

Low-temperature generation of strong basicity *via* an unprecedented guest–host redox interaction†

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An unprecedented guest–host redox strategy is developed to generate strong basicity on mesoporous silica, which breaks the tradition of thermally induced decomposition of precursors. New materials possessing ordered mesostructure, strong basicity, and excellent catalytic activity are thus successfully fabricated at a low temperature.

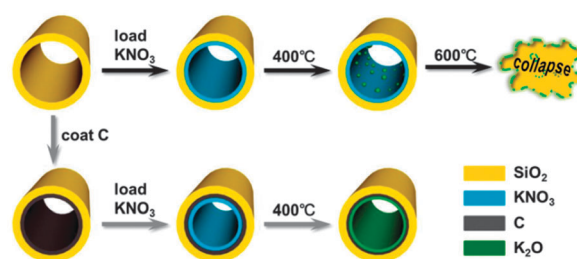
Mesoporous solid strong bases are extremely desirable for use in environmentally benign and economical catalytic processes, since they can catalyze a range of reactions under mild conditions and reduce waste production.¹ Their large pore openings favor mass transfer and avoid deactivation resulting from coke formation that usually takes place in microporous catalysts.² To date many attempts have been made to construct mesoporous materials with strong basicity. Among candidates with mesostructure, mesoporous silica is the optimal choice of support, because of its low cost, high stability, and good synthetic controllability.³ The generation of strong basicity on mesoporous silica, therefore, has been attracting great attention ever since its discovery.

Some interesting mesoporous solid bases can be prepared by incorporating nitrogen into mesoporous silica⁴ and by grafting organic basic groups onto mesoporous silica.⁵ A methylation method was also utilized to improve the strength of nitrogen-incorporated solid bases, due to the donation of an electron from the methyl group to the adjacent nitrogen atom.⁶ Nevertheless, the basicity of these materials is quite weak in addition to the rigorous synthetic conditions. Aiming to enhance the base strength, the introduction of metal oxides with strong basicity (*e.g.* K₂O) was tried. The preparation generally includes loading of base precursors (*e.g.* KNO₃) and subsequent calcination to decompose precursors to the corresponding metal oxides. Unlike other supports, the decomposition of base precursors on mesoporous silica is rather difficult. According to our previous investigation, only a tiny amount of KNO₃ can be decomposed on silica, even when the sample was activated at a high temperature of 600 °C.⁷ Further increasing the temperature can lead to the decomposition of KNO₃, but the resultant strongly basic

species inevitably react with siliceous supports. Hence, the obtained materials only possess weak basicity and the mesostructure is severely destroyed. Despite great efforts, the generation of strong basicity on mesoporous silica has remained a challenge to date.

Herein, we develop a strategy to generate strong basicity on mesoporous silica by using an unprecedented guest–host redox interaction. A layer of carbon is precoated on mesoporous silica SBA-15 prior to the introduction of base precursor KNO₃ (Scheme 1), which endows the host with reducibility. The formation of basic sites is thus realized by the redox interaction between KNO₃ and the carbon layer. Such a redox process can be completed at a temperature of 400 °C, which is obviously lower than that of the conventional thermally induced decomposition of KNO₃ (>600 °C). More importantly, the residual carbon layer prevents the siliceous frameworks from being corroded by newly formed basic species. Hence, a new kind of solid base possessing both ordered mesostructure and high base strength, which is extremely desirable for catalysis, was successfully fabricated. We also demonstrate that the mesoporous basic materials exhibit excellent catalytic activity in heterogeneous transesterification reactions, which is much superior to that of various typical strongly basic catalysts.

The carbon layer was coated on SBA-15 by using furfuryl alcohol as the source (see ESI† for details). Four samples were obtained with a carbon content of 3.7, 8.1, 13.3, and 28.9 wt% (measured by thermogravimetry (TG), Fig. S1, ESI†) and denoted as CS-*m* (*m* = 1–4, a larger number means higher carbon content). After coating carbon, the ordered mesostructure is preserved as evidenced by low-angle X-ray



Scheme 1 Promoting low-temperature conversion of KNO₃ and strong basicity generation on mesoporous silica by carbon pre-coating.

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diffraction (XRD), N_2 sorption, and transmission electron microscopy (TEM) results (Fig. S2–S4, ESI[†]), while the surface areas and pore volumes decrease with the increase in carbon content. Infrared (IR) spectra in Fig. S5 (ESI[†]) show that the band at 960 cm^{-1} , which originated from silanols (Si–OH) becomes weak after carbon coating.⁸ This is due to the interaction between carbon and the siliceous support, leading to consumption of silanols and dispersion of carbon on the surface.

The base precursor KNO_3 was introduced into CS-*m* supports by impregnation and subsequent activation at $400\text{ }^\circ\text{C}$, producing the samples KCS-*m* ($m = 1\text{--}4$). In a similar process, KNO_3 was introduced into SBA-15 and activated at 400 and $600\text{ }^\circ\text{C}$, resulting in the formation of KS(400) and KS(600), respectively. Two kinds of crystalline phases, namely orthorhombic and hexagonal phases, were formed for KNO_3 supported on SBA-15 and CS (Fig. S6, ESI[†]).⁷ It is hard to identify any residual diffraction lines of KNO_3 on CS supports upon activation at $400\text{ }^\circ\text{C}$, whereas the lines with high intensity are still visible for KNO_3 on SBA-15. This demonstrates that the carbon layer plays a significant role in the conversion of KNO_3 . Upon increasing the temperature to $600\text{ }^\circ\text{C}$, the decomposition of KNO_3 can proceed on pure SBA-15, but the mesostructure was destroyed completely as will be discussed later. IR spectra of samples before and after activation were also recorded to examine the conversion of KNO_3 (Fig. S7, ESI[†]). All samples before activation give rise to an obvious vibration band at 1384 cm^{-1} assigned to nitrate.⁹ Activation at $400\text{ }^\circ\text{C}$ only slightly weakens the band of nitrate for KS. For the samples containing a carbon interlayer, nonetheless, the band intensity drops evidently and keeps declining with the increase in carbon content. The TG technique was employed to gain a deep insight into the conversion of KNO_3 on different supports. On pure SBA-15, the decomposition of KNO_3 can be divided into three stages centered at about 440 , 590 , and $670\text{ }^\circ\text{C}$ (Fig. 1). It is noticeable that on carbon-coated SBA-15, KNO_3 converts at a temperature as low as $410\text{ }^\circ\text{C}$. The TG data, in combination with the above XRD and IR results, clearly show that the carbon layer promotes the conversion of KNO_3 at much low temperatures.

Structural characterization of samples after potassium modification was performed by various approaches. The diffraction lines in low-angle XRD patterns are observable for KCS samples even though the intensity varies with the carbon content (Fig. S8, ESI[†]). Because the majority of KNO_3 is not decomposed at $400\text{ }^\circ\text{C}$, the diffraction lines for KS(400) can be well recognized. Upon increasing the activation temperature to $600\text{ }^\circ\text{C}$, the decomposition of KNO_3 can take place, but all of the diffraction lines disappear. The N_2 sorption isotherms of KCS are of type IV with an H1 hysteresis loop, which is characteristic of materials with cylindrical mesopores (Fig. S9, ESI[†]). A negligible amount of N_2 is adsorbed in KS(600), corresponding to a pretty low surface area ($3\text{ m}^2\text{ g}^{-1}$) and pore volume ($0.01\text{ cm}^3\text{ g}^{-1}$). TEM is another important technique to characterize the long-range channel ordering. As displayed in Fig. S4B (ESI[†]), the periodic ordering of the mesostructure is well preserved for KCS samples. On the basis of these results, it is conclusive that the carbon layer avoids the corrosion of siliceous frameworks by generated basic species, leading to the production of materials with ordered mesostructure.

The basic properties of resultant materials were initially analyzed by the amount of basic sites. In the case of KS(400) and KS(600), the amount of basic sites is only 0.52 and 0.02 mmol g^{-1} due to the

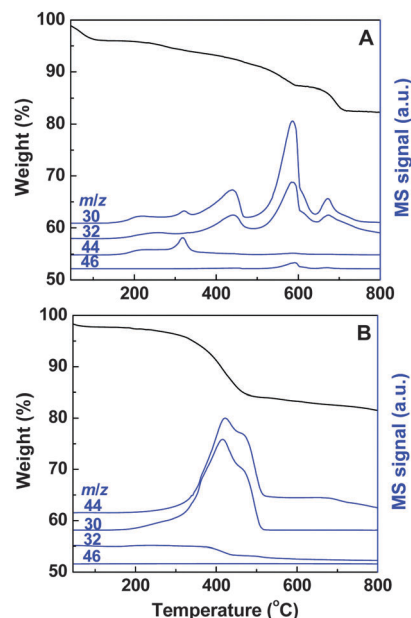


Fig. 1 (A) TG and MS analysis of (A) KS and (B) KCS-3 before activation.

reaction of strongly basic species with silica and/or incomplete decomposition of KNO_3 (Fig. 2). Interestingly, for the sample containing 3.7 wt\% of carbon, KCS-1, the amount of basic sites increases to 1.3 mmol g^{-1} . The amount of basic sites keeps rising with the increase in carbon content and reaches 1.97 mmol g^{-1} for KCS-3 and KCS-4, which is in good agreement with the theoretical value (1.98 mmol g^{-1}) and implies the thorough conversion of KNO_3 to basic sites. The basicity of materials was further determined by use of temperature programmed desorption of the CO_2 (CO_2 -TPD) technique. Only a tiny amount of CO_2 was desorbed at $105\text{ }^\circ\text{C}$ for KS(600) as shown in Fig. 3. This desorption peak becomes more intense and a small peak at $560\text{ }^\circ\text{C}$ emerges for KS(400). In the case of KCS-3, the intensity of peaks at both low and high temperatures increases sharply. Moreover, the desorption of CO_2 lasts up to $800\text{ }^\circ\text{C}$, mirroring the existence of superbasic sites on KCS samples.

The obtained materials were utilized to catalyze the synthesis of dimethyl carbonate (DMC) through the transesterification of ethylene carbonate and methanol.¹⁰ As a versatile green chemical, DMC has been proposed as a carbonylating agent, a fuel additive, and a methylating agent. The traditional synthesis of DMC is carried out by use of homogeneous strong bases, while increasing attention has been paid to the development of heterogeneous catalysts recently. As presented in Fig. 4, no DMC is formed at all even after reaction for

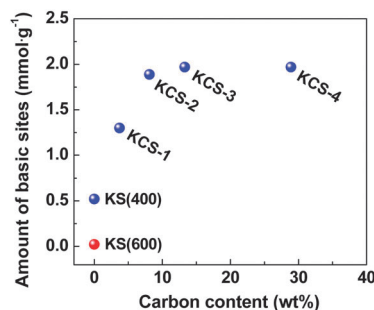


Fig. 2 Amount of basic sites as a function of carbon content for samples.

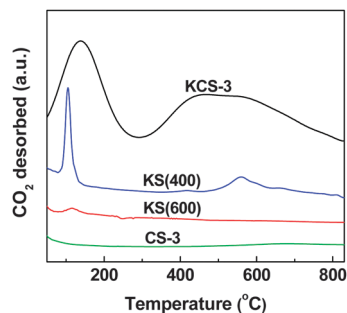


Fig. 3 CO₂-TPD profiles of CS, KS, and KCS samples.

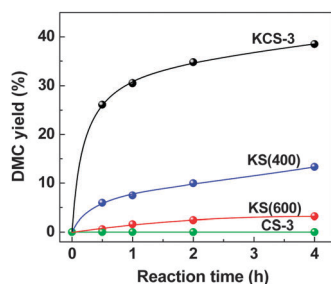
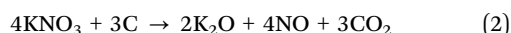
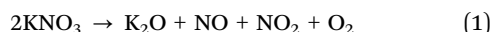


Fig. 4 The yield of DMC under the catalysis of different samples.

4 h over the sample without potassium (CS-3). Under the catalysis of KS(400) and KS(600), the yield of DMC is 13.3 and 3.2%, respectively. The coating of a carbon interlayer results in an obvious increase in catalytic activity (Fig. 4 and Fig. S10, ESI†). It is surprising that the yield of DMC reaches as high as 38.6% over KCS-3, which is obviously superior to those over KS(400) and KS(600) despite the same potassium content. To deeply understand the catalytic performance of our materials, some well-known solid bases were employed for comparison. Upon catalysis with the classic solid base MgO, only 7.6% of DMC is produced. The zeolite possessing strong basicity, CsX, gives a yield of 6.1%. A solid superbases CaO/ZrO₂ was also used to catalyze the reaction, and the yield of DMC is only 15.1%. Apparently, our materials exhibit excellent catalytic performance in DMC synthesis, and are much better than various typical solid bases.

To examine the mechanism of KNO₃ conversion, gaseous products generated in the process were monitored using a mass spectrometer (MS). Four signals with *m/z* values of 30, 32, 44, and 46 were detected and can be, respectively, attributed to NO, O₂, CO₂, and NO₂ (Fig. 1). The decomposition of KNO₃ on SBA-15 predominantly produces NO and O₂ along with a small amount of NO₂. In the presence of the carbon layer, however, the conversion of KNO₃ proceeds in a quite different way and the main products are NO and CO₂. Accordingly, the conversion of KNO₃ to basic species K₂O on SBA-15 and CS supports can be tentatively described by eqn (1) and (2), respectively.



As can be seen from the TG curve, the weight loss of KCS-3 is 16.1 wt%. Taking into account that the support CS-3 itself gives rise to a weight loss of 3.5 wt% upon heating (Fig. S11, ESI†),

the weight loss derived from the reaction of KNO₃ with carbon should be 12.6 wt%, which agrees well with the theoretical value (12.5 wt%). This confirms the pathway of KNO₃ conversion displayed in eqn (2). From the viewpoint of converting all supported KNO₃ (20 wt%), a minimum carbon content of 5.3 wt% is necessary, which comprises 1.8 wt% of carbon that reacted with KNO₃ and 3.5 wt% of carbon that is lost in the process. It is thus reasonable that only part of KNO₃ is converted in KCS-1, since the carbon content (3.7 wt%) is less than 5.3 wt%. In terms of the above analysis, it is safe to say that the conversion of KNO₃ on CS supports results from the redox reaction between the guest and the host.

In general, the preparation of solid strong bases is performed by introducing precursors into porous supports followed by calcination to form basic species. However, two factors hinder the generation of strong basicity on mesoporous silica by use of this renowned method. One is the difficulty in the decomposition of base precursors on mesoporous silica, and the other is the reaction between strongly basic species and siliceous frameworks. In the present study, we design a delicate strategy by precoating a carbon layer, and both weaknesses can be overcome. The carbon layer adjusts the surface properties and endows the host with reducibility. The basic oxide can thus be produced *via* the guest–host redox reaction, which breaks the tradition of thermally induced decomposition. This strategy significantly decreases the treatment temperature and the conversion of precursors can reach as high as 100%. By using pure mesoporous silica as the support, the decomposition of KNO₃ is possible if the calcination temperature is high enough. However, the formed strongly basic species inevitably react with siliceous frameworks, which results in the collapse of mesostructure and the formation of weakly basic species. In this regard, the carbon interlayer plays a more important role in enhancing the alkali-resistant ability of the host, which avoids the reaction of strongly basic species with siliceous frameworks that occurs in the traditional process. The present strategy may open up a new way for the fabrication of functional materials by taking advantage of guest–host interaction.

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