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1 Introduction

For the demands of sustainable development and green chemistry, the use of heterogeneous catalysts instead of traditional homogeneous ones has received increasing attention. Among various heterogeneous catalysts, mesoporous solid superbases are highly attractive for applications in environmentally friendly and economical catalytic processes. They can catalyze diverse reactions under mild conditions and reduce waste production.¹⁻⁴ Their large pore sizes favor mass transfer and avoid deactivation derived from coke formation that usually happens in microporous catalysts.5-7 To date, many attempts have been made to generate strong basicity on mesoporous hosts. Since the discovery of mesoporous silica M41S by Kresge et al.,⁸ a series of mesoporous materials have been synthesized through the surfactant templating approach. Among various candidates with a mesostructure, mesoporous silicas are the best choice for a support, owing to their high stability, low and tuneable pore symmetry.9-11 Moreover, the cost.

Constructing mesoporous solid superbases by a dualcoating strategy[†]

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Great attention has been paid to the development of mesoporous solid superbases due to their versatile catalytic activity under mild conditions. In this paper, a dualcoating strategy was designed to generate superbasicity on mesoporous silica SBA-15 by precoating ZrO₂ prior to the loading of base precursor (KNO₃). The ZrO₂ interlayer performs two functions by enhancing the guest-host interactions to promote the decomposition of KNO₃ at low temperatures, and by improving the alkali-resistance of the siliceous host, which simultaneously overcomes two weaknesses of mesoporous silicas. As a result, new dualcoating composites possessing both an ordered mesostructure and superbasicity were successfully fabricated. However, direct modification of SBA-15 with KNO3 results in a sample with only weak basicity and a collapsed mesostructure. Interestingly, both the amount and dispersion degree of ZrO_2 play an important role in the generation of strong basicity. An intact layer can be formed on SBA-15 provided that the content of ZrO₂ is higher than 30 wt% and the ammonia/water-induced hydrolysis (AIH) method is employed. The mesostructure cannot be preserved if the content of ZrO₂ is lower than 30 wt% or if conventional coating methods (i.e. impregnation and grinding) are used. The obtained materials containing ZrO₂ are active in heterogeneous synthesis of dimethyl carbonate (DMC) and the vield of DMC can reach 28.4%, which is obviously higher than that over the material without a ZrO_2 coating (9.8%). The present strategy may open a new way for the design and synthesis of functional materials with strong basicity.

> functionalization of mesoporous silicas is easy to realize by either element incorporation into frameworks or modification on the surface.¹²⁻¹⁵ Therefore, the generation of strong basicity on mesoporous silicas has been attracting extensive attention ever since their discovery.

> Grafting organic basic groups onto silanols offers an interesting method to form basic sites on mesoporous silicas.16-18 However, the basicity that is derived from organic groups (such as amine groups) is generally weak. In addition, these organicinorganic hybrid materials can only be used at low temperatures, owing to the degradation of organic building blocks at elevated temperatures. By treating mesoporous silicas or Alsubstituted silicas with gaseous ammonia, the oxygen in the frameworks can be partially displaced by nitrogen and generate oxynitride frameworks, which produces a new kind of solid base with a mesostructure.19-21 Recently, a methylation method was also used to enhance the strength of nitrogen-doped mesoporous silica, taking account of the donation of an electron from the methyl group to the nitrogen atom.²² Nevertheless, temperatures higher than 900 °C have to be employed in the process of nitrogen doping, and the strength of the basic sites is still weak. To improve the base strength, alkaline metal oxides with strong basicity (such as potassium and cesium oxides) have been employed to modify mesoporous silica. These materials were generally prepared by the introduction of precursors (such

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as KNO3 and CH3COOCs), followed by calcination at high temperatures to decompose the precursors.^{23,24} Unfortunately, the obtained materials only exhibit weak basicity and the mesostructure of the supports is severely deteriorated. This is because strongly basic species can react with silica, especially at high temperatures. The modification of mesoporous silica by various alkaline and alkaline earth metal oxides was investigated.²⁴ The ordered mesoporous structure is always destroyed completely by the introduction of alkaline metal oxides. However, the introduction of CaO into mesoporous silica SBA-15 produces a composite with superbasicity and an ordered mesostructure. Further investigations show that solid strong bases can also be obtained from other alkaline earth metal oxide modification. It is known that alkaline metal oxides possess quite different properties as compared with alkaline earth metal oxides. However, the generation of strong basicity on mesoporous silica through alkaline metal oxide modification remains a challenge up to now.

Through an in-depth analysis of host and guest properties, we consider that there are two factors which hinder the generation of strong basicity on mesoporous silica. The first factor is the weak guest-host interactions between the base precursor (*e.g.* KNO₃) and silica, leading to difficulty in the conversion of the base precursor to basic species. According to our previous investigation, only a small amount of KNO₃ can be decomposed on silica, even if the sample was activated at a high temperature of 600 °C.²⁵ The second factor is the poor alkali-resistance of mesoporous silica, which results in the collapse of the mesoporous structure after the formation of strongly basic species.²⁴ Aiming to generate strong basicity on mesoporous silica, both of these two weaknesses must be overcome.

In the present study, we developed a dualcoating strategy to generate strong basicity on mesoporous silica. Mesoporous silica SBA-15 was precoated with a layer of ZrO2 prior to the introduction of the base precursor KNO₃. The ZrO₂ interlayer plays a double role by enhancing the interaction of the guest with the host and improving the alkali-resistance of the siliceous host. Our results show that the decomposition temperature of the base precursor was lowered apparently, and superbasic sites were successfully formed on mesoporous silica SBA-15. More importantly, we demonstrated that the dispersion degree of ZrO₂ had an important effect on the mesostructure and basicity of the resulting materials. By use of the ammonia/ water-induced hydrolysis (AIH) approach, a well-dispersed ZrO₂ interlayer can be created, and the dispersion degree is obviously higher than that derived from conventional methods (i.e. impregnation and grinding). The structural and basic properties of the obtained materials were characterized by various methods. The basic catalytic performance of these new dualcoating materials was also evaluated.

2 Experimental section

2.1 Materials synthesis

Synthesis of SBA-15. Mesoporous silica SBA-15 was synthesized according to the reported method.^{26,27} Three grams of triblock copolymer P123 (EO₂₀PO₇₀EO₂₀) was dissolved in 22.5 g

of distilled water and 90 g of aqueous HCl solution (2 M) with stirring at 40 °C. After the formation of a homogeneous solution, 6.38 g of tetraethylorthosilicate (TEOS) was added and stirred at this temperature for 24 h. Finally, the resulting gel was transferred to a Teflon-lined autoclave and kept at 120 °C for 24 h under static conditions. The as-prepared sample was recovered by filtration, washed with water, and air-dried at room temperature. The removal of template was carried out at 550 °C in an air flow for 5 h with a heating ramp of 2 °C min⁻¹.

Coating ZrO₂ on SBA-15. ZrO₂ was introduced to SBA-15 by three different methods, namely, AIH, impregnation, and grinding, in which ZrO(NO₃)₂ was used as the precursor for ZrO₂. The typical process for ZrO₂ coating by the AIH method was as follows.28 The required amount of precursor was dissolved in deionized water, followed by the addition of SBA-15 under stirring for 24 h. The mixture was evaporated at 80 °C followed by drying at 100 °C for 4 h. The precursor-loaded SBA-15 was put in an open glass vial and kept inside an autoclave containing NH₃-H₂O solution without direct contact between the solid and solution. The tightly closed autoclave was then heated to 60 °C for 0.5 h. Finally, the solid was dried at room temperature for 6 h and then at 100 °C for 12 h, and calcined at 500 °C for 5 h in air to get the sample denoted as ZS(A)-n, where n is the mass percentage of ZrO_2 . For impregnation, the required amount of precursor was dissolved in deionized water, followed by the addition of SBA-15 under stirring for 24 h. The mixture was evaporated at 80 °C and then heated at 100 °C for 4 h. The solid was calcined at 500 °C in an air flow for 5 h. The resultant material was denoted as ZS(I)-*n*, where *n* is the mass percentage of ZrO₂. In the case of solvent-free modification, the required amount of precursor was manually ground together with 1 g of SBA-15 sample in a mortar at room temperature for about 0.5 h. The resulting homogeneous powder was calcined at 500 °C in an air flow for 5 h and denoted as ZS(G)-*n*, where *n* is the mass percentage of ZrO₂.

Introduction of potassium species. The base precursor, KNO_3 , was introduced by wet impregnation. An identical amount of KNO_3 (25 wt%) was used for all samples. Typically, 0.25 g of KNO_3 was dissolved in 15 mL of deionized water, followed by the addition of 0.75 g of host. After stirring at room temperature for 24 h, the mixture was evaporated at 80 °C and subsequently dried at 100 °C for 4 h. The obtained solid was calcined at 550 °C in a N₂ flow for 200 min to decompose KNO_3 . The final samples were respectively represented as KS, KZS(A)-*n*, KZS(I)-*n*, and KZS(G)-*n* for potassium species supported on SBA-15, ZS(A)-*n*, ZS(I)-*n*, and ZS(G)-*n*, where *n* is the mass percentage of ZrO₂.

2.2 Materials characterization

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker D8 Advance diffractometer with Cu K α at 40 kV and 40 mA. The N₂ adsorption–desorption isotherms were measured using a Belsorp II system at -196 °C. The samples were degassed at 300 °C for 4 h prior to analysis. The pore diameter was calculated from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images of the materials were captured in a JEM-2010 UHR electron microscope operated at 200 kV. Fourier transform infrared (IR) spectra of the samples diluted with KBr were performed on a Nicolet Nexus 470 spectrometer. UV-visible diffuse reflectance (UV-vis) spectra of the samples were recorded using a UV-2401PC spectrophotometer, and $BaSO_4$ was used as an internal standard.

The base strength (H_{-}) of the materials was detected by using a series of Hammett indicators.²⁹ The amount of basic sites was measured by standard acid–base titration.³⁰ Temperature-programmed desorption of CO₂ (CO₂-TPD) was performed using a BELSORP BEL-CAT-A instrument. The samples were pretreated at 550 °C for 200 min under N₂ flow prior to the adsorption of CO₂ at room temperature. After the physically adsorbed CO₂ was purged by a He flow (99.999%) at room temperature, the sample was heated to 800 °C, and the CO₂ liberated was detected by mass spectrometry.

2.3 Catalytic tests

Dimethyl carbonate (DMC) was synthesized from the transesterification of ethylene carbonate and methanol. In a typical process, methanol (0.5 mol), ethylene carbonate (0.1 mol), and catalyst (0.5 wt% of methanol) were added to a 50 mL threenecked glass flask with a water-cooled condenser. All catalysts were pretreated at 550 °C in a N₂ flow (99.999%, 30 mL min⁻¹) for 200 min prior to reaction. The reaction was conducted at 65 °C with stirring for a given period of time. After the reaction was finished, the products and unreacted substrates were recovered from the flask and subjected to centrifuging. The obtained upper liquid was then analyzed by a Varian 3800 gas chromatograph equipped with a flame ionization detector.

3 Results

3.1 Coating ZrO₂ on mesoporous silica

Fig. 1A shows the low-angle XRD patterns of parent SBA-15 and ZrO_2 -coated SBA-15 samples. The (100), (110), and (200) reflections can be well discerned after the introduction of ZrO_2 , indicating that the ordered mesostructure is well preserved

despite the modification methods (i.e. AIH, impregnation, and grinding). In general, the intensity of the (100) reflection should decline with the introduction of metal oxides because of the decreasing scatter contrast between the pore walls and pore space. However, the (100) reflection of the samples containing 10-30 wt% of ZrO₂ derived from the AIH method is obviously more intense than that of parent SBA-15. This can be attributed to the formation of a smooth ZrO₂ layer on the internal walls of SBA-15, similar to what happened in CuO- or Y₂O₃-coated SBA-15.³¹⁻³³ Such a smooth layer contributes to the spatial order, giving rise to the diffraction line itself. Interestingly, the intensity of the (100) reflection decreases in the order ZS(A)-30 > ZS(I)-30 > ZS(G)-30, despite the same Zr content. That means that ZrO₂ coated by the AIH method has the highest dispersion degree, while aggregated ZrO₂ may be formed in the sample from grinding, as can be proven by the wide-angle XRD results. As shown in Fig. 1B, only a broad peak at 2θ of 23° , originating from amorphous silica, is detected for parent SBA-15. In the case of ZS(A) and ZS(I), no new diffraction peak emerges. However, the diffraction peaks ascribed to tetragonal ZrO₂ (JCPDS no. 50-1089) become visible for ZS(G),²⁹ which reflects the dispersion degree of ZrO2 in different samples and confirms the low-angle XRD patterns.

Fig. S1[†] presents the N_2 adsorption–desorption results for different samples. The isotherms of all Zr-containing samples are of type IV with an H1 hysteresis loop, similar to that of parent SBA-15. This reflects that the mesoporous structure is well preserved after the introduction of ZrO₂. It is worth noting that the samples ZS(I)-30 and ZS(G)-30 give a tail in the isotherms. The hysteresis remains open up to a relative pressure of 0.50 for ZS(I)-30 and 0.44 for ZS(G)-30, which is apparently delayed in contrast to ZS(A)-30, which closes at a relative pressure of 0.64. This indicates that the introduction of ZrO₂ by the AIH method can form a smoother layer, resulting in lessblocked mesopores.³⁴

UV-vis spectroscopy is known to be a very sensitive probe for the characterization of metal oxide dispersion and metal ion coordination environment. Valuable information can be obtained from the position of absorption bands. As displayed in Fig. 2, the sample ZS(A)-30 exhibits an absorption band at 205 nm, which corresponds to ligand-to-metal charge transfer



Fig. 1 (A) Low-angle and (B) wide-angle XRD patterns of (a) SBA-15, (b) ZS(A)-5, (c) ZS(A)-10, (d) ZS(A)-20, (e) ZS(A)-30, (f) ZS(A)-40, (e1) ZS(I)-30, and (e2) ZS(G)-30 samples.



Fig. 2 UV-vis spectra of (a) reference $ZrO_2,$ (b) ZS(I)-30, (c) ZS(A)-30, and (d) ZS(G)-30 samples.

from an O^{2-} to a highly dispersed Zr^{4+} ion.²⁸ In the case of ZS(I)-30, the band appears at 210 nm. This red-shift of absorption mirrors a decrease in dispersion of Zr species and an increase in the coordination number, probably owing to the formation of some Zr-O-Zr bonds. On the contrary, reference ZrO₂ shows an intense and broad band at 230 nm due to full connectivity of Zr-O-Zr linkages,³⁵ revealing the aggregation of Zr species in bulk oxide. A broad band at 210–230 nm can be observed in the spectrum of ZS(G)-30, indicating that at least part of the ZrO₂ is aggregated in the sample. On the basis of the aforementioned results, it is concluded that the dispersion degree of ZrO₂ in the samples derived from different methods decreases in the order ZS(A) > ZS(I) > ZS(G).

The dispersion of ZrO₂ can also be related to the amount of residual silanol groups (Si-OH) in the samples after ZrO₂ modification.^{31,32} The bending vibrations of Si-OH give rise to the band at 960 cm⁻¹, which can be easily identified in parent SBA-15 (Fig. S2[†]). The introduction of ZrO₂ by the AIH method leads to an obvious decrease of the band at 960 cm^{-1} . Such a band was almost invisible when the ZrO₂ loading exceeds 20 wt %. This is due to the interaction between ZrO₂ and SBA-15, leading to the consumption of silanol groups and subsequently the dispersion of ZrO₂ on the surface.^{32,36} It is noticeable that the amount of silanol groups is different for ZS(A)-30, ZS(I)-30, and ZS(G)-30 in spite of the same Zr content. The band at 960 cm⁻¹ is obviously more intense in the IR spectrum of ZS(G)-30, which indicates that fewer silanol groups were consumed in the process of grinding, leading to the aggregation of ZrO₂. The IR results thus provide further evidence of the dispersion degree of ZrO₂-coated SBA-15 prepared by the three different methods (i.e. AIH, impregnation, and grinding).

3.2 Structural characterization of mesoporous solid base

To obtain mesoporous solid bases, KNO_3 was introduced to SBA-15 precoated with ZrO_2 . Strongly basic species K_2O are supposed to be generated from the decomposition of KNO_3 during activation. Structural characterization of the resultant materials was performed by various techniques. Fig. 3 illustrates the low-angle XRD patterns of the potassium-

functionalized samples. In the absence of ZrO_2 , the mesoporous structure of pure SBA-15 is destructed by strongly basic K₂O formed in the process of activation. Similarly, coating 5–20 wt% of ZrO_2 by the AIH method fails to protect the siliceous host as well, and the mesostructure of SBA-15 seldom remains. When the amount of ZrO_2 reaches 30 wt%, the main peak for a hexagonal lattice emerges in the low-angle XRD pattern. Apparently, the existence of a ZrO_2 interlayer on SBA-15 avoids the contact of strongly basic potassium species with the siliceous frameworks, preventing the mesostructure from corroding. For the three samples with an identical Zr content, the mesostructure decreases in the order KZS(A)-30 > KZS(I)-30 > KZS(G)-30. These results demonstrate that the effect of ZrO₂ on the protection of the host structure is not only related to the amount, but also to the dispersion degree.

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Fig. 4 presents the N_2 adsorption-desorption data of the samples after potassium loading. For the samples coated with 0–20 wt% of ZrO_2 , the N_2 uptake in the mesoporous region is negligible, indicative of the damage to the mesostructure. It is worth noting that an obvious hysteresis loop is observed in the isotherm of KZS(A)-30, which reflects the preservation of the mesoporous structure after precoating 30 wt% of ZrO_2 through the AIH method. In the case of KZS(I)-30, the shape of the isotherm changes and the hysteresis extends to high pressures, suggesting partial destruction of the ordered mesoporous networks. According to the isotherm of KZS(G)-30, it is clear that its mesostructure was severely destroyed, in spite of it having the same Zr content as KZS(A)-30 and KZS(I)-30.

TEM is an important technique to characterize mesostructure. The images of typical samples after potassium loading were taken and shown in Fig. 5. The sample KZS(A)-30 exhibits a highly ordered mesostructure, implying that the structure of parent SBA-15 is well maintained. In comparison with KZS(A)-30, the periodic ordering of KZS(I)-30 is worse and the mesostructure is partially damaged. For the sample KZS(G)-30, the pore system of SBA-15 is completely destroyed, while some large pores are generated due to the corrosion of the siliceous host by strongly basic species. It is worth noting that sporadic mesostructure in a small area can be observed in the sample KS without a ZrO_2 coating. This is due to the fact that the majority



Fig. 3 Low-angle XRD patterns of (a) KS, (b) KZS(A)-5, (c) KZS(A)-10, (d) KZS(A)-20, (e) KZS(A)-30, (f) KZS(A)-40, (e1) KZS(I)-30, and (e2) KZS(G)-30 samples.

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Fig. 4 (A) N_2 adsorption–desorption isotherms and (B) pore size distributions of (a) KS, (b) KZS(A)-5, (c) KZS(A)-10, (d) KZS(A)-20, (e) KZS(A)-30, (f) KZS(A)-40, (e1) KZS(I)-30, and (e2) KZS(G)-30 samples.



Fig. 5 TEM images of (A) KS, (B) KZS(A)-30, (C) KZS(I)-30, and (D) KZS(G)-30. Scale bars represent 50 nm.

of KNO₃ cannot be decomposed during activation under the same conditions, as will be discussed later. On the basis of the above-mentioned results, it is clear that the mesostructure decreases in the order KZS(A)-30 > KZS(I)-30 > KZS(G)-30. This order is in good agreement with the dispersion degree of ZrO₂ in SBA-15, pointing out that a well-dispersed ZrO₂ layer is beneficial for the protection of mesostructure.

3.3 ZrO₂-promoted decomposition of KNO₃

Fig. 6A shows the wide-angle XRD patterns of potassium-containing samples before activation. The characteristic diffraction lines of KNO₃ in the orthorhombic phase (JCPDS no. 74-2055) and/or hexagonal phase (JCPDS no.76-1693) are detected.^{25,37} Activation leads to the conversion of the orthorhombic phase to the hexagonal one in the sample KS (Fig. 6B), while the diffraction lines are still evident. That means that the decomposition of KNO₃ on pure mesoporous silica is quite difficult, even at high temperature of 550 °C. Similar results were also reported previously for KNO₃ supported on bulk silica.²⁵ Coating 5 wt% of ZrO₂ leads to a sharp decrease of crystalline KNO₃. When the content of ZrO₂ is higher than 20 wt%, the diffraction lines of KNO₃ disappear for the samples derived from both AIH and impregnation methods. However, the characteristic peaks for KNO₃ are still visible in the XRD pattern of KZS(G)-30 prepared by grinding, revealing the existence of residual KNO₃. Apparently, the ZrO₂ layer modifies the surface properties of SBA-15 and subsequently promotes the decomposition of supported KNO₃. Moreover, the effect of an interlayer strongly depends on the dispersion degree of ZrO₂.

IR spectra of different samples before and after activation at 550 °C were recorded to examine the decomposition of KNO₃. As shown in Fig. S3,[†] all samples before activation reveal an obvious band at 1383 cm⁻¹ that can be attributed to the asymmetric stretching vibrations of N-O in nitrate.³⁸⁻⁴⁰ Activation only slightly weakens the band at 1383 cm^{-1} in the sample KS, reflecting that a large amount of KNO₃ remains undecomposed in the sample. In the case of the KZS(I)-30 and KZS(G)-30 samples, the intensity of such a band decreased significantly after activation under the same activation conditions, while the amount of residual KNO₃ in KZS(G)-30 is larger than that in KZS(I)-30. It is worth noting that the characteristic band of nitrate disappears in the sample KZS(A)-30, indicating that KNO₃ is completely decomposed by activation. The difference spectra of the samples before and after activation were provided in Fig. S4.[†] The decomposition of KNO₃ on different supports is well reflected by the difference spectra. A large absorbance change at 1383 cm⁻¹ is observed for the sample KZS(A)-30 before and after activation, which is in agreement with the complete decomposition of KNO₃. On the contrary, the difference between the sample KS before and after activation is very small, indicating that the majority of KNO3 does not decompose. Therefore, the decomposition of KNO3 on different supports is in line with the dispersion degree of ZrO₂, namely KZS(A)-30 > KZS(I)-30 > KZS(G)-30.



Fig. 6 Wide-angle XRD patterns of (a) KS, (b) KZS(A)-5, (c) KZS(A)-10, (d) KZS(A)-20, (e) KZS(A)-30, (f) KZS(A)-40, (e1) KZS(I)-30, and (e2) KZS(G)-30 samples (A) before and (B) after activation. ∇ and \blacklozenge denote KNO₃ of orthorhombic and hexagonal phases, respectively.



Fig. 7 (A) TG and (B) DTG curves of (a) KS, (b) KZS(A)-30, (c) KZS(I)-30, and (d) KZS(G)-30 samples before activation. TG and DTG curves are plotted offset for clarity.

Aiming to have deep insight into the decomposition behavior of KNO₃ on ZrO₂-coated SBA-15, the TG technique was utilized. Fig. 7 depicts the TG and DTG curves of KS, KZS(A)-30, KZS(I)-30, and KZS(G)-30 samples before activation. All supported samples give a weight loss centered at around 100 °C ascribed to the desorption of physically adsorbed water. For the unsupported sample, the decomposition of bulk KNO₃ gives a single weight loss centered at around 700 °C (Fig. S5[†]). In the case of KNO₃ supported on SBA-15, the decomposition can be tentatively assigned to two stages, while the DTG peak at about 700 °C is much more intense. This indicates that the loading of KNO3 on SBA-15 has no obvious effect on the decrease of decomposition temperature. However, the coating of ZrO₂ results in an apparent decrease of the decomposition temperature of KNO₃. The decomposition occurs at around 500, 530, and 560 °C for KNO3 supported on ZS(A)-30, ZS(I)-30, and ZS(G)-30, respectively. Obviously, the coating of a ZrO_2 layer promotes the decomposition of KNO₃ at much lower temperatures. Among various supports, KNO3 supported on ZS(A)-30 derived from the AIH method has the lowest decomposition temperature, which is 200 °C lower as compared with KNO3 on pure SBA-15.

3.4 Basicity and catalytic performance of dualcoating materials

After the decomposition of supported KNO₃ to K₂O, strongly basic sites are supposed to be produced. The basic properties of the resultant materials were first characterized by the detection of the base strength and amount of basic sites. Parent SBA-15 exhibits a base strength (H_{-}) of less than 9.3. Coating ZrO_2 on SBA-15 does not affect such a base strength. After functionalization with potassium species, the resulting materials derived from different supports show quite different base strengths. The samples KS, KZS(A)-5, and KZS(A)-10 possess a base strength of 9.3. For the sample KZS(A)-20, a base strength of 15.0 is detected. That means that no strongly basic sites are formed when the content of ZrO₂ is lower than 20 wt%. Interestingly, basic sites with a high strength of 27.0 emerge on samples KZS(A)-30 and KZS(A)-40. According to the definition,^{41,42} a solid material that has basic sites with a strength higher than 26.5 can be regarded as a solid superbase. This is direct evidence of the generation of superbasicity on potassium-functionalized SBA-15 precoated with ZrO₂ by the AIH method. Such a high strength is also detected on the sample KZS(I)-30 prepared by impregnation, while a base strength of 18.4 is measured on the sample KZS(G)-30 derived from grinding. In terms of the results above, it is clear that the amount of ZrO₂ should be large enough to form an intact interlayer between the basic species and silica. In other words, the ZrO₂ layer should cover the surface of silica completely; otherwise, the reaction of strongly basic species with silica may take place, leading to the formation of materials with weak basicity and a collapsed mesostructure. Although the sample KZS(G)-30 contains the same amount of ZrO2 as KZS(A)-30, aggregation takes place for ZrO₂ introduced by grinding. Some silica surface uncovered by ZrO2 is thus exposed, and the reaction of strongly basic species with silica is still unavoidable.

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The amount of basic sites on parent SBA-15 is 0 mmol g^{-1} . Coating ZrO₂ leads to a slight increase in the amount of basic sites due to the amphoteric properties of ZrO₂. For instance, the amount of basic sites for the sample ZS(A)-30 is 0.20 mmol g^{-1} . For the sample KZS(A)-30, the amount of basic sites reaches 2.54 mmol g^{-1} , which is consistent with the theoretical value (2.47 mmol g^{-1}) supposing that all supported KNO₃ is converted to K₂O. However, the amount of basic sites on KZS(I)-30 and KZS(G)-30 is only 2.18 and 0.85 mmol g^{-1} due to the reaction of strongly basic species with silica and/or incomplete decomposition of KNO₃.

The CO₂-TPD technique was employed to further examine the basicity of the potassium-modified samples (Fig. 8). An obvious desorption peak at about 790 °C emerges for the sample KZS(A)-30. The desorption of CO₂ at such a high temperature demonstrates the existence of superbasic sites, which confirms the results for base strength. In addition, a broad desorption peak at 150 °C was observed in the sample KZS(A)-30. Such a peak is also detected on the other two samples containing ZrO₂. The samples KZS(I)-30 and KZS(G)-30 show a desorption peak at high temperatures as well, whereas the desorption temperatures are obviously lower as compared with KZS(A)-30. The sample KS only shows a weak, broad desorption peak centered at about 250 °C, owing to the reaction of strongly basic species with silica.

The obtained solid bases were also applied to catalyze the synthesis of DMC via the transesterification of ethylene carbonate and methanol.43,44 As a versatile green chemical, DMC has been proposed as a methylating agent instead of methyl halides and dimethyl sulfate, which are toxic and corrosive. DMC is also used as a carbonylating agent, polar solvent, and fuel additive. Conventionally, the synthesis of DMC is carried out in the presence of homogeneous basic catalyst, whereas the development of heterogeneous catalysts attracts much attention recently. Fig. 9 shows the catalytic performance of different samples. Under the catalysis of KS, the yield of DMC is only 9.8% at a reaction time of 4 h. However, the yield of DMC reaches 28.4% on KZS(A)-30 under the same reaction conditions. This demonstrates the importance of a ZrO₂ layer coated by the AIH method. About 22.5% and 15.7% of DMC is yielded over KZS(I)-30 and KZS(G)-30, which is lower than that over KZS(A)-30, but



Fig. 8 CO₂-TPD profiles of (a) KZS(A)-30, (b) KZS(I)-30, (c) KZS(G)-30, and (d) KS samples.



Fig. 9 The yield of DMC as a function of reaction time on (a) KZS(A)-30, (b) KZS(I)-30, (c) KZS(G)-30, and (d) KS samples.

higher than that over KS. On the basis of the results above, it is evident that the catalytic performance of different samples is strongly dependent on their mesostructure and basicity.

4 Discussion

Conventionally, a solid strong base can be prepared by introduction of a base precursor to a host and subsequent calcination to decompose the precursor, forming strongly basic sites. The same approach has also been attempted to generate strong basicity on mesoporous silicas. However, two difficulties hinder the application of such a classic approach when mesoporous silicas are employed as hosts. On the one hand, the decomposition of the precursor is quite difficult because of the weak interactions between the precursor and silica. The majority of KNO₃ cannot be decomposed on SBA-15, even at a high temperature of 550 °C, as described above. The increase of temperature to 700 °C can lead to the decomposition of KNO₃, while such a high temperature will accelerate the reaction of strongly basic species with silica and destroy the mesostructure completely. On the other hand, the alkali-resistance of silica is poor, which is different from zirconia and alumina which are well-known hosts for solid strong bases.^{29,42,45} The mesoporous structure can be severely damaged due to the reaction between strongly basic species and silica, even if the amount of basic species is quite small, as shown above. Hence, it is difficult to generate strong basicity on mesoporous silicas by the classic approach, namely direct incorporation of precursor followed by calcination.

To overcome the difficulties in basicity generation on mesoporous silica, a dualcoating strategy was developed in the present study. A layer of ZrO_2 was precoated on mesoporous silica before loading the base precursor KNO_3 (Scheme 1). The ZrO_2 interlayer plays a double role by enhancing the guest-host interactions to promote the decomposition of the precursor and by preventing the siliceous frameworks from corroding by the formed basic species. In comparison with unmodified SBA-15, the decomposition temperature of KNO_3 was obviously lowered on ZrO_2 -coated SBA-15. All of the loaded KNO_3 can be converted to the strongly basic species K_2O after activation for the sample



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Scheme 1 Comparison of potassium species loaded on SBA-15 as well as on ZrO₂-coated SBA-15 prepared through different approaches.

KZS(A)-30. The use of ZrO₂ as a promoter to enhance the guesthost interactions is associated with its electronegativity. According to the reported method,⁴⁶ the electronegativity of the cations in ZrO₂ and SiO₂ can be calculated to be 11.97 and 17.10, respectively. With the reduction of electronegativity, the metaloxygen interactions become weaker and the coordination ability of lattice oxygen increases.⁴⁷ Because the electronegativity of Zr⁴⁺ is obviously smaller than that of Si⁴⁺, the coordination ability of oxygen in ZrO₂ with the precursor should be higher. Therefore, coating mesoporous silica with ZrO₂ enables the surface to provide enhanced guest-host interactions, weakening the bond of K⁺ and NO₃⁻ and promoting the decomposition of KNO₃. As a result, the decomposition of KNO₃ can take place at lower temperatures on SBA-15 by precoating ZrO₂.

In addition to promoting the decomposition of KNO₃, ZrO₂ coating also improves the alkali-resistance of the host. The formation of a ZrO2 interlayer avoids the direct contact of basic sites with the siliceous frameworks, thus preventing the host from being corroded by strongly basic species. As a result, the mesoporous structure of the resultant materials is well preserved and mesoporous solid superbases are successfully prepared. It should be stated that the amount of ZrO₂ is of great importance for the protection of the mesoporous structure. The amount of ZrO₂ should be large enough to form an intact layer (at least a monolayer) on the surface of SBA-15. Otherwise, the reaction of strongly basic species with silica is still inevitable due to the exposed silica surface that is not covered by ZrO₂. Assuming that each ZrO₂ molecule exists in the tetragonal form with a unit cell constant (a_0) of 0.5128 nm, its coverage is 0.2630 nm². Therefore, for the formation of a monolayer on SBA-15 with a surface area of 690 m² g⁻¹, about 35 wt% of ZrO_2 is required.48 Taking into consideration that some small micropores are inaccessible to zirconium compounds, the amount of ZrO₂ for the formation of a monolayer should be lower than 35 wt%. According to the present investigation, the mesostructure can be preserved when the content of ZrO_2 exceeds 30 wt% for the AIH method, which is consistent with the theoretical value. Hence, aiming to effectively protect the host structure, the amount of ZrO₂ should be higher than 30 wt% from the viewpoint of forming an intact layer.

It is interesting to note that the dispersion degree of ZrO₂ plays an essential role in the preparation of mesoporous solid bases. Besides the AIH method, the introduction of ZrO₂ by impregnation and grinding was also carried out. However, the resultant samples after potassium functionalization exhibit quite different properties. As described above, the sample KZS(A)-30 exhibits an ordered mesostructure. Nevertheless, the mesoporous structure of KZS(I)-30 was partially damaged and that of KZS(G)-30 was destroyed completely despite an identical ZrO₂ content. Correspondingly, their basicity and catalytic performance decrease in the same order. In terms of the results from various characterization techniques, it is clear that the dispersion degree of ZrO₂ in the materials derived from different methods declines in the order ZS(A) > ZS(I) > ZS(G). The good dispersion of ZrO₂ by the AIH method is related to the pre-hydrolysis of the precursor ZrO(NO₃)₂ in the presence of ammonia/water vapor. In such a low-temperature process, the intermediate $Zr(OH)_4$ tends to distribute inside the pores evenly, resulting in a composite with a uniform coating of ZrO₂ on the surface after calcination.28 The AIH method has also been applied to coat other metal oxides on mesoporous silicas.49 By use of the conventional methods (i.e. impregnation and grinding), it is impossible to form an intact layer on SBA-15, and aggregation of ZrO₂ occurs to a greater or lesser extent. Therefore, both the amount and dispersion degree of ZrO₂ play a significant role in the preparation of mesoporous solid bases.

To date, the synthesis of mesoporous solid superbases derived from a siliceous host remains a challenge in spite of great efforts. In this study, we developed a dualcoating strategy to overcome both of the weaknesses of mesoporous silicas by precoating a layer of metal oxide before loading the base precursor. The ZrO_2 interlayer not only enhances the guest-host interactions (promoting the decomposition of base precursor at low temperatures), but also improves the alkali-resistant ability of the host (preventing siliceous frameworks from destruction). Ordered mesoporous materials with superbasicity were thus successfully constructed. The present strategy should enable various basic species to be introduced to mesoporous silicas with a range of pore symmetries, resulting in the fabrication of new solid superbases with high potential in adsorptive and catalytic applications.

5 Conclusions

The dualcoating strategy provides an effective approach to generate strong basicity on mesoporous silica. On the one hand, the ZrO_2 interlayer enhances the guest-host interactions, leading to the decomposition of the base precursor KNO₃ at much lower temperatures as compared with KNO₃ supported on pure SBA-15. On the other hand, the alkaliresistance of the silica host is greatly improved by precoating a layer of ZrO_2 , and the mesostructure can be well preserved after the formation of strongly basic sites. Hence, materials possessing both an ordered mesostructure and superbasicity with a high strength of 27.0 were successfully constructed. Not only the amount, but also the dispersion degree of ZrO_2 has an important effect on the generation of strong basicity. When

the amount of ZrO_2 is higher than 30 wt%, an intact layer can be produced by use of the AIH method. Nonetheless, aggregation takes place if ZrO_2 was introduced by impregnation or grinding, which is not beneficial for the protection of the mesostructure.

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