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Ni-PC@SBA-15 derived from nano-sized Ni-MOF-74 confined in SBA-15 as highly active catalyst for gas phase catalytic hydrodechlorination of 1,2-dichloroethane

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A novel catalyst consisting of metallic Ni and porous carbon (PC) confined in SBA-15 was fabricated by the confined pyrolysis of nano-sized Ni-MOF-74 that was *in-situ* grown in the mesopores of SBA-15. Due to the intimate contact between Ni and PC in fine Ni-PC composite resulting from the confinement effect of mesoporous SBA-15, the catalyst displayed prominent catalytic activity and selectivity in the gas phase catalytic hydrodechlorination of 1,2-dichloroethane.

Gas phase catalytic hydrodechlorination (HDC) is an attractive avenue to convert chlorinated organic pollutants into less toxic and valuable hydrocarbons.¹ Supported Ni-based catalysts are cost-effective and highly selective catalysts despite of their relatively lower catalytic activities as compared with noble metal catalysts.² Additionally, carbonaceous materials and SiO₂ are widely adopted catalyst supports due to their excellent resistance against corrosive HCl formed in the HDC processes. For Ni-based catalysts supported on carbon and SiO₂, however, large metal particles are generally formed and metal particle growth commonly occurs during the preparation and reaction processes because of the lack of strong metal-support interaction, resulting in low catalytic activity. Numerous hierarchically structured Ni-based catalysts, such as core-shell, volk-shell, lamellar and embedded catalysts, have been explored to enhance metal dispersion and catalytic stability.³ Metal-organic frameworks (MOFs) can be easily converted into nano-sized metal particles supported on porous carbon (PC) through pyrolysis under controlled atmosphere, providing facile and one-step synthesis of supported metal catalysts.⁴

However, the direct pyrolysis of MOFs also results in large metal particles due to aggregation of metal particles at high carbonization temperature.⁵ To enhance the dispersion of MOFs, hybridizing MOFs with SiO₂ or carbonaceous materials has been explored and the hybrid materials exhibited promising performances in gas adsorption, storage and electrochemical reactions.⁶ Notably, confining nanoparticles in well-defined channels is an effective approach to enhance particle dispersion and inhibit particle aggregation. However, studies using confined MOFs as precursors to prepare supported catalysts are still very limited in the literature.^{6f, 6g}

Herein, we fabricated highly dispersed Ni-PC composite located in the pores of an ordered mesoporous silica (i.e., SBA-15) using nano-sized Ni-MOF-74 confined in SBA-15 as the precursor. SBA-15 was selected as the matrix to host Ni-PC particles due to its ordered mesopore structure, high pore volume and large surface area.⁷ The preparation route of the catalysts is described in Scheme 1 and the details of preparation procedure are given in ESI $\ensuremath{^\dagger}$. Briefly, a desired amount of nano-sized Ni-MOF-74 was in-situ grown inside the mesopores of SBA-15 (denoted as xNi-MOF-74@SBA-15, x=1, 4, 17, where x represented theoretical Ni loading amount). Subsequently, the highly dispersed Ni-PC composite confined in SBA-15 pores was readily obtained upon direct pyrolysis of xNi-MOF-74@SBA-15 at 450 °C under N₂ atmosphere. The resultant catalyst is denoted as xNi-PC@SBA-15. For comparison, PC supported Ni catalyst (denoted as Ni@PC) was prepared by direct carbonization of pristine Ni-MOF-74. To investigate the role of PC, 1Ni-PC@SBA-15 was calcined in air to obtain a catalyst without carbon (denoted as 1Ni@SBA-15). A Ni-based catalyst supported on SBA-15 with similar Ni



Scheme 1. Schematic illustration of the fabrication of Ni-PC@SBA-15 catalysts derived from nano-sized Ni-MOF-47 confined in SBA-15.

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loading amounts prepared by the conventional impregnation method was also involved as comparison (denoted as 1Ni/SBA-15). The gas phase catalytic HDC of 1,2-dichloroethane was used to evaluate the catalytic performances of the catalysts.

The contents of Ni in the catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and the results are listed in Table S1 in ESI[†]. Ni@PC had a Ni content of 73.66 wt.%, significantly higher than that of xNi-PC@SBA-15 (ranging from 0.89 to 17.0 wt.%). The X-ray diffraction (XRD) patterns of nano-sized Ni-MOF-74 and xNi-MOF-74@SBA-15 are presented in Fig. S1a. In consistence with the previous study,⁸ pristine Ni-MOF-74 exhibited two weak and broad peaks at 20 of 6.8 (110) and 11.9° (300), reflecting its low crystallinity due to the small crystal size in the nanometer range (i.e., < 10 nm). As for 17Ni-MOF-74@SBA-15, diffraction peaks of nano-sized Ni-MOF-74 were indentified along with that of amorphous SiO₂ (the broad peak centered at 20 of 22.4°), indicating that nano-sized Ni-MOF-74 was formed in SBA-15. However, the diffraction peaks characteristic of nano-sized Ni-MOF-74 were not observed in 1Ni-MOF-74@SBA-15 and 4Ni-MOF-74@SBA-15, likely due to the low loading amount of nano-sized Ni-MOF-74 and its dilution on SBA-15 support.9 Similar observations were reported for other confined MOF nanocrystals.9,10 Ni@PC presented very sharp and narrow diffraction peaks at 44.4, 51.9 and 76.5° assigned to metallic Ni,¹¹ reflecting the formation of large and well crystallized Ni particles on PC upon pyrolysis of nano-sized Ni-MOF-74. In parallel, the diffraction peaks characteristic of metallic Ni were clearly observed in 17Ni-PC@SBA-15. However, peaks of metallic Ni were not identified in 1Ni-PC@SBA-15 and 4Ni-PC@SBA-15 (see Fig. S1b), suggesting the formation of small Ni particles with high dispersions. Consistent results were provided by the X-ray photoelectron spectra (XPS) of Ni 2p (Fig. S2 in ESI[†]). As shown in Fig. S2, besides metallic Ni, NiO and Ni(OH)₂ species can also be found in Ni-based catalysts due to the oxidation of surface metallic Ni when exposed to air. In Ni@PC, the majority of Ni species were in the form of metallic Ni. 17Ni-PC@SBA-15 had a lower content of metallic Ni as compared with Ni@PC. However, the XPS peaks of metallic Ni were absence in 1Ni-PC@SBA-15 and 4Ni-PC@SBA-15, attributed to their very small Ni particles with high surface to bulk ratios that were more prone to oxidation upon exposure to air.

The infrared (IR) spectra of nano-sized Ni-MOF-74 and xNi-MOF-74@SBA-15 are displayed in Fig. S3a. For pristine nano-sized Ni-MOF-74, the IR bands characteristic of MOF-74 appeared at 1552, 1416 and 1193 cm⁻¹, which were assigned to the asymmetric and symmetric stretching vibrations of -COO⁻ from the carboxylic acid, and the vibrational band of C-O respectively.^{10,12,13} As for xNi-MOF-74@SBA-15, besides very strong bands at 1056 and 809 cm⁻¹ from asymmetric and symmetric stretching vibrations of Si-O in SBA-15,^{11,14} the IR bands of Ni-MOF-74 were also clearly identified. Additionally, the intensities of IR bands assigned to Ni-MOF-74 increased with the loading of Ni-MOF-74, confirming the successful growth of Ni-MOF-74 in SBA-15. The IR spectra of the xNi-PC@SBA-15 catalysts were similar to that of SBA-15 (see Fig. S3b, ESI[†]) and the bands characteristic of organic components were not visible, suggesting complete decomposition and carbonization of organic moisture from Ni-MOF-74 after pyrolysis. Fig. S4 (ESI [†]) shows thermogravimetric analysis (TGA) profiles of Ni-MOF-74 and xNi-MOF-74@SBA-15. The 74@SBA-15 (395-405 °C). The diffuse reflectance ultraviolet-visible (DR-UV/Vis) spectra of xNi-MOF-74@SBA-15 (presented in Fig. S5, ESI⁺) were similar to that of pristine nano-sized Ni-MOF-74, which were also typical for MOF-74.16,17 This further confirmed the formation of Ni-MOF-74 in SBA-15. Additionally, all UV absorbance bands of xNi-MOF-74@SBA-15 were slightly blueshifted in comparison with Ni-MOF-74, likely attributed to the formation of smaller crystals of Ni-MOF-74 due to the confinement effect of SBA-15.¹⁸ The N₂ adsorption-desorption isotherms and pore size distributions of SBA-15 and xNi-MOF-74@SBA-15 are shown in Fig. S6 and the parameters are listed in Table S2, ESI [†]. All isotherms displayed clear capillary condensation with typical IV sorption behavior, attributed to the mesopore structure of SBA-15. Due to the pore occupation and lower surface area of nano-sized Ni-MOF-74 with low crystallinity,⁸ xNi-MOF-74@SBA-15 possessed lower surface area than pristine SBA-15. In parallel, the BET surface area and pore volume of xNi-PC@SBA-15 were also lower as compared with SBA-15 (Fig. S7 and Table S1), due to the formation of Ni-PC particles in the mesopores of SBA-15.

Fig. S8 (ESI [†]) shows the scanning electron microscopy (SEM) images of xNi-MOF-74@SBA-15. It is seen that Ni-MOF-74 was aggregated nanocrystals (Fig. S8a). 1Ni-MOF-74@SBA-15 and 4Ni-MOF-74@SBA-15 exhibited the ropelike domains of SBA-15 (Fig. S8b and c), suggesting that Ni-MOF-74 was mainly dispersed inside the pores of SBA-15 in these two materials. For 17Ni-MOF-74@SBA-15, a uniform Ni-MOF-74 layer was observed outside SBA-15 (Fig. S8d), indicative of the growth of partial Ni-MOF-74 on SBA-15 external surface due to excess Ni-MOF-74 loading. The SEM images and elemental mapping of Ni@PC and xNi-PC@SBA-15 catalysts are displayed in Fig. S9. For all Ni-based catalysts, the elemental distributions were homogeneous.

The morphology of xNi-MOF-74@SBA-15 was further characterized by the transmission electron microscopy (TEM) images (presented in Fig. S10 in ESI[†]). Consistent with previous observations,⁸ pristine nano-sized Ni-MOF-74 showed a 'continuous' solid morphology. Ordered arrays of SBA-15 channels were clearly observed in the images of xNi-MOF-74@SBA-15. In line with the SEM results, nano-sized Ni-MOF-74 was found both in the pore and on the surface of 17Ni-MOF-74@SBA-15. TEM images of Ni@PC and xNi-PC@SBA-15 catalysts are shown in Fig. 1. For Ni@PC catalyst, very large Ni particles (with size in the range of 4-22 nm) could be clearly identified due to severe metal aggregation, while small Ni particles were evenly distributed in xNi-PC@SBA-15, attributed to the effectively confinement effects from SBA-15. Notably, in 1Ni-PC@SBA-15, Ni particles (with size in the range of 0.4-6 nm) were smaller than the pore diameter of SBA-15 (8.09 nm), reflecting that majority of Ni particles could be confined in the mesopores of SBA-15. A small portion of Ni particles were likely located on the external surface of SBA-15 in 4Ni-PC@SBA-15 and 17Ni-PC@SBA-15, as suggested by their larger particle sizes. The average Ni particle sizes of the catalysts

Page 2 of 5

2 | J. Name., 2012, 00, 1-3

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Fig. 1. The TEM images and Ni particles size distribution of differentNi-basedcatalysts.

were further quantified according to a surface area weighted diameter: $^{19} \ \ \,$

$$d_s = \sum n_i d_i^3 / \sum n_i d_i^2$$

where n_i is the number of counted Ni particles with diameter of d_i and the total number of particles ($\sum n_i$) is larger than 120.

The average Ni particle sizes of Ni@PC, 1Ni-PC@SBA-15, 4Ni-PC@SBA-15 and 17Ni-PC@SBA-15 were calculated to be 11.88, 2.45, 4.37 and 9.88 nm, respectively. On the basis of Ni particle sizes, the dispersion of active Ni sites can be further determined using the equation:²⁰ Dispersion (%) = 96.7/d_s (nm). The dispersions of Ni in 1Ni-PC@SBA-15, 4Ni-PC@SBA-15, 17Ni-PC@SBA-15 and Ni@PC were calculated to be 39.47%, 22.13%, 9.79% and 8.14%, respectively, reflecting a dispersion order of 1Ni-PC@SBA-15 > 4Ni-PC@SBA-15 > 17Ni-PC@SBA-15 > Ni@PC.

To verify the role of carbon in xNi-PC@SBA-15, temperature-programmed hydrogen desorption (H₂-TPD) profiles of 1Ni-PC@SBA-15 and 1Ni@SBA-15 are compared and the results are presented in Fig. S11. Both 1Ni-PC@SBA-15 and 1Ni@SBA-15 displayed two desorption peaks. The desorption peaks at 50-300 °C were assigned to hydrogens weakly adsorbed on the surface of Ni particles, while the high temperature peaks at 400-600 °C were attributed to spilled hydrogens,²¹ migrating from Ni metal surface to the surface of PC and SBA-15. Notably, the ratio of spilled hydrogens to adsorbed hydrogens of 1Ni-PC@SBA-15 was 44.5, much larger than that of 1Ni@SBA-15 (26.8). This suggested the substantially enhanced H-spillover effect of 1Ni-PC@SBA-15. The marked enhancement of H-spillover effect in 1Ni-PC@SBA-15 was likely due to the formation of Ni-carbon composites, in which the intimate contact between Ni particles and carbon with large interfacial perimeter strongly facilitated H-spillover from Ni particles into carbon surface.²²

The gas phase catalytic HDC of 1,2-dichloroethane was used to evaluate the catalytic performances of the catalysts. Besides trace methane and ethane, ethylene was the main product from the catalytic HDC of 1,2-dichloroethane on Nibased catalysts. Ethylene selectivities of all catalysts were above 90% (Fig. S12 in ESI \ddagger), representing their remarkable

catalytic merit. Fig. 2 shows the catalytic HDC of 1,2dichloroethane on the catalysts as a function of reaction time on stream (TOS). The conversion of 1,2-dichloroethane remained nearly constant on all catalysts during the test TOS, indicative of the high catalytic stability of Ni-based catalysts. Consistently, the morphologies and Ni particle sizes of the tested catalysts were not significantly changed after use (see TEM images in Fig. S13 in ESI[†]). However, 1,2-dichloroethane conversions on Ni-based catalysts varied with their structural properties. At 10 h of TOS, the conversions of 1,2dichloroethane on 1Ni-PC@SBA-15, 4Ni-PC@SBA-15 and 17Ni-PC@SBA-15 were 40.3%, 55.9% and 65.5%, respectively. The gradually increased 1,2-dichloroethane conversion was ascribed to the increase of active Ni sites with Ni loadings. It should be noted that the conversions of xNi-PC@SBA-15 catalysts were comparable to or even higher than that of Ni@PC (43.2%), despite of their much lower Ni loading (4-80 times lower than that in Ni@PC). This suggested the remarkable enhancement effects on xNi-PC@SBA-15 for catalytic HDC of 1,2-dichloroethane. The higher catalytic activities of xNi-PC@SBA-15 catalysts can be tentatively explained in terms of the dispersion of Ni particles. TEM results showed that owing to the confinement effects of SBA-15, much higher Ni dispersion was obtained on xNi-PC@SBA-15 catalysts than that of Ni@PC. Thus, xNi-PC@SBA-15 had more active sites and hence higher catalytic activities. The exceptional advantages of xNi-PC@SBA-15 catalysts were also manifested in comparison with SBA-15 supported Ni catalyst prepared by the conventional impregnation method (i.e., 1Ni/SBA-15, Fig. S14). At 10 h of TOS, the conversion of 1,2dichloroethane on 1Ni/SBA-15 was 18.9%, less than half of the conversion of 1Ni-PC@SBA-15.

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To further evaluate the catalytic performances of the catalysts, turnover frequency (TOF) values were calculated by normalizing the 1,2-dichloroethane conversion by exposed Ni sites. The TOF values of Ni@PC, 1Ni-PC@SBA-15, 4Ni-PC@SBA-15 and 17Ni-PC@SBA-15 were 2.64, 42.04, 21.83, and 14.41 h⁻¹, respectively. This reflected a catalytic activity order of 1Ni-PC@SBA-15 > 4Ni-PC@SBA-15 > 17Ni-PC@SBA-15 >> Ni@PC, which was consistent with their Ni dispersion order. This trend could be well interpreted in terms of the strong interaction between Ni particles and supports, which is favorable for the formation of spilled hydrogens. Previous studies showed that the spilled hydrogens formed on the metal-support interface



Fig. 2. (a) Conversion as a function of time on stream and (b) turnover frequency for gas phase catalytic hydrodechlorination of 1,2-dichloroethane over different Nibased catalysts.

Accepted Manuscri

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played an important role in the HDC reaction on Ni-based catalysts.^{23,24} For both Ni@PC and xNi-PC@SBA-15 catalysts, Ni particles were in intimate contact with the carbonaceous residual. Furthermore, smaller Ni particle had larger Ni-carbon interfacial area due to more effective Ni-carbon contact. Thus, stronger H-spillover effect could be expected on catalysts with smaller Ni particle size. Accordingly, owing to the higher Ni dispersion, xNi-PC@SBA-15 catalysts exhibited significantly higher TOF values than Ni@PC. The crucial role of H-spillover effect could be further verified by comparing the catalytic performances of 1Ni-PC@SBA-15 and 1Ni@SBA-15 without carbon residual. 1Ni@SBA-15 had similar Ni loading amount and particle size with that of 1Ni-PC@SBA-15 (see Fig. 1 and Table S1), whereas its conversion of 1,2-dichloroethane (24.5%) was much lower than that of 1Ni-PC@SBA-15 (40.3%). Consistently, the TOF value of 1Ni@SBA-15 was 28.86 h⁻¹, lower than that of 1Ni-PC@SBA-15 (42.04 h⁻¹). H₂-TPD results showed that more effective formation of spilled hydrogens was evoked on 1Ni-PC@SBA-15 than on 1Ni@SBA-15, clearly confirming the important role of H-spillover effect.

In summary, we successfully prepared a novel Ni-PC composite confined in SBA-15 (Ni-PC@SBA-15) by the confined pyrolysis of nano-sized Ni-MOF-74 that was in-situ grown in the mesopores of SBA-15, and introduced it for the gas phase catalytic HDC reaction. In comparison with Ni-PC composite prepared by direct pyrolysis of Ni-MOF-74 (Ni@PC), very small Ni particles with even size distribution are achieved on Ni-PC@SBA-15 due to the confinement effect from ordered mesopores of SBA-15. Additionally, the intimate contact between Ni particles and carbon in fine Ni-PC composite favored highly effective formation of spilled hydrogens. As a result, Ni-PC@SBA-15 exhibited superior catalytic activity and selectivity in the gas phase catalytic HDC of 1,2-dichloroethane to ethylene. The findings in this work highlight that Ni-PC@SBA-15 can be used as a highly active and selective catalyst in gas phase catalytic HDC reaction. The study also provides important knowledge to the fabrication of MOFsderived materials with high metal dispersion.

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Conflicts of interest

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There are no conflicts to declare.

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Novel Ni-porous carbon composite confined in SBA-15 was fabricated for highly effective and selective gas phase catalytic hydrodechlorination of 1,2-dichloroethane.