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# Significant Decrease in Activation Temperature for the Generation of Strong Basicity: A Strategy of Endowing Supports with Reducibility

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# Supporting Information

ABSTRACT: Mesoporous solid strong bases are quite attractive due to their good catalytic performance for applications as environmentally friendly catalysts in various reactions. However, pretty harsh conditions are usually compulsory for the fabrication of strong basicity by using traditional thermal activation (e.g., 700 °C for the activation of base precursor KNO<sub>3</sub> supported on mesoporous Al<sub>2</sub>O<sub>3</sub>). This is energy intensive and harmful to the mesoporous structure. In this study, we report a strategy of endowing supports with reducibility (ESWR) by doping low-valence Cr<sup>3+</sup> into mesoporous Al<sub>2</sub>O<sub>3</sub>, so that the activation temperature for basicity generation is decreased significantly. Fascinatingly, KNO<sub>3</sub> on mesoporous Al<sub>2</sub>O<sub>3</sub> can be motivated to basic sites



completely at the temperature of 400 °C via the ESWR strategy, which is much lower than the conventional thermal activation (700 °C). We have demonstrated that the redox reciprocity between KNO<sub>3</sub> and  $Cr^{3+}$  is responsible for the low-temperature conversion, and Cr6+ is formed quantitatively as the oxidation product. The obtained solid bases possessing ordered mesostructure and strong basicity provide promising candidates for base-catalyzed synthesis of dimethyl carbonate via transesterification. The catalytic activity is obviously higher than a typical solid base like MgO as well as a series of reported basic catalysts containing alkali metal and alkaline-earth metal oxides.

#### 1. INTRODUCTION

Mesoporous solid strong bases have drawn much attention in recent decades, because they can catalyze a series of reactions such as Michael addition, Knoevenagel condensation, and transesterification reaction in gentle conditions with few pollution issues.<sup>1</sup> It is known that the high specific surface areas and the affluent porous structure of mesoporous solid strong bases are beneficial for rapid mass transfer and avert active site deactivation caused by carbon deposition that usually happens in microporous catalysts.<sup>2-4</sup> As heterogeneous catalysts, mesoporous solid bases present some advantages over liquid base catalysts, such as higher selectivity, easier separation, and better reusability.<sup>5,6</sup> Hence, numerous attempts have been made in the past decades to synthesize mesoporous solid strong bases for heterogeneous catalysis.<sup>7–9</sup>

With the development of ordered mesoporous materials, remarkable efforts have been made to prepare solid strong bases based on these kinds of materials. Mesoporous silica has received great attention since the first mesoporous silica, M41S, was discovered.<sup>10,11</sup> The thermal treatment of mesoporous silica SBA-15 or MCM-41 by nitrogen-containing gases at high temperature was reported to generate basic sites.<sup>12-15</sup> The basicity is relatively weak since it is originated from partial replacement of oxygen in the siliceous framework by nitrogen.<sup>16-18</sup> Grafting organic basic groups such as aminopropyl groups is another alternative to from basicity on mesoporous silica.<sup>19–22</sup> However, the resultant catalysts also present poor basicity in addition to low thermal stability due to the existence of organic amino groups. In order to enhance the base strength, the method of loading alkaline metal oxides on mesoporous materials is employed. Because the alkali resistance of mesoporous silica is relatively weak, serious structural degradation is difficult to avoid after the introduction of strongly basic species. As a result, mesoporous Al<sub>2</sub>O<sub>3</sub> as a typical nonsiliceous oxide with strong alkali resistance becomes an ideal support of choice.<sup>23</sup> To fabricate strong basicity, a base precursor like KNO<sub>3</sub> is first loaded onto

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mesoporous  $Al_2O_3$  followed by thermal activation to decompose the precursor to basic sites. It should be stated that a quite high temperature (ca. 700 °C) is required to decompose KNO<sub>3</sub> on  $Al_2O_3$ . The high-temperature activation consumes lots of energy and leads to the degradation of the mesoporous structure. Therefore, it is a pronounced challenge to prepare solid bases with a mesoporous structure and strong basicity at a low temperature.

In the present study, we report the preparation of mesoporous solid strong bases through a strategy of endowing supports with reducibility (ESWR) by doping low-valence  $Cr^{3+}$  into mesoporous  $Al_2O_3$ , for the first time. The reducibility of support caused by  $Cr^{3+}$  doping leads to a significant decrease in activation temperature. The supported KNO<sub>3</sub> can be completely motivated to strongly basic sites at 400 °C, which is much lower than the 700 °C required for the conventional thermal activation on undoped mesoporous  $Al_2O_3$  (Scheme 1). Our results also show that the low-

Scheme 1. Scheme Depicting the Conversion of  $KNO_3$  on the Supports  $mAl_2O_3$  and mCA



temperature conversion of KNO<sub>3</sub> is caused by its redox interaction with  $Cr^{3+}$ , and  $Cr^{6+}$  is yielded quantitatively as the oxidation product. This breaks the convention of thermal pyrolyzation of base precursors that is extensively reported in literature. The resultant solid bases with ordered mesostructure and strong basicity are quite active in base-catalyzed synthesis of dimethyl carbonate via transesterification. The catalytic activity is superior to the classic solid base MgO as well as a variety of reported basic catalysts containing alkali metal and alkaline-earth metal oxides.

# 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** P123  $(EO_{20}PO_{70}EO_{20})$ , chromium nitrate nonahydrate, sodium hydroxide, and aluminum isopropoxide were purchased from Sigma-Aldrich. Potassium nitrate, nitric acid, ethanol, methanol, ethanediol, ethylene carbonate, and phenolphthalein were purchased from Sinopharm. All chemicals were used directly without any further purification. Deionized water was used in all experiments.

**2.2.** Materials Synthesis. 2.2.1. Synthesis of Cr-Doped Mesoporous  $Al_2O_3$ . Cr-doped mesoporous  $Al_2O_3$  was synthesized as follows.<sup>24</sup> In a typical synthesis process, 1.0 g of P123 was dissolved in 20.0 mL of ethanol with vigorous magnetic stirring. Then, quantitative aluminum isopropoxide and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were sequentially added. Then, 1.6 mL of 67.0 wt % nitric acid was added. After it

was stirred for 5 h at room temperature, the obtained mixture was treated at 60 °C for 48 h to volatilize ethanol. The bluish green parent materials were crushed to powders and calcined in an air flow at 700 °C for 4 h. The obtained Cr-doped mesoporous  $Al_2O_3$  were labeled as mCA(n), where n = 1, 2, and 3 represents the molar ratio of Cr/Al varied from 1/7, 1/5, and 1/3, respectively. The mesoporous  $Al_2O_3$  without Cr doping was also made by the same method without the addition of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and the obtained material was labeled as  $mAl_2O_3$ .

2.2.2. Preparation of Solid Bases. The base precursor of  $KNO_3$  was loaded onto  $mAl_2O_3$  by the wet impregnation method. In a typical process, 0.3 g of  $KNO_3$  (30 wt %) was dissolved into 10 g of deionized water with magnetic stirring. Then, 0.7 g of  $mAl_2O_3$  was added, and after it was stirred for 2 h, the mixture was evaporated at about 75 °C in a water bath kettle. After that, the material was dried at 80 °C for 24 h. The obtained solid was denoted as 30KA. By using mCA(n) as the support and adjusting the loading amount of  $KNO_3$  (varied from 10 to 30 wt %) and n (1, 2, and 3) represents the molar ratio of Cr/Al (1/7, 1/5, and 1/3). The products were then activated at a certain temperature (400 or 700 °C) in an Ar flow for 3 h to motivate supported  $KNO_3$  to basicity. The obtained samples were labeled as yKCA-t (or yKA-t), where t denotes the activation temperature.

2.3. Materials Characterization. X-ray diffraction (XRD) patterns of these samples were recorded on a Bruker D8 Advance diffractometer with monochromatic Cu K $\alpha$  radiation in the  $2\theta$  range from 0.6° to 6° and 5° to 80° at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a PHI5000 VersaProbe spectrometer (UIVAC-PHI) with monochromatic Al K $\alpha$  radiation, and the binding energies were corrected to C 1s at 284.6 eV.<sup>25,26</sup> The N<sub>2</sub> adsorption-desorption isotherms were measured using an ASAP2020 system at -196 °C. Before the test, the samples were evacuated for 4 h in the degas port at 200 °C. The multipoint Brunauer-Emmet-Teller (BET) surface area was estimated over the relative pressure range from 0.04 to 0.20. The total pore volume was calculated using the amount adsorbed at a relative pressure of 0.99. The pore size distributions of the mesoporous materials were analyzed by the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (TEM) images were performed on a JEM-2010 UHR electron microscope. The obtained catalyst powders were measured by UV-visible (UV-vis) diffuse reflectance spectra on a UV-2401PC spectrophotometer, and BaSO<sub>4</sub> was used as the standard. Scanning electronic microscopy (SEM) images were recorded on Hitachi S4800 instrument, and the elemental distribution of materials was recorded by energy dispersive X-ray spectroscopy (EDX) mapping. Thermogravimetric mass spectrometry (TG-MS) was carried out on a thermobalance (STA-499C, NETZSCH). Then, 10 mg of sample was heated from room temperature to 900 °C with a heating rate of 5 °C min<sup>-1</sup> in Ar (20 mL min<sup>-1</sup>). The gaseous products derived from pyrolyzation of the samples were analyzed by MS. Fourier transform infrared spectrometry (FTIR) measurements of the samples were carried out on a Nicolet Nexus 470 spectrometer by means of the conventional KBr pellet technique. To prepare the KBr tablets, about 2 mg of the sample was mixed with 200 mg of KBr powder, and the mixture was pressed into a transparent sheet. The basicity and the basic strength distribution of the catalyst was studied by carbon dioxide temperature-programmed desorption (CO<sub>2</sub>-TPD) experiments on a BELSORP BEL-CAT-A apparatus. Before the test, the samples were activated at 400 °C for 3 h prior to the adsorption of CO<sub>2</sub> at 50 °C. After the physically adsorbed CO<sub>2</sub> was purged by a He flow (99.999%) at room temperature for 30 min, the sample was heated to 800 °C, and the CO<sub>2</sub> liberated was detected via a mass spectrometer (HAL201, HIDEN).<sup>27</sup> To measure the amount of total basic sites of these samples, 50 mg of sample was added into 10.0 mL of a certain concentration of aqueous HCl (0.05 mol  $L^{-1}$ ). The suspension was vibrated for 24 h, and the undissolved portion was separated by a centrifuge. The serum was titrated with 0.01 mol L<sup>-1</sup> aqueous NaOH for determining the excess of acid.<sup>28</sup>

**2.4. Catalytic Tests.** DMC was synthesized via the transesterification of ethylene carbonate and methanol.<sup>29-31</sup> The typical process was as follows. First, 16 g of methanol, 8.88 g of ethylene carbonate, and 50 mg of catalyst were added to a 100 mL threenecked glass flask with a water-cooled condenser device. The reaction was conducted at 70 °C with stirring for a prescribed period of time. After the reaction, the upper liquid mixture was centrifuged and analyzed via an Agilent 7890A gas chromatography equipped with a flame ionization detector (FID).

# 3. RESULTS AND DISCUSSION

**3.1.** Conversion of the Base Precursor  $KNO_3$  on Different Supports. The motivation of the base precursor  $KNO_3$  on mesoporous  $Al_2O_3$  with or without Cr doping was studied by TG-MS. As shown in Figure 1A, 30KA presents an



**Figure 1.** Conversion of KNO<sub>3</sub> on the supports (A) 30KA and (B) 30KCA(2). The MS signals of 30, 32, 44, and 46 can be ascribed to NO,  $O_2$ ,  $N_2O$ , and  $NO_2$ , respectively.

obvious weight loss at about 700 °C attributed to the decomposition of KNO<sub>3</sub>, indicating the high temperature for the formation of basicity on undoped mesoporous Al<sub>2</sub>O<sub>3</sub>. On typical Cr-doped support mCA(2), the conversion of KNO<sub>3</sub> occurs at about 400 °C (Figure 1B). This reflects that the presence of Cr lowers the temperature for KNO<sub>3</sub> conversion significantly. The effect of Cr content in the mCA was examined as well. In the case of 30KCA(1) with a lower Cr atom content (Figure S1), some KNO<sub>3</sub> was converted at about 400 °C with more converted at >600 °C, suggesting that Cr in 30KCA(1) is not enough to convert KNO<sub>3</sub> fully. For the sample 30KCA(3) with a high Cr content (Figure S2), the complete conversion of base precursor also takes place at 400 °C. This indicates the importance of Cr content in the conversion of KNO<sub>3</sub>, and the mCA(2) with a Cr/Al molar ratio of 1/5 is suitable for complete KNO3 conversion. The gaseous products derived from the samples during thermal treatment were analyzed by MS. Four MS signals with m/zvalues of 30, 32, 44, and 46 could be detected, and they are ascribed to NO, O<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub>, respectively (Figure

1).<sup>15,32</sup> The decomposition of KNO<sub>3</sub> on  $mAl_2O_3$  predominantly produces NO,  $O_2$ , and NO<sub>2</sub>, along with a small amount of N<sub>2</sub>O (Figure 1A). In the case of the *m*CA, however, the main products are NO, N<sub>2</sub>O, and NO<sub>2</sub>. The different gaseous products derived from KA and KCA indicate different pathways for KNO<sub>3</sub> conversion.

Wide-angle XRD patterns were recorded to characterize the different samples. As shown in Figure S3, mAl<sub>2</sub>O<sub>3</sub> only shows amorphous XRD peaks.<sup>33-36</sup> After the introduction of base precursor, a series of diffraction peaks ascribed to KNO<sub>3</sub> can be observed. It is noticeable that after activation at 400 °C, the sample 30KA-400 still gives intense diffraction peaks of KNO<sub>3</sub>, indicating that only a small quality of KNO<sub>3</sub> is decomposed. In the case of 30KA-700 activated at 700 °C, the diffraction peaks of KNO<sub>3</sub> disappears, proving that the decomposition of KNO<sub>3</sub> only takes place at high temperatures on  $mAl_2O_3$ . The doping of Cr on mesoporous Al<sub>2</sub>O<sub>3</sub> leads to the formation of evident XRD peaks at  $2\theta$  of 24.7, 33.9, 36.5, 55.4, and 65.7°, which corresponds to (012), (104), (110), (116), and (300) crystal faces of  $Cr_2O_3$  (JCPDS no. 84-0315).<sup>37-42</sup> The intensity of these diffraction peaks increases gradually with the augment of Cr content (Figure S4). After the loading of  $KNO_3$ , the diffraction peaks of KNO<sub>3</sub> (JCPDS no. 01-0493) appear, and the diffraction intensity increases with the enhancement of KNO<sub>3</sub> loading (Figures 2A and S5). As shown in Figure 2B,



Figure 2. Wide-angle XRD patterns of KCA(2) series samples with different KNO<sub>3</sub> loadings (A) before and (B) after calcination at 400  $^{\circ}$ C.

the diffraction peaks of KNO<sub>3</sub> disappear after activation at 400 °C on the support mCA(2) regardless of KNO<sub>3</sub> content, which is much lower than that on  $mAl_2O_3$  (700 °C). This proves that the presence of  $Cr_2O_3$  promotes the conversion of KNO<sub>3</sub>. Interestingly, after activation the peaks of  $Cr_2O_3$  decrease progressively with increasing KNO<sub>3</sub> content. This is due to the transformation of  $Cr_2O_3$  to other Cr oxides caused by the redox interaction between  $Cr_2O_3$  and KNO<sub>3</sub>. This phenomenon can also be clearly seen from Figure S6 where the  $Cr_2O_3$  diffraction peaks decline after activation. Moreover, there are no diffraction peaks that originate from  $Cr_2O_3$ , and the remaining peaks of KNO<sub>3</sub> can be observed in 30KCA(1)-400 with low Cr content. This suggests that the amount of  $Cr_2O_3$ 

in the sample is relatively small and not sufficient for the thorough conversion of  $KNO_3$ . These results thus confirm the data from TG-MS.

XPS spectra were further collected to characterize the samples. The presence of K, Cr, and Al elements in the samples can be verified from the spectra (Figures 3 and S7-



Figure 3. XPS spectra of different samples. (A) N 1s and (B) Cr 2p before calcination as well as (C) N 1s and (D) Cr 2p after calcination.

S9). Particularly, the conversion of  $KNO_3$  can be monitored by N 1s XPS spectra before and after activation, as shown in Figure 3A and 3C. Before activation, the N 1s spectra show an XPS peak derived from  $NO_3^-$  at the binding energy of 407 eV.43,44 After activation, the N 1s peak disappears for the samples 30KCA(3)-400 and 30KCA(2)-400 with a high Cr content, proving that the supported KNO<sub>3</sub> is completely converted. However, for the sample 30KCA(1)-400 with a low Cr content, an evident peak at the binding energy (BE) of 407 eV is still detected, indicating that only part of KNO3 is converted. Figures S10 and S11 exhibit the FT-IR spectra of different samples before and after activation. For mCA(1) and mCA(2), the band at 1384 cm<sup>-1</sup> belongs to carbonate species on the mixed oxide surface formed by adsorption of atmospheric CO2.45 All samples containing KNO3 give an obvious IR band at 1384 cm<sup>-1</sup> attributed to N-O vibration.<sup>46,47</sup> After activation at 400 °C, the sample 30KCA(1)-400 still has a strong vibration band of nitrate, which indicates that KNO<sub>3</sub> is only partially converted.<sup>48,49</sup> For the KCA(2)-400 series samples, the band of nitrate drops sharply, and there is only a peak left at  $1384 \text{ cm}^{-1}$  derived from the support, which indicates the entire conversion of KNO<sub>3</sub> in the presence of sufficient Cr in the supports (Figure S11).

Based on the above results, it is obvious that the doping of low-valence  $Cr^{3+}$  into  $mAl_2O_3$  accelerates the motivation of the base precursor significantly. Complete conversion of KNO<sub>3</sub> can be realized at the temperature of 400 °C, which is much lower than the decomposition temperature for KNO<sub>3</sub> on

undoped  $mAl_2O_3$  (700 °C). The existence of Cr has an important effect on the conversion of KNO<sub>3</sub>, which is different from the traditional thermal decomposition of base precursors. Moreover, the loading amount of Cr influences the activation of KNO<sub>3</sub>. When the Cr/Al molar ratio is less than 1/7 for the sample 30KCA(1), only partial KNO<sub>3</sub> is converted after activation. Nevertheless, for the samples 30KCA(2) and 30KCA(3) with a Cr/Al molar ratio higher than 1/5, KNO<sub>3</sub> can be completely converted under the same activation conditions.

3.2. Proposed Activation Mechanism for Basicity **Generation.** By doping low-valence  $Cr^{3+}$  into  $mAl_2O_3$ , the conversion of supported KNO3 is achieved at a low temperature of 400 °C. The conversion of  $KNO_3$  on mCAshould be attributed to the redox interaction considering the reducibility of Cr<sup>3+</sup> and the oxidizability of KNO<sub>3</sub>. The transformation of Cr valence during redox was thus explored. The Cr 2p XPS spectra of the samples before and after activation were shown in Figure 3B and 3D. In the case of 30KCA(1), 30KCA(2), and 30KCA(3) before activation, there are two peaks at the BE of 586.5 and 577.2 eV associated with Cr<sup>3+</sup> species.<sup>50</sup> After activation at 400 °C, two new peaks appear in at the BE values of 589.4 and 580.4 eV and can be ascribed to  $Cr^{6+}$  species.<sup>51,52</sup> This demonstrates that  $Cr^{3+}$  in *m*CA was oxidized to  $Cr^{6+}$  during the conversion of KNO<sub>3</sub>. Clearly, the contents of Cr<sup>6+</sup> are obviously larger than Cr<sup>3+</sup> in the samples 30KCA(3)-400 and 30KCA(2)-400, but for the sample 30KCA(1)-400, only Cr<sup>6+</sup> species is detected, indicating the complete transformation of  $Cr^{3+}$  to  $Cr^{6+}$ .

To further investigate the valence transformation of Cr, diffuse reflectance UV-vis spectra of the sample before and after activation were recorded (Figure S12). For the sample 30KCA(2), two absorption bands corresponding to Cr<sup>3+</sup> appear at about 455 and 600 nm. After activation, the UVvis spectrum of 30KCA(2)-400 exhibits two new absorption peaks at around 274 and 360 nm assigned to Cr<sup>6+</sup> species.<sup>53</sup> Meanwhile, the peaks of Cr<sup>3+</sup> species decline obviously, indicating that a large amount of  $Cr^{3+}$  was converted to  $Cr^{6+}$ . It is known the transformation of the valence state of metal is often accompanied by a change in color. The digital photos of samples with different loading amounts of KNO3 before and after activation at 400 °C were taken and are shown in Figure 4. The color of 10KCA(2) is dark green and becomes lighter with the increase of KNO<sub>3</sub> loading. After activation at 400 °C, the color of these samples changes to yellow green due to the



Figure 4. Digital photos of the samples before and after calcination.

valence variation of  $Cr^{3+}$  to  $Cr^{6+}$ . In the case of 30KCA(1), the color is dark yellow due to the low content of Cr (Figure S13). It is obvious that the color changes to luminous yellow after activation, giving further evidence of the transformation of  $Cr^{3+}$  to  $Cr^{6+}$ .

From TG-MS results of the sample 30KA (Figure 1A), the decomposition of KNO<sub>3</sub> on  $mAl_2O_3$  predominantly produces NO, O<sub>2</sub>, NO<sub>2</sub>, and N<sub>2</sub>O. So, the decomposition of KNO<sub>3</sub> to basic sites on  $mAl_2O_3$  could be depicted through the following equation:  $6KNO_3 \rightarrow 3K_2O + 2NO + N_2O + 4O_2 + 2NO_2$ . But in the presence of the Cr atoms, the main products are NO, N<sub>2</sub>O, and NO<sub>2</sub> (Figures 1B, S1, and S2). Therefore, by combining XPS and UV-vis data, the conversion of KNO<sub>3</sub> to basic sites on mCA could be depicted through the following equation:  $8KNO_3 + 3Cr_2O_3 \rightarrow 4K_2O + 6CrO_3 + 2NO + N_2O$ + 4NO<sub>2</sub>. Quantitative analysis of the consumption of  $Cr^{3+}$  for the conversion of KNO<sub>3</sub> in the 30KCA series samples was conducted. Theoretically, due to the low Cr content in 30KCA(1), only 72.6% of KNO3 is converted to K2O even though all  $Cr^{3+}$  is oxidized to  $Cr^{6+}$ . Therefore, partial KNO<sub>3</sub> is not converted and the structure of 30KCA(1) is destroyed because of the insufficient Cr doping. Further increasing the Cr content, the quantitative analysis of XPS presents that 94.7% of  $Cr^{3+}$  was oxidized to  $Cr^{6+}$  for the 30KCA(2) sample, which is close to the theoretical value (98%) provided that all supported KNO3 is converted. Similarly, in the case of 30KCA(3), the quantitative analysis of XPS exhibits that about 78.9% of  $Cr^{3+}$  is oxidized to  $Cr^{6+}$ , which is consistent with the theoretical value of 73.3%.

The aforementioned results demonstrate that the low activation temperature in Cr-doped  $mAl_2O_3$  originated from the redox reaction between the base precursor and the support. In the process of activation, KNO<sub>3</sub> is converted to K<sub>2</sub>O and low-valence  $Cr^{3+}$  is transformed to high-valence  $Cr^{6+}$ , which has been evidenced by various approaches including XPS and UV–vis spectra as well as color change. Quantitative analysis shows that  $Cr^{3+}$  in 30KCA(1) is not sufficient for the conversion of supported KNO<sub>3</sub>, while  $Cr^{3+}$  in 30KCA(2) and 30KCA(3) with increasing Cr contents is enough for the conversion of supported KNO<sub>3</sub>. The theoretical values are in good agreement with the measured ones according to various characterizations. We also analyzed the coordination number (CN) of  $Cr^{6+}$ , and the CN of  $Cr^{6+}$  should be 6 in the samples after calcination, such as 30KCA(2)-400.

3.3. Structural Properties of the Obtained Solid Bases. Various techniques were used to examine the structure of the obtained mesoporous solid bases, since mesoporosity is important for the materials. Figure 5 exhibits the N<sub>2</sub> adsorption-desorption isotherms and the pore size distributions of different samples. The textural properties such as surface area and pore volume are displayed in Tables 1 and S2. It is obvious that all of the samples have typical type-IV curves, which is the representative characteristic of a mesoporous structure.<sup>54,55</sup> The isotherms have a clear condensation step at  $p/p_0 = 0.5-0.9$  with a uniform mesoporous size of around 8 nm. For the KCA(2)-400 samples, the hysteresis loop and pore volume exhibits a decreasing tendency with increasing KNO<sub>3</sub> content, and the meso-structure remains intact in these solid catalysts. The KA sample without Cr doping was also investigated as a comparison. In order to decompose KNO<sub>3</sub>, the KA sample was activated at 700 °C. As shown in Figure S14 and Table 1, the sample 30KA-700 after activation presents very low N<sub>2</sub> uptake, indicating the serious damage of



Figure 5. (A)  $N_2$  adsorption–desorption isotherms and (B) pore size distributions of the KCA(2) series samples.

Table 1. Physicochemical Characteristics of Different Samples

|  |                                  |                                 | amount of basic sites $(mmol g^{-1})$ |          |
|--|----------------------------------|---------------------------------|---------------------------------------|----------|
| sample   | $S_{\rm BET}~({\rm m^2~g^{-1}})$ | $V_{\rm p}~({\rm cm^3~g^{-1}})$ | theoretical <sup>a</sup>              | measured |
| $mAl_2O_3$   | 255                              | 0.45                            | 0                                     | 0.28     |
| mCA(2)   | 177                              | 0.40                            | 0                                     | 0.22     |
| 30KA-400   | 95                               | 0.29                            | 2.94                                  | 0.31     |
| 30KA-700   | 29                               | 0.11                            | 2.94                                  | 2.88     |
| 10KCA(2)-400   | 156                              | 0.43                            | 0.98                                  | 0.94     |
| 20KCA(2)-400   | 98                               | 0.23                            | 1.96                                  | 1.92     |
| 30KCA(2)-400   | 68                               | 0.22                            | 2.94                                  | 2.90     |
| <sup><i>a</i></sup> Theoretical values based on the amount of KNO <sub>3</sub> loaded. |                                  |                                 |                                       |          |

the mesoporous structure. In addition, the Cr content has an effect on the structure of materials, and the materials with higher Cr content show a better mesostructure after activation (Figures 5, S15, and S16).

Low-angle XRD was also applied to test the mesostructure of samples. As exhibited in Figure 6, the support mCA(2) has a



Figure 6. Low-angle XRD patterns of the samples mCA(2), 10KCA(2)-400, 20KCA(2)-400, and 30KCA(2)-400.

strong diffraction peak at around 1° along with a weak one at about 1.7°, corresponding to the crystal faces of (100) and (110). This indicates an ordered two-dimensional hexagonal mesoporous structure.<sup>21,32</sup> These diffraction peaks are also observed in KCA(2)-400 series samples regardless of the KNO<sub>3</sub> content, demonstrating that the mesoporous structure

was preserved after KNO<sub>3</sub> loading and subsequent activation. For the sample 30KA-700 without Cr doping, no diffraction peak is detected despite that the support  $mAl_2O_3$  shows an ordered mesostructure, suggesting that the mesostructure is degraded after activation. The samples with different Cr content were studied as well (Figures S17–S19). All of the supports before KNO<sub>3</sub> loading give clear diffraction peaks ascribed to the mesoporous structure. Nevertheless, the diffraction peak in the low-angle XRD pattern of 30KCA(1)-400 is quite weak, if it appears at all. This indicates the destruction of the mesostructure due to the low Cr content. For the samples KCA(2)-400 and KCA(3)-400 with high Cr loading, the mesostructure can be well maintained after activation. This is consistent with the N<sub>2</sub> adsorption results.

TEM characterization was carried out to further examine the structure of the materials. As shown in Figure 7a and 7b, TEM



Figure 7. TEM images of the samples (a) 30KCA(2) and (b) 30KCA(2)-400. SEM and EDX mapping images of the sample 30KCA(2)-400.

images of 30KCA(2) and 30KCA(2)-400 show an ordered structure with long-range ordered mesopores. This suggests that the introduction of KNO<sub>3</sub> and subsequent conversion to basic sites do not damage the mesoporous structure. For other supports like  $mAl_2O_3$  and mCA(1), periodic mesoporous structure is also observed from TEM images (Figures S20 and S21). Nonetheless, the loading of KNO<sub>3</sub> and activation results in the obvious change of pore structure. Instead of parallel pore channels observed in the supports, an unordered pore arrangement is detected for 30KCA(1)-400 and 30KA-700. This reflects the degradation of ordered mesoporous structure after the formation of basic sites in the samples without Cr or with a low Cr content. EDX mapping images of different samples were taken and are shown in Figures 7, S22, and S23. The existence of K, Cr, O, and Al atoms is evidenced, and these atoms are uniformly distributed in the samples.

From the results mentioned above, it is found that the doping of a suitable amount of Cr leads to the formation of

solid base with a good mesoporous structure. On the contrary,  $mAl_2O_3$  without Cr doping shows a collapsed mesostructure after the introduction of basic sites. This indicates the importance of Cr doping in the preservation of ordered structure of solid bases. In addition, the doping amount of Cr has an effect on the structure of the materials. High Cr content is beneficial to the preservation of the mesoporous structure, while low Cr content may lead to the damage of the structure provided that Cr is not sufficient for the conversion of supported base precursor.

3.4. Basicity and Catalytic Performance of Solid Bases. The basic properties of different samples were first measured by acid-base titration. As shown in Tables 1 and S1, the supports  $mAl_2O_3$ , mCA(1), mCA(2), and mCA(3) give a tiny amount of basic sites, indicating the negligible basicity of the supports. For the sample 30KA-400 activated at 400 °C, the amount of total basic sites is only 0.31 mmol  $g^{-1}$ , which is comparable to the support and indicates that a very small amount of  $KNO_3$  is decomposed on  $mAl_2O_3$ . Further increasing to the activation temperature to 700 °C, the sample 30KA-700 presents 2.88 mmol  $g^{-1}$  of the amount of basic sites, which is close to the theoretical value (2.94 mmol  $g^{-1}$ ) and proves that KNO<sub>3</sub> is motivated to basic sites despite the collapse of the mesostructure at such a high activation temperature. Interestingly, for the sample 10KCA(2)-400activated at 400 °C, the amount of basic sites is 0.94 mmol  $g^{-1}$ , which is consistent with the theoretical value (0.98 mmol  $g^{-1}$ ). The amount of basic sites continue to increase with the increasing amount of KNO<sub>3</sub>. The amount of basic sites reaches 1.92 mmol  $g^{-1}$  for 20KCA(2)-400 and 2.90 mmol  $g^{-1}$  for 30KCA(2)-400, which is in line with the theoretical values (1.96 and 2.94 mmol  $g^{-1}$ , respectively). This demonstrates the full decomposition of KNO3 to basic sites in Cr-doped materials at relatively low temperatures. In addition, the amount of Cr has an effect on the amount of basic sites (Table S1). For the sample 30KCA(1)-400 with a low Cr content, partial KNO3 is converted and the amount of basic sites is lower than theoretical value; for the samples 30KCA(2)-400 and 30KCA(3)-400 with suitable Cr contents, KNO<sub>3</sub> can be fully motivated to basic sites.

CO<sub>2</sub>-TPD was applied to further measure the basicity of the obtained materials (Figure 8). The CO<sub>2</sub> desorption peaks can be provisionally divided into three parts named as  $\alpha$ ,  $\beta$ , and  $\gamma$  at about 90, 150, and 500 °C, which are originated from weak, medium, and strong basic sites, respectively. For the sample mCA(2), only a small desorbed peak of CO<sub>2</sub> ascribed to weak basicity is detected, certifying the poor basicity of pure support.



**Figure 8.** CO<sub>2</sub>-TPD profiles of the samples *m*CA(2), 10KCA(2)-400, 20KCA(2)-400, and 30KCA(2)-400.

It can be seen that the profile of the 10KCA(2)-400 shows a big CO<sub>2</sub> desorption peak derived from weak basicity and a small desorption peak from strong basicity, indicating the increase of basicity after introducing KNO<sub>3</sub>. With increasing the KNO<sub>3</sub> loading, the desorption peaks at the  $\beta$  and  $\gamma$  parts increase obviously, suggesting the enhancement of medium and strong basic sites. Especially, a sharp CO<sub>2</sub> desorption peak is observed at high temperature in the sample 30KCA(2)-400; this reflects that a large amount of strong basicity is formed for the sample with high KNO<sub>3</sub> loading. These results confirm the above titration data and suggest that the resultant solid bases are promising candidates for catalysis.

The obtained strong base catalysts were used to synthesize dimethyl carbonate (DMC) via the transesterification of ethylene carbonate and methanol. DMC is a versatile green chemical and can be utilized as a fuel additive, carbonylating agent, and methylating agent.<sup>31,56</sup> Much attention has been paid to the synthesis of DMC by using heterogeneous catalysts instead of conventional homogeneous ones.<sup>57,58</sup> As presented in Figures 9 and S24, the supports without potassium loading



**Figure 9.** (A) Transesterification reaction of methanol with ethylene carbonate catalyzed by mCA(2), 10KCA(2)-400, 20KCA(2)-400, and 30KCA(2)-400, as well as (B) comparison of catalytic activity with typical reported solid bases.

exhibit a DMC yield less than 10% after the reaction for 4 h. The limited amount of basic sites on these samples is the key to the low yield of DMC. As shown in Figure 9A, the introduction of KNO<sub>3</sub> leads to an obvious increase of catalytic activity. The yield of DMC is 27.1% over the sample 10KCA(2)-400. Further enhancement of KNO<sub>3</sub> loading results in the increase of catalytic activity, and the yield of DMC reaches 45.7% over the sample 30KCA(2)-400. A variety of catalysts used for the catalysis of the same reaction were employed for comparison, as shown in Figure 9B and Table S2. In general, the catalytic activity of alkali metal oxides increases with element period, namely, K > Na > Li. The DMC yield is 12.2% over Li<sub>2</sub>O/SBA-15 and 28.4% over K<sub>2</sub>O/ZrO<sub>2</sub>/SBA-15.

Nevertheless, the DMC yield is only 6.1% under the catalysis of the zeolite CsX. This is because the small pore size of CsX hinders the reactions. Over the benchmark solid base MgO, about 7.6% of DMC is yielded. For the alkaline-earth metal oxide CaO/ZrO<sub>2</sub>, the yield of DMC is only 15.1%, which is obviously lower than that for the K2O-modified catalysts. It is easy to find that K<sub>2</sub>O/SBA-15 shows a better catalytic activity than catalysts containing other active sites. Surprisingly, our catalyst 30KCA(2)-400 gives a DMC yield of 45.7%, which is obviously superior to that of K<sub>2</sub>O/SBA-15 as well as those for other reported catalysts. To prove the heterogeneous nature of catalyst 30KCA(2)-400, the catalyst was removed by hotfiltration during catalysis. The catalyst 30KCA(2)-400 was removed after 1 h for the reaction between methanol and ethylene carbonate. The yield was 22.6% in 1 h and remained at this level in 3 h (Figure S25). However, the yield reached 45.7% for the reaction without filtration of catalyst, indicating the heterogeneous nature during catalysis. The sample 30KCA(2)-400 also shows ideal reusability for catalyzing the DMC systhesis (Figure S26). After four cycles, the DMC yield remained at around 42%, indicating the active species not leaching.

Apparently, the characterization of basicity shows that the obtained solid bases possess strong basicity, and the basicity increases when the amount of  $KNO_3$  is enhanced. The strong basicity, along with the ordered mesoporous structure, makes the present catalysts active in the synthesis of DMC through transesterification reactions. The catalytic activity of 30KCA(2)-400 is superior to a variety of catalysts with active sites that ranged from alkali metal to alkaline-earth metal oxides.

#### 4. CONCLUSIONS

We have developed an ESWR method to fabricate mesoporous strong bases via doping low-valence  $Cr^{3+}$  into  $mAl_2O_3$ . In the process of activation, the base precursor KNO<sub>3</sub> is reduced to strongly basic K<sub>2</sub>O while low-valence Cr<sup>3+</sup> is oxidized to highvalence Cr<sup>6+</sup>. This strategy breaks though the tradition of thermal-induced pyrolyzation of base precursors. Consequently, the strongly basic sites can be formed on mCA at 400 °C, which is much lower than that on  $mAl_2O_3$  (700 °C). In addition to being energy-saving, the activation at low temperature is beneficial to the preservation of the ordered mesoporous structure, which is different from the collapse of structure occurred in  $mAl_2O_3$ . The obtained materials with strong basicity and ordered mesostructure show high activity in transesterification reactions and are more active than a great many reported solid strong base catalysts. The present work may open up an avenue for the preparation of functional materials by tailoring the surface characteristic of supports.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00759.

Tables with comparisons of the experimental and TG-MS analyses, XRD patterns, XPS spectra, IR spectra, UV-vis spectra,  $N_2$  adsorption-desorption isotherms, pore size distributions, TEM images, SEM and EDX mapping images, filtration and reusability test, and other complementary data (PDF)

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#### Notes

The authors declare no competing financial interest.

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