Because each hydroxyl group is isolated on the rims of CD, the basic sites, resulted from point-to-point molecular grafting, can be dispersed at a molecular level in the obtained materials.

The introduction of inorganic precursors to porous supports is a widely used method for the preparation of solid strong bases. In the subsequent high-temperature calcination, strong basicity can be generated from the decomposition of precursors. Nonetheless, high-temperature calcination is an energy-intensive process, and the shrinkage and even collapse of pore structure are almost inevitable. Furthermore, the dispersion degree of active species, which is crucial to catalytic activity, is quite limited by using this method. In this study, we design a strategy to construct solid strong bases by taking advantage of molecular precursor grafting. This strategy allows the formation of strong basicity at room temperature, which avoids the degradation of support structure in conventional processes and of course, saves lots of energy. More importantly, the obtained materials show a molecular-level dispersion of basic sites, which are particularly expected for catalysis but impossible to realize by conventional methods. We also demonstrated that these materials are highly efficient in the catalytic synthesis of DEC, and also superior to some typical solid strong bases. The strong basicity, together with the high dispersion degree of lithium sites, is believed to account for the activity. The present materials may offer promising candidates for applications in a range of reactions catalyzed by bases. The dispersion of active species is extremely desirable for the preparation of high-performance functional materials. Our strategy should enable diverse active species to be introduced to a series of supports, resulting in the construction of new types of materials with highly dispersed active sites and great potential in various applications such as catalysis and adsorption.

Notes and references

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