

Article pubs.acs.org/cm

# Direct Fabrication of Strong Basic Sites on Ordered Nanoporous Materials: Exploring the Possibility of Metal-Organic Frameworks

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# Supporting Information

ABSTRACT: Heterogeneous strong base catalysts possessing ordered nanoporous structure are highly expected due to their high activity and shape selectivity in diverse reactions. However, their fabrication remains a great challenge because quite high temperatures (600-700 °C) are compulsory for the generation of strong basicity on conventional ordered nanoporous materials (i.e., zeolites and mesoporous silicas). Here, we report for the first time direct fabrication of strong basic sites on metal-organic frameworks (MOFs) by using guest-host redox (GHR) interaction between base precursors and low-valence metal centers (e.g., Cr<sup>3+</sup>), which breaks the tradition of thermo-induced decomposition of base precursors. It is fascinating that base precursor KNO3 can be converted to strong basic species on MIL-53(Cr) at 300 °C, which is much lower than that on zeolite Y (700 °C) and mesoporous silica SBA-15 (600 °C). The resultant solid base exhibits strong basicity, ordered nanoporous structure, and high activity and shape selectivity in base-catalyzed reactions.



## INTRODUCTION

To satisfy the requirements of green and sustainable catalytic processes, the replacement of conventional homogeneous catalysts with their heterogeneous analogues is of significant interest.<sup>1-4</sup> Among heterogeneous catalysts, solid strong bases have received growing attention due to some remarkable merits over liquid bases, such as low corrosiveness, few disposal issues, and easy recycle of catalysts.<sup>5</sup> These solid strong bases can catalyze diverse reactions including halogenation, Knoevenagel condensation, Michael addition, and transesterification reaction, to name just a few. It is known that selectivity of target products is crucial for most reactions.<sup>6,7</sup> To enhance the selectivity, catalysts with ordered nanoporous structure are frequently expected. Only reactants (or products) with a matching dimension can access active sites in the pores of catalysts (or escape from the pores), and selective synthesis is thus realized. Zeolites and mesoporous silicas are two kinds of representative ordered nanoporous materials, and are widely used for the preparation of catalysts with enhanced selectivity.<sup>8-11</sup> Many attempts have also been made to create basic sites on zeolites and mesoporous silicas, such as ion exchange, nitrogen doping, and amino groups grafting. Some interesting solid bases with ordered nanoporous structure can be prepared, while most of these solid bases show only weak basicity.<sup>12,13</sup> To enhance the base strength, alkaline metal oxides with strong basicity (such as K<sub>2</sub>O) have been attempted to incorporate into zeolites and mesoporous silicas. The preparative process includes introduction of a precursor (such as KNO<sub>3</sub>), followed by calcination at a high temperature to decompose the precursor.<sup>14,15</sup> For example, 600 °C is required to decompose KNO3 on mesoporous silica SBA-15. Unfortunately, the obtained materials exhibit weak basicity, and the structure of supports is severely damaged. This is caused by the reactions between strong basic species and supports at high temperatures. To avoid such reactions, a dual-coating strategy was designed in which mesoporous silicas were coated with an alkali-resistant interlayer (e.g., Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>).<sup>16,17</sup> However, the coating process is relatively complicated, and, after coating, the surface areas of mesoporous silicas are obviously declined. Vapor-induced conversion of nitrate precursors was also reported by utilizing the reactions between vapors (e.g., methanol) and precursors.<sup>18,19</sup> Basic sites can be produced at relatively low temperatures (e.g., 400 °C by use of methanol), and the degradation of siliceous supports is hindered to some extent. Nevertheless, toxic organic vapors are involved in the process of vapor-induced conversion. Although elaborate efforts have been dedicated, direct fabrication of strong basic sites on ordered nanoporous materials remains a great challenge.

Metal-organic frameworks (MOFs) are porous crystalline materials assembled from organic linkers and metal ion (or cluster) nodes. Because of their adjustable structure, diverse functionality, and large surface areas, MOFs are highly promising for applications in catalysis.<sup>20-22</sup> MOFs possess ordered nanopores with a size ranging from micropore to mesopore, which bridges the gap between zeolites and mesoporous silicas.<sup>23</sup> The emergency of MOFs creates new opportunities for the fabrication of solid strong bases with ordered nanoporous structure. Nonetheless, the predominant approach for generation of basicity on MOFs is still the introduction of amino groups, either coordinatively grafted

Received: December 7, 2017 Revised: February 6, 2018



**Figure 1.** (a) Scheme depicting the conversion of KNO<sub>3</sub> on the zeolite Y. (b) Scheme depicting the conversion of KNO<sub>3</sub> on the mesoporous silica SBA-15. (c) Scheme depicting the conversion of KNO<sub>3</sub> on the metal–organic framework MIL-53(Cr). On the basis of TG analysis, the activation temperatures for K@Y, K@SAB-15, and K@MIL-53(Cr) are 700, 600, and 300 °C, respectively.

onto open metal sites or covalently bonded to organic linkers.<sup>24,25</sup> Hence, only weak basicity can be formed on the resultant materials. It is interesting to note that the frequently employed precursors of strong bases, nitrates, own oxidizability. Meanwhile, metal centers at low valence states possess reducibility in many MOFs, which is absent in zeolites and mesoporous silicas. By taking advantage of the redox reaction between guest and host, it is expected that precursors can be converted to strong basic sites at a low temperature. This may lead to the fabrication of a new kind of solid strong bases with ordered nanoporous structure, which is unlikely to be realized on conventional support zeolites and mesoporous silicas.

Here, we report the direct fabrication of strong basic sites on MOFs by using a guest-host redox (GHR) strategy, for the first time, which breaks the tradition of thermal decomposition of base precursors. As a proof of concept, MIL-53(Cr) containing Cr metal centers at a low valence state  $(Cr^{3+})$  was used as the host, and a typical base precursor KNO3 was employed as the guest (Figure 1). MIL-53(Cr) is built up from infinite chains of corner-sharing  $Cr^{3+}O_4(OH)_2$  octahedra, interconnected by terephthalate groups to create a 3D framework.<sup>26</sup> It is intriguing that the GHR interaction makes the conversion of KNO<sub>3</sub> on MIL-53(Cr) occur at the temperature of about 300 °C. Such a temperature is much lower than the thermal decomposition of KNO<sub>3</sub> on zeolite Y  $(\sim 700 \ ^{\circ}C)$  and SBA-15  $(\sim 600 \ ^{\circ}C)$  as well as all porous supports reported until now. As a consequence, strong basicity is directly generated on MIL-53(Cr), and the ordered nanoporous structure of support is well maintained. This is impossible to realize via the conventional thermal method, because the structure of supports is seriously destroyed under harsh conditions for the decomposition of precursors. The GHR process can be confirmed by gaseous products as well as the formation of  $Cr^{6+}$  from  $Cr^{3+}$  in MIL-53(Cr). We also demonstrate that the resultant solid base K@MIL-53(Cr) is active as heterogeneous catalysts in both Knoevenagel

condensation and transesterification reactions. The catalytic results reflect the selectivity upon a series of reactants and superior activity to various classic solid base catalysts.

#### EXPERIMENTAL SECTION

**Chemicals and Materials.** Tetragonal zirconium dioxide (*t*-ZrO<sub>2</sub>) was prepared by the calcination of zirconium oxychloride octahydrate ZrOCl<sub>2</sub> 8H<sub>2</sub>O (Aladdin, 98%) at 400 °C in an air flow for 4 h with a heating rate of 2 °C min<sup>-1</sup>. Gases were all from Nanjing Ruier. Other chemicals including EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (P123; Sigma-Aldrich, analytical reagent), tetraethylorthosilicate (TEOS; Sigma-Aldrich, 98%), hydrochloric acid (Sigma-Aldrich, ≥99%), chromium nitrate nonahydrate (Sigma-Aldrich, 99%), terephthalic acid (Aladdin, 99%), hydrofluoric acid (Adamas-beta, 40%), zeolite molecular sieve (NaY; Aladdin, >99%), silicon dioxide (Sinopharm, analytical reagent),  $\gamma$ -aluminum oxide (Aladdin, analytical reagent), monoclinic zirconium dioxide (m-ZrO<sub>2</sub>; Aladdin, analytical reagent), potassium nitrate (Sinopharm, analytical reagent), benzaldehyde (Sinopharm, analytical reagent), malononitrile (Sinopharm, analytical reagent), ethyl cyanoacetate (Sinopharm, analytical reagent), ethyl acetoacetate (Aladdin, analytical reagent), diethyl malonate (Aladdin, analytical reagent), ethylene carbonate (Sinopharm, analytical reagent), phenolphthalein (Sinopharm, analytical reagent), and sodium hydroxide (Sigma-Aldrich, 98%) were used directly without any further purification. Deionized water was generated by a Milli-Q integral pure and ultrapure water purification system and used in all experiments.

**Synthesis of SBA-15.** Mesoporous silica SBA-15 was synthesized according to the literature reported previously.<sup>18,27</sup> First, 3 g of triblock copolymer P123 ( $EO_{20}PO_{70}EO_{20}$ ) was dissolved in 90 g of aqueous HCl solution (2 M) and 22.5 g of deionized water with stirring at 40 °C. Next, 6.38 g of silica source tetraethylorthosilicate (TEOS) was added to the homogeneous solution and stirred at this temperature for 24 h. Finally, the as-prepared gel was moved to a Teflon-lined autoclave and remained at 100 °C for 24 h. The resulting product was recovered by filtration, washing, and drying at room temperature. Calcination was carried out at 550 °C in an air flow for 5 h with a heating rate of 2 °C min<sup>-1</sup> to remove the template of pure SBA-15.

Synthesis of MIL-53 (Cr). MIL-53 (Cr) was hydrothermally synthesized by using the published procedure.<sup>28</sup> First, chromium

nitrate nonahydrate Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (3.1972 g, 8 mmol), terephthalic acid HO<sub>2</sub>C-(C<sub>6</sub>H<sub>4</sub>)-CO<sub>2</sub>H (1.3244 g, 8 mmol), hydrofluoric acid (0.16 g, 8 mmol), and H<sub>2</sub>O (40.2982 g) were mixed. Reactants were stirred for 1 h under the airtight space before introducing the resulting suspension in a Teflon-lined steel autoclave, and the temperature was kept at 220 °C for 3 days. A grayish-green powder was obtained with traces of terephthalic acid. Next, the free terephthalic acid was evacuated by solvothermal exchange with DMF (1 g of MIL-53(Cr) in 50 mL of DMF) at 150 °C for 15 h. After being cooled to room temperature, the powder was impregnated in the methanol for 3 days and replaced three times to remove the DMF molecules. Eventually, dichloromethane was replaced by the anhydrous methanol to obtain the green product MIL-53 (Cr).

**Preparation of Solid Bases.** The base precursor KNO<sub>3</sub> was introduced by wet impregnation. An identical amount of KNO<sub>3</sub> (10 wt %) was put into the different supports. Typically, 0.1 g of KNO<sub>3</sub> was dissolved in 15 mL of deionized water, followed by addition of 0.9 g of NaY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.86), SBA-15, MIL-53(Cr), SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, *m*-ZrO<sub>2</sub>, and *t*-ZrO<sub>2</sub>. After being stirred at room temperature for 2 h, the mixture was evaporated at 60 °C and subsequently dried at 100 °C for 4 h. The obtained solid was denoted as K@Y, K@SBA-15, K@MIL-53(Cr), K@SiO<sub>2</sub>, K@ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, K@*m*-ZrO<sub>2</sub>, and K@*t*-ZrO<sub>2</sub>. For the conversion of base precursor KNO<sub>3</sub> to basic sites, the samples K@Y, K@SBA-15, and K@MIL-53(Cr) separately were calcined at 700, 300 and 600, 300 °C in an inert gas for 2 h. The final materials were represented as K@Y-700, K@SBA-15-300 and K@SBA-15-600, K@MIL-53(Cr)-300.

Characterization and Measurement. X-ray diffraction (XRD) patterns of materials were recorded using a Bruker D8 Advance diffractometer with monochromatic Cu K $\alpha$  radiation in the  $2\theta$  range from 0.6° to 8° and from 5° to 80° at 40 kV and 40 mA along with the scanning speed of 0.5°/min. To determine the surface area of the assynthesized materials, N2 adsorption-desorption isotherms were measured by ASAP 2020 at -196 °C. The temperature selected to perform the degasification step was different with regard to NaY, SBA-15, and MIL-53(Cr), and the degasification time was 4 h. The Brunauer-Emmett-Teller (BET) surface area was calculated with the relative pressure ranging from 0.05 to 0.35. The total pore volume was determined from the amount adsorbed at the relative pressure of about 0.99. The pore size distribution of various materials was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. For exploring the conversion of KNO<sub>3</sub>, Fourier transform infrared (IR) spectra of the samples diluted with KBr in a good proportion of 1:150 were carried out on a Nicolet Nexus 360 spectrometer with a spectra resolution of 8 cm<sup>-1</sup>. Transmission electron microscopy (TEM) images were captured to analyze the structural characterization of the materials in a JEM-2010 UHR electron microscope operated at 200 kV. The morphology of prepared samples was examined by HITACHI S-4800 SEM, and the elemental distribution of materials was determined by energy dispersive X-ray spectroscopy (EDX). EDX was performed in the scanning electron (SE) mode, and the accelerating voltage was 20 kV. TG analysis was performed on a thermobalance (STA-499C, NETZSCH). Ten milligrams of sample was heated from room temperature to 800 °C at the rate of 10  $^{\circ}$ C min<sup>-1</sup> in the flow of N<sub>2</sub> (25 mL min<sup>-1</sup>). The gaseous products derived from decomposition were analyzed by MS. TP-MS combines with temperature programming and mass spectrometry (HAL201, HIDEN), and its voltage is 70 eV. The condition of determination is the same as TG-MS. UV-visible diffuse reflectance (UV-vis) spectra of the samples were recorded with a UV-2401PC spectrophotometer, and BaSO4 was used as an internal standard. XPS measurement was done on a PHI5000VersaProbe spectrometer (UIVAC-PHI) with monochromatic Al  $K_{\alpha}$  radiation, and the binding energies were referred to  $C_{1s}$  at 284.6 eV.

To measure the amount of basic sites, 50 mg of sample after activation was added to 10 mL of aqueous HCl and  $CH_3COOH$  (0.05 M). The solid–liquid mixture was separated by a centrifuge after the sample suspension was shaken for 24 h. The remaining acid in liquid phase was titrated with a standard base (0.01 M aqueous NaOH)

where phenolphthalein was employed as an indicator. The amount of HCl consumed was used to calculate the basicity.

Knoevenagel Condensation Reaction. The catalytic performance of sample K@MIL-53(Cr)-300 was evaluated by Knoevenagel condensation reaction.<sup>29</sup> The catalysts (0.05 g) needed to experience activation at 300 °C, and then it was placed in a 10 mL two-necked glass flask containing a water-cooled condenser. The equimolar quantities of benzaldehyde (1 mmol) and other four substrates (malononitrile, ethyl cyanoacetate, ethyl acetoacetate, and diethyl malonate) were added to the absolute ethyl alcohol (2.5 mL). After the reaction mixtures were stirred at 70 °C for 1 h, the product was cooled to 25 °C and the *n*-dodecane (0.4 g) as an internal standard was injected. A centrifuge separates the supernatant, which was tested by means of a gas chromatograph (GC, Agilent 7890A) equipped with a FID and a JWDB-5 95% dimethyl-1-(5%)-diphenylpolysiloxane column.

**Transesterification Reaction.** With the prepared solid base catalyst, the compound dimethyl carbonate (DMC) can be produced via the transesterification of methanol and ethylene carbonate.<sup>14</sup> Typically, methanol (0.5 mol), ethylene carbonate (0.1 mol), and catalyst (0.5 wt % of methanol) were added to a three-necked glass flask with a water-cooled condenser. The reaction was conducted at 65  $^{\circ}$ C with stirring for a given period of time. After the reaction was completed, the reaction mixtures were recovered from the flask and subjected to centrifuging. The obtained upper liquid was then analyzed by use of a gas chromatograph (GC, Agilent 7890A) equipped with a FID and a JWDB-5 95% dimethyl-1-(5%)-diphenylpolysiloxane column.

#### RESULTS AND DISCUSSION

Aiming to create strong basicity, base precursor KNO<sub>3</sub> was introduced to three supports with ordered nanoporous structure, the zeolite Y, the mesoporous silica SBA-15, and the MOF MIL-53(Cr), by impregnation. The obtained samples were denoted as K@Y, K@SBA-15, and K@MIL-53(Cr), respectively. These samples were subjected to thermal treatment at different temperatures to convert KNO<sub>3</sub>, which results in the formation of K@Y-T, K@SBA-15-T, and K@ MIL-53(Cr)-T (where T represents the treatment temperature). Strong basicity is anticipated to generate through the conversion of KNO3 to alkaline metal oxide K2O. It is noticeable that KNO<sub>3</sub> exhibits a quite different conversion behavior on different supports. Thermogravimetry-mass spectrometer (TG-MS) technique was first adopted to examine the conversion of KNO<sub>3</sub>. Four signals with m/z values of 30, 32, 44, and 46 were detected, and they stemmed from NO,  $O_2$ ,  $N_2O/CO_2$ , and  $NO_2$ , respectively (Figure 2). The intensity of these signals is sort of different for the three samples, indicating different pathways for KNO3 conversion. However, the signal of NO (m/z = 30) that originated from KNO<sub>3</sub> is predominant in all samples. The signal of NO, in combination with the weight loss, can be utilized to compare the conversion behavior of KNO<sub>3</sub> on different supports.

All samples give a weight loss at temperatures lower than 200 °C, which is assigned to desorption of physically adsorbed water. In addition to this weight loss, K@Y presents another weight loss centered at 700 °C ascribed to the conversion of KNO<sub>3</sub>. In the case of K@SBA-15, the majority of KNO<sub>3</sub> was decomposed at about 600 °C with the minority at 300 °C. The conversion of KNO<sub>3</sub> to basic sites on zeolite Y and mesoporous silica SBA-15 could be depicted respectively through the following equations:  $4\text{KNO}_3 \rightarrow 2\text{K}_2\text{O} + 4\text{NO} + 2\text{O}_2$  and  $6\text{KNO}_3 \rightarrow 3\text{K}_2\text{O} + 4\text{NO} + \text{N}_2\text{O} + 5\text{O}_2$ . For the decomposition of KNO<sub>3</sub>, the gaseous products include O<sub>2</sub>. Actually, there is still a certain amount of residual carbon-containing compounds



**Figure 2.** Conversion of KNO<sub>3</sub> on different porous supports: (a) K@ Y, (b) K@SBA-15, and (c) K@MIL-53(Cr) monitored by TG-MS. C represents the conversion of KNO<sub>3</sub>, and *D* represents the degradation of support. The MS signals 30, 32, 44, and 46 can be ascribed to NO,  $O_2$ ,  $N_2O/CO_2$ , and NO<sub>2</sub>, respectively.

in SBA-15 after the removal of template.<sup>30,31</sup> Such carboncontaining compounds can react with O2, leading to the formation of  $CO_2$ . As a result, the signal of  $O_2$  is not observed in the TG-MS data. Noteworthily, K@MIL-53(Cr) shows two weight losses at 300 and 500 °C, which correspond to two different signals with m/z values of 30 and 44 in MS curves, respectively. NO is the unique origin of the signal of m/z = 30and is thus associated with the conversion of KNO<sub>3</sub>. However, the signal of m/z = 44 at 500 °C comes from CO<sub>2</sub> due to the degradation of MOFs.<sup>32</sup> Thus, the predominant products from the decomposition of KNO3 include NO, N2O, and O2 as shown in the following equation: 24KNO\_3 + 8Cr^{3+}  $\rightarrow$  12K\_2O +  $12NO + 6N_2O + 8Cr^{6+} + 21O_2$ . This reflects that KNO<sub>3</sub> is converted at 300 °C on MIL-53(Cr), and the structure of support is intact at such a low temperature. Nevertheless, the conversion of KNO3 on zeolite Y and mesoporous silica SBA-15 takes place mainly at 700 and 600 °C, which is much higher than that on MIL-53(Cr). On the basis of TG-MS results, the activation temperature of KNO<sub>3</sub> supported on different porous materials can be identified.

It is surprising that the conversion of KNO<sub>3</sub> on MIL-53(Cr) takes place at a temperature as low as 300 °C, which has never been reported on any supports to our knowledge. Several classic porous supports, SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> in monoclinic and tetragonal crystallite (*m*-ZrO<sub>2</sub> and *t*-ZrO<sub>2</sub>), were employed for comparison (Table S1 and Figures S1–S4). KNO<sub>3</sub> loaded on SiO<sub>2</sub> and *m*-ZrO<sub>2</sub> is decomposed at high temperatures of

700 and 730 °C, respectively. However, the decomposition temperature decreases to 400 and 470 °C on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and *t*-ZrO<sub>2</sub>, respectively. There are octahedral vacancies on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and *t*-ZrO<sub>2</sub>, and K<sup>+</sup> of KNO<sub>3</sub> is able to insert in the vacancies in the preparation process.<sup>33</sup> This enhances the guest—host interaction and promotes the decomposition of KNO<sub>3</sub> at relatively low temperatures. Hence, KNO<sub>3</sub> can be decomposed at lower temperatures on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and *t*-ZrO<sub>2</sub> than that on SiO<sub>2</sub> and *m*-ZrO<sub>2</sub>. In any case, the base precursor KNO<sub>3</sub> on MIL-53(Cr) can be converted at an unexpectedly low temperature of 300 °C, which is unachievable on zeolites and mesoporous silicas as well as any other porous supports reported until now.

Fourier transform infrared (IR) spectra of different samples were recorded to further examine the conversion of KNO<sub>3</sub>. The samples K@Y, K@SBA-15, and K@MIL-53(Cr) all display a strong characteristic band at 1383 cm<sup>-1</sup> that originates from the asymmetric stretching vibration of N–O in nitrate.<sup>34</sup> According to TG-MS results, K@Y was activated at 700 °C, and after treatment the characteristic band of KNO<sub>3</sub> disappeared (Figure S5), indicating the decomposition of KNO<sub>3</sub>. Similarly, thermal treatment at 600 °C led to vanishing of the characteristic band of KNO<sub>3</sub> on K@SBA-15 (Figure S6). Because TG-MS results show that KNO<sub>3</sub> is partially decomposed at 300 °C, the IR spectrum of K@SBA-15-300 was measured as well. However, the characteristic band of KNO3 in K@SBA-15-300 is slightly weaker than that in K@SBA-15. This means that only a small amount of KNO3 on SBA-15 is decomposed at 300 °C. In the IR spectrum of MIL-53(Cr), two intense bands at 1537 and 1385 cm<sup>-1</sup> attributed to symmetrical and asymmetric stretching vibrations of carbonyl groups are detected (Figure S7). Interestingly, the characteristic band of KNO3 overlaps the asymmetric stretching vibration of carbonyl groups. Despite the difficulty, it is possible to identify the conversion of KNO<sub>3</sub> by comparing the relative intensity of the band at 1385 cm<sup>-1</sup> with that at 1537 cm<sup>-1</sup>. The relative intensity of the band at 1385 cm<sup>-1</sup> first increases after loading KNO<sub>3</sub> and then decreases after activation, revealing the conversion of KNO3 upon thermal treatment at 300 °C.

Various techniques were employed to characterize the structure of resultant materials. Characteristic peaks of zeolite Y are observed in the wide-angle X-ray diffraction (XRD) patterns of pristine Y and K@Y, while only a broad peak ascribed to amorphous frameworks is visible in K@Y-700 (Figure 3a). This mirrors that the structure of zeolite is retained after the introduction of base precursor KNO<sub>3</sub>, and is completely destroyed after activation at 700 °C aiming to convert the precursor to basic sites. In the case of SBA-15 with mesostructure, no diffraction peaks appear in wide-angle XRD patterns due to the pore size at mesoporous scale (Figure S8). The periodic pore arrangement can be revealed by three diffraction peaks in the low-angle XRD patterns, which are indexed as the (100), (110), and (200) reflections (Figure 3d). Because only a small number of KNO3 are decomposed on SBA-15 at 300 °C, the diffraction peaks are partially weakened for the sample K@SBA-15-300. When the activation temperature is increased to 600 °C, all diffraction lines disappear, which indicates the complete degradation of structure for the sample K@SBA-15-600. Interestingly, the activated sample K@ MIL-53(Cr)-300 exhibits almost the same XRD patterns as that of pristine MIL-53(Cr) and K@MIL-53(Cr) before activation (Figure 3g). This means that the ordered structure of MIL-53(Cr) is well preserved after the formation of basic sites,



**Figure 3.** (a) Wide-angle XRD patterns of the zeolite Y, K@Y, and K@Y-700 samples. (b and c) TEM images of the zeolite Y and K@Y-700. (d) Low-angle XRD patterns of SBA-15, K@SBA-15, K@SBA-15, S00, and K@SBA-15-600 samples. (e and f) TEM images of SBA-15 and K@SBA-15-600. (g) Wide-angle XRD patterns of MIL-53(Cr), K@MIL-53(Cr), and K@MIL-53(Cr)-300 samples. (h and i) TEM images of MIL-53(Cr) and K@MIL-53(Cr)-300.

whereas that of zeolite Y and mesoporous silica SBA-15 is destroyed completely.

N<sub>2</sub> adsorption and electron microscopy give further information on the structure of materials. For the activated samples K@Y-700 and K@SBA-15-600, the adsorption amount of N<sub>2</sub> declines dramatically in contrast to pristine zeolite Y and mesoporous silica SBA-15 (Figures S9 and S10). Moreover, the BET surface area decreases from 745 m<sup>2</sup> g<sup>-1</sup> for Y zeolite to 40  $m^2~g^{-1}$  for K@Y-700 (Table S2). Similarly, the BET surface area of K@SBA-15-600 is 70  $m^2~g^{-1}$ , which is much lower than that of SBA-15 (943 m<sup>2</sup> g<sup>-1</sup>). Unlike zeolite and mesoporous silica, the adsorption amount of N2 only decreases slightly after incorporating basic species to MIL-53(Cr) (Figure S11). A similar tendency is also observed for BET surface areas of the samples based on MIL-53(Cr). In both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of pristine zeolite Y (Figures S12a and 3b), cubic crystals can be identified. However, the cubic crystals disappear, and amorphous phases become visible in the images of K@Y-700 (Figures S12b and 3c). SBA-15 presents a rod-like morphology in the SEM image, which is partially degraded on K@SBA-15-300 and completely destroyed on K@SBA-15-600 (Figure S13). Similarly, ordered mesopores can be seen from the TEM image of SBA-15, while the damage of mesostructure takes place in K@SBA-15-300 and K@SBA-15-600 (Figures 3e,f and S14). On the contrary, the original crystalline morphology of MIL-53(Cr) is well retained after incorporating basic K species from both SEM and TEM images (Figures 3h,i and S15). EDX and elemental mapping analysis indicate the existence of K that uniformly distributed in the samples K@Y, K@SBA-15, and K@MIL-53(Cr), despite the presence or absence of ordered structure after activation (Figures S16–19).

On the basis of the results from different characterization techniques, it is safe to say that at the temperature for KNO<sub>3</sub>

conversion, the structure of zeolite Y and mesoporous silica SBA-15 is seriously destroyed. However, the structure of MIL-53(Cr) remains intact when supported KNO<sub>3</sub> is entirely converted to basic sites.

The basic properties of obtained materials were characterized. To measure the base strength, Hammett titration was employed. The base strength  $(H_{-})$  of K@Y-700 and K@SBA-15-300 is less than 9.3, and that of K@SBA-15-600 is 15.0. In the case of MIL-53(Cr)-300, it is difficult to observe the color change of indicator due to the dark green color of the sample. The amount of basic sites was measured as well. For the sample K@Y-700, the amount of basic sites is only 0.04 mmol  $g^{-1}$  due to the reaction of basic species with the zeolite support (Figure S21). When SBA-15 was used as the support, the amount of basic sites for K@SBA-15-300 is just 0.06 mmol  $g^{-1}$  due to the incomplete conversion of KNO<sub>3</sub>, while that for K@SBA-15-600 is 0.39 mmol  $g^{-1}$  because of the reaction between basic species and silica support. Remarkably, in the case of K@MIL-53(Cr)-300, the amount of basic sites reaches 0.92 mmol  $g^{-1}$ , which is close to the theoretical value (0.99 mmol  $g^{-1}$ ). Acetic acid was also used to measure basicity of samples in consideration that HCl is a strong acid. The amount of basic sites for the samples K@Y-700, K@SBA-15-300, K@SBA-15-600, and K@MIL-53(Cr)-300 is 0.05, 0.07, 0.38, and 0.95 mmol g<sup>-1</sup>, respectively, which is in good agreement with the values obtained by using HCl. The experimental error for basicity using both HCl and acetic acid varies between 0.01 and 0.02 mmol  $g^{-1}$ . On the basis of these results, it is obvious that the precursor KNO3 can be fully converted to basic sites on MIL-53(Cr).

The new solid base K@MIL-53(Cr)-300 was first applied to catalyze Knoevenagel condensation. Knoevenagel condensation is a well-known reaction between an aromatic aldehyde and a compound containing active methylene group. This reaction is useful for the formation of a C–C bond and usually catalyzed by relatively weak or medium strong base.<sup>36,37</sup> In this study, Knoevenagel condensation of benzaldehyde with different active methylene compounds was examined (Table 1). Under the same conditions, the reaction of benzaldehyde with

Table 1. Knoevenagel Condensation of Benzaldehyde with Different Active Methylene Compounds Catalyzed by K@ MIL-53(Cr)-300<sup>*a*</sup>

0 + [ E	.EWG WG → ᢕ	EWG EWG	
pKa	Knoevenagel prod-	Molecular	Yield
	uct	dimension	(%)
		11.492	94.8
11.1	ĊN ĊN	Å×7.739 Å	
13.1		13.931	81.6
13.1		Å×7.891 Å	01.0
14.3		12.585	20.1
17.5		Å×9.648 Å	20.1
16.4		12.733	0.0
10.4	Ĩ,	Å×9.261 Å	0.8
	• + E pKa 11.1 13.1 14.3 16.4	$ \begin{array}{c} \mathbf{O} + \underbrace{\mathbf{EWG}}_{\mathbf{WG}} \longrightarrow \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	CN       EWG       EWG         pK <sub>a</sub> Knoevenagel prod-       Molecular         uct       dimension         i1.1       Á×7.739 Å         13.1       Molecular         NC       13.931         i4.3       Molecular         i6.4       Molecular

<sup>&</sup>quot;Reaction conditions: 1 mmol of benzaldehyde, 1 mmol of active methylene compounds, 50 mg of catalyst, 2.5 mL of ethanol, 70 °C, 1 h. EWG = electron-withdrawing group such as CN, COOR, and COR.

malononitrile gives a high yield of 94.8%. In the case of ethyl cyanoacetate, the yield decreases to 81.6%. It is worth noting that the yield is only 20.1% for the reaction of benzaldehyde with ethyl acetoacetate, and the yield is less than 1.0% for the reaction involving diethyl malonate. Two factors are considered to account for the significant difference in reactivity. The first factor is the acidity of active methylene compound. The acidity decreases in the order of malononitrile  $(pK_a = 11.1) >$  ethyl cyanoacetate ( $pK_a = 13.1$ ) > ethyl acetoacetate ( $pK_a = 14.3$ ) > diethyl malonate ( $pK_a = 16.4$ ), which is in good agreement with the reactivity. Because the active methylene compound functions as a donor molecule in base-catalyzed Knoevenagel condensation, the reactivity declines with the increase of  $pK_a$ values of the donor molecule. The other factor is steric hindrance. The yield of target products generally decreases with the increase of reactant/product molecular dimension. For the reactions of benzaldehyde with ethyl acetoacetate and diethyl malonate, the yields are obviously lower than those with malononitrile and ethyl cyanoacetate. Taking into account that the pore size of MIL-53(Cr) is 7.85 Å,<sup>28</sup> the shape selectivity will become obvious when reactant/product molecules possess comparable sizes. According to the molecular sizes shown in Table 1 and Figure S22, the Knoevenagel products of malononitrile (11.492 Å  $\times$  7.739 Å) and ethyl cyanoacetate  $(13.931 \text{ Å} \times 7.891 \text{ Å})$  are able to transport from the pores of catalyst considering molecular vibration. Nevertheless, transportation of Knoevenagel products of ethyl acetoacetate (12.585 Å  $\times$  9.648 Å) and diethyl malonate (12.733 Å  $\times$ 9.261 Å) is apparently difficult. The results reflect that the yield of diethyl 2-benzylidenemalonate is rationally reduced on account of the limited space in the K@MIL-53(Cr).

Besides benzaldehyde, the aromatic aldehyde with larger molecule size, 1-naphthaldehyde, was applied to react with four methylene substrates (Figure 4). The yield is 30.3% for the reaction of 1-naphthaldehyde with ethyl cyanoacetate (30.3%), and is much lower than that of benzaldehyde (81.6%). Similarly, the yield for the reaction of 1-naphthaldehyde with malononitrile, ethyl acetoacetate, and diethyl malonate is 77.6%, 2.0%, and 0.2%, respectively, which is lower than that of benzaldehyde (94.8%, 20.1%, and 0.8%, respectively). Moreover, the reaction between ethyl cyanoacetate and two different steric substrates benzaldehyde and 1-naphthaldehyde was carried out in one pot. The reaction with benzaldehyde leads to a high yield of 61.8%, which is obviously higher than that with 1-naphthaldehyde (14.6%). These results can thus demonstrate the shape selectivity of the present solid base K@ MIL-53(Cr)-300.

To prove the heterogeneous nature of K@MIL-53(Cr)-300, hot-filtration during catalysis to remove the catalyst was conducted. In the heterogeneous case, it should be no catalytic activity after the removal of catalysts. The catalyst K@MIL-53(Cr)-300 was removed after 10 min for the reaction between benzaldehyde and ethyl cyanoacetate. The yield was 34.9% in 10 min and kept at this level in 60 min. However, the yield reached 81.6% for the reaction without filtration of catalyst. These results can thus demonstrate the heterogeneous nature during catalysis. Meanwhile, recycle experiments were conducted to test the catalytic efficiency. The recovered catalyst K@MIL-53(Cr)-300 shows similar activity as compared to the fresh one in the reaction between benzaldehyde and ethyl cyanoacetate. The yield remains at a high level of 79.1% at the fifth run, which is comparable to that of the first run (81.6%). This indicates no degradation of K@MIL-53(Cr)-300 during



**Figure 4.** (a) Knoevenagel condensation of benzaldehyde or 1naphthaldehyde with different active methylene compounds over K@ MIL-53(Cr)-300. (b) Filtration test of the catalyst K@MIL-53(Cr)-300 for the reaction between benzaldehyde and ethyl cyanoacetate. (c) Recycling experiments of K@MIL-53(Cr)-300 for the reaction between benzaldehyde and ethyl cyanoacetate.

catalysis. The K/Cr ratio of K@MIL-53(Cr)-300 before and after reaction was tested as well. On the basis of the SEM-EDX spectra (Figure S20), the K/Cr ratio of K@MIL-53(Cr)-300 is 0.23 after reaction, which is comparable to the value before reaction (0.21). This mirrors that there is no leaching of K in the reaction processes.

The obtained solid base K@MIL-53(Cr)-300 was further used for the synthesis of dimethyl carbonate (DMC) via the transesterification of ethylene carbonate and methanol, which is catalyzed by materials with strong basicity.<sup>19</sup> DMC is a versatile green chemical and has been utilized as a carbonylating and methylating agent as well as a promising fuel additive.<sup>38,39</sup> Traditionally, DMC is synthesized in the presence of homogeneous catalysts, whereas increasing attention has been paid to the development of heterogeneous catalysts. As listed in Table 2, the yield of DMC increases with the prolonged reaction time over all catalysts. Under the catalysis of K@MIL-53(Cr)-300, the yield of DMC reaches 26.9% after the reaction for 4 h. It is interesting to compare the catalytic activity of K@ MIL-53(Cr)-300 with some well-known solid bases. Under the same reaction conditions, the yield of DMC is only 7.6% over the benchmark solid base MgO. For the strongly basic zeolite KL, the yield of DMC is 4.0%. The zeolite CsX with even stronger basicity than KL was also employed. CsX gives a DMC yield of 6.1%, which is higher than that over KL but much lower

Table 2.	Transesteri	fication <b>R</b>	eaction	of M	lethan	ol with
Ethylene	Carbonate	Catalyzed	l by Va	rious	Solid	Bases <sup>a</sup>

0 <sup>0</sup> , + H₃C-OH → <sup>0</sup> , 0							
Catalyst	DMC yield (%)						
,	0.5 h	1 h	2 h	4 h			
K@MIL-53(Cr)-300	6.2	8.8	15.8	26.9			
MgO	1.3	2.9	4.7	7.6			
KL	1.0	2.5	3.0	4.0			
CsX	3.0	4.5	5.2	6.1			
<sup><i>a</i></sup> Reaction conditions: carbonate, 50 mg of cat	0.5 mol of alyst, 20 mL	methanol of metha	, 0.1 mol nol, 65 °C	of ethylene			

than that over K@MIL-53(Cr)-300. On the basis of these results, it is safe to say that the present material K@MIL-53(Cr)-300 owns strong basicity in addition to shape selectivity in catalysis.

By use of the GHR strategy, KNO<sub>3</sub> can be converted to basic sites at a low temperature of 300 °C on MIL-53(Cr). This strategy is obviously different from thermal decomposition of KNO<sub>3</sub> on conventional supports including zeolite and mesoporous silica, which is usually conducted at quite high temperatures (600-700 °C). The low-temperature conversion of KNO<sub>3</sub> on MIL-53(Cr) can be ascribed to the redox interaction between KNO3 and Cr metal centers at a low valence state  $(Cr^{3+})$ , which is absent in conventional supports. To verify the mechanism, the K-containing MIL-53(Cr) was analyzed by X-ray photoelectron spectroscopy (XPS) and compared to pristine MIL-53(Cr). The Cr 2p region was studied in detail. For pristine MIL-53(Cr), the Cr  $2p_{3/2}$  and Cr  $2p_{1/2}$  spectra at the binding energies (BE) of 577.6 and 587.1 eV are observed (Figure 5a), which are attributed to  $Cr^{3+}$ species.<sup>40</sup> In the case of K@MIL-53(Cr)-300, two shoulder peaks at BE values of 579.3 and 588.7 eV ascribed to Cr<sup>6+</sup> appear (Figure 5b), indicating that Cr<sup>3+</sup> in MIL-53(Cr) is partially oxidized to Cr<sup>6+</sup> during the reduction of KNO<sub>3</sub> to basic species. To confirm the generation of Cr<sup>6+</sup>, diffuse reflectance UV-vis spectra of the support MIL-53(Cr) and solid base K@ MIL-53(Cr)-300 were recorded. MIL-53(Cr) presents three pronounced absorption bands at about 295, 455, and 596 nm, which are assigned to the d-d transition of Cr<sup>3+</sup> species (Figure 5c). For the sample K@MIL-53(Cr)-300, a new peak at 263 nm becomes visible along with the blue shift of the peak at 295 nm caused by ligand-to-metal charge transfer, implying the formation of Cr<sup>6+,41</sup> Taking into consideration that the content of KNO3 is 10 wt % in the sample, 8.4% of Cr3+ should be oxidized to  $Cr^{6+}$  provided that all KNO<sub>3</sub> is reduced to K<sub>2</sub>O. The quantitative analysis of XPS shows that 9.2% of Cr<sup>6+</sup> is yielded, which is in line with the theoretical value. The organic ligands in MIL-53(Cr) with an empty antibonding orbital (unsaturated hydrocarbons and double bonds) can accept electrons from metal ions. In the redox process, electron transfer from the d orbital of metal ions to the  $\pi^*$  orbital of ligands takes place, leading to the decline in the peaks of 455 and 596 nm.<sup>42,43</sup> Hence, the generation of basic sites on MIL-53(Cr) is caused by the guest-host redox interaction, in which KNO<sub>3</sub> is reduced to  $K_2O$  and  $Cr^{3+}$  is oxidized to  $Cr^{6+}$ . This makes the formation of basic sites on MIL-53(Cr) at a quite



Figure 5. XPS of (a) MIL-53(Cr) and (b) K@MIL-53(Cr)-300 samples. (c) UV–vis spectra of MIL-53(Cr) and K@MIL-53(Cr)-300 samples.

low temperature, and the ordered nanoporous structure is well maintained.

#### CONCLUSION

We have demonstrated direct fabrication of strong basic sites on MOFs by using the GHR strategy between base precursors and metal centers at a low valence state, for the first time. This breaks the tradition of thermo-induced decomposition of base precursors. As a result, base precursor KNO<sub>3</sub> can be converted to strong basic species on MIL-53(Cr) at 300 °C, which is much lower than the thermal decomposition of KNO<sub>3</sub> on representative nanoporous supports zeolite Y (~700 °C) and mesoporous silica SBA-15 (~600 °C) as well as any porous supports reported to date. Strong bases with ordered nanoporous structure are successfully fabricated from MOFs, while weak basicity and collapsed structure are observed on zeolites and mesoporous silicas due to the reactions between strong basic species and supports at high temperatures. The resultant new solid base exhibits high activity and shape selectivity in Knoevenagel condensation and transesterification reactions, and the activity is higher than various classic solid base catalysts. The present strategy may open an avenue for the fabrication of various functional materials by use of guest-host interaction.

ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b05102.

Experimental details and additional data (PDF)

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21722606, 21576137, and 21676138) and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions.

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