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*In situ* creation of multi-metallic species inside porous silicate materials with tunable catalytic properties<sup>†</sup>

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Porous metal silicate (PMS) material PMS-11, consisting of uniformly distributed multi-metallic species inside the pores, is synthesized by using a discrete multi-metal coordination complex as the template, demonstrating high catalytic activity and selectivity in hydrogenation of halogenated nitrobenzenes by synergistically activating different reactant molecules *via* Ni and Co transition metal centers, while Gd<sup>III</sup> Lewis acid sites play a role in tuning the catalytic properties.

The catalytic sites, consisting of multiple redox-active metal species, demonstrate superior catalytic properties in numerous reactions, derived from the distinct electron-deficient/rich functions of individual metals that could synergistically activate different reactant molecules.<sup>1,2</sup> Because metallic species are easily aggregated, they are traditionally stabilized by organic ligands or immobilized in porous matrices.<sup>3</sup> However, the mismatched pore sizes and structures, and incompatibility of porous supports to metallic species often results in metal aggregation, which would heavily deteriorate the catalytic properties.<sup>4</sup>

Among numerous porous support matrices for immobilization of redox-active metal species, porous silicate materials, which are very stable in a harsh environment, represent one class of the most ideal porous matrices for developing industrially applicable catalysts.<sup>5</sup> Because the affinity between silica and redox-active metals is very weak, it is a challenge to introduce and subsequently stabilize redox-active metal sites inside porous silicate materials, due to the easy sintering and agglomeration nature of metallic species.<sup>6</sup> Since porous silicate materials were traditionally synthesized by using organic templates, it would be a very promising strategy for *in situ* production and subsequent immobilization of metallic species into porous silicate materials by using discrete metal–organic complexes instead of traditional organic templates. Similar to the traditional synthesis strategy for porous silicate materials, the uniform shapes and sizes of metal–organic templates would be able to define the uniform distribution of pore sizes and shapes in porous silicate materials. Superior to the traditional strategy for immobilization of metallic species in porous silicate materials, the constituents and sizes of *in situ* generated and encapsulated redox-active metallic species in porous silicate materials are systematically tunable to improve the catalytic properties by tuning the synthesis methods and annealing conditions. Because many transition metal ions have similar coordination ability and coordination environments, they easily form isostructural complexes, indicating that the metal constituents in porous metal silicate (PMS) materials are arbitrarily tunable to optimize the catalytic properties.

As shown in Scheme 1,  $[Ni_2Gd_2]$  is a coordination complex, consisting of two Ni<sup>II</sup> and two Gd<sup>III</sup> ions connected by hydroxymethylpyridine and benzoate ligands.<sup>7</sup> Because Co<sup>II</sup> and Ni<sup>II</sup> ions with similar coordination ability easily form isostructural



Scheme 1 Schematic representation of the synthetic procedures for PMS-11.

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**Fig. 1** (a) PXRD profiles of [NiGd], [NiCoGd<sub>2</sub>], the PMS-11 precursor and PMS-11 (the number in the parenthesis represents the annealing temperature). (b) Nitrogen adsorption/desorption isotherms for the PMS-11 precursor and PMS-11 (the inset shows the pore size distributions for the PMS-11 precursor and PMS-11). (c) SEM and (d) TEM images of PMS-11.

complexes, the Ni<sup>II</sup> ions could be partially or fully replaced by  $Co^{II}$  ions with any ratio to form a series of isostructural coordination complexes, which have been confirmed by PXRD and ICP-MS analysis (Fig. 1a). Additionally, rare earth metal ions with unique orbital structures and 4f electrons might be able to improve the catalytic properties by synergistic cooperation with transition metal centers.<sup>8</sup> We report herein a PMS material, denoted as PMS-11, consisting of Ni<sup>0</sup>, Co<sup>0</sup> and Gd<sup>III</sup> metal species, which was templated by [NiCoGd<sub>2</sub>] with a Ni: Co:Gd ratio of 1:1:2 and subsequently annealed at 600 °C under a N<sub>2</sub> atmosphere, demonstrating excellent catalytic properties in hydrogenation of halogenated nitrobenzenes to produce halogenated anilines with almost quantitative conversion and selectivity.

The TGA curve shows that the weight loss of the PMS-11 precursor that occurred between 200 and 570 °C under a nitrogen atmosphere, which is similar to the thermal behaviors of [NiCoGd<sub>2</sub>], should be ascribed to pyrolysis of the organic ligands (Fig. S1, ESI†). Accordingly, the PMS-11 precursor was pyrolyzed at different temperatures. There is no sharp diffraction PXRD peak for the PMS-11 precursor and the annealed products at 400, 500 and 600 °C, indicating that metal species were well-distributed without aggregation in the solid materials (Fig. 1a and Fig. S2, ESI†). When the temperature was increased to 700 °C, there appeared the characteristic diffraction peaks ascribed to silica (JCPDS No. 39-1425).<sup>9</sup> Further increasing the temperature to 800 °C, the crystallization degree of PMS-11 was highly improved.

In the FT-IR spectrum of the PMS-11 precursor, the peaks at 470, 795 and 1100 cm<sup>-1</sup> are attributed to the vibration of Si–O bonds, the peaks at 640 and 720 cm<sup>-1</sup> are the vibration of the pyridine ring in hydroxymethylpyridine, and the peaks at 1400, 1545 and 1602 cm<sup>-1</sup> correspond to the stretching vibration of

carboxylate moieties of benzoate (Fig. S3, ESI<sup>†</sup>).<sup>9,10</sup> The vibration peaks for organic ligands were gradually weakened when raising the annealing temperature, while the vibration of the Si–O bonds becomes stronger, indicating gradual decomposition of the organic ligands in PMS-11.

 $N_2$  sorption measurements revealed that PMS-11 and its precursor exhibit the typical type IV isotherms consisting of hysteresis loops. PMS-11 takes up 465 cm<sup>3</sup> g<sup>-1</sup> N<sub>2</sub> at 77 K and 1 bar, resulting in a microporous BET surface area of 232 m<sup>2</sup> g<sup>-1</sup>, which is much higher than that of the PMS-11 precursor (47 m<sup>2</sup> g<sup>-1</sup>). The micropore size in PMS-11 is mainly around 2.0 nm, which is very close to the size of [NiCoGd<sub>2</sub>] in PMS-11 (~1.9 nm), indicating that the pore characteristics of PMS-11 depend on the metalorganic template (Fig. 1b and Table S1, ESI†). The SEM image shows that there are loosely packed nanoparticles in PMS-11, which are similar to those in its precursor (Fig. 1c and Fig. S4, ESI†). TEM and STEM-EDS elemental mapping images show the uniform morphology of the annealed materials at different temperatures, while the metallic species is dispersed in the material without aggregation (Fig. S5–S8, ESI†).

The surface chemical states and binding energies of Ni and Co species in PMS-11 were studied by X-ray photoelectron spectroscopy (XPS) (Fig. S9, ESI<sup>†</sup>). The binding energies of Ni<sup>0</sup> 2p<sub>3/2</sub> and 2p<sub>1/2</sub> for PMS-11 are located at 855.6 and 873.3 eV, while the  $Ni^{2+} 2p_{3/2}$  and  $2p_{1/2}$  peaks are located at 861.5 and 879.7 eV, respectively (Fig. 2a).<sup>11</sup> The strong peaks at 779.2 and 795.3 eV are the characteristic binding energies of Co<sup>0</sup>, and the peaks at 784.3 and 801.2 eV correspond to  $Co^{2+}$  (Fig. 2b). Compared with those of the PMS materials whose templates contain Ni<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> and Gd<sup>III</sup>, Co<sup>II</sup> and Gd<sup>III</sup>, and Ni<sup>II</sup> and Co<sup>II</sup>, the Ni 2p peaks for PMS-11 shifted to the high binding energy field, while the Co 2p peaks shifted to the low binding energy field, indicating that electron transfer occurred after the introduction of Gd<sup>III</sup> and Co<sup>0</sup> species in PMS-11 (Fig. S10 and S11, ESI<sup>+</sup>). The above results demonstrate that the introduction of Co and Gd species in Ni-based catalysts could tune the



Fig. 2 (a) High resolution Ni 2p and (b) Co 2p XPS spectra for different PMS materials (the letters in the parentheses represent the encapsulated metal species).

electron and orbital properties, which might exhibit unique catalytic properties.

Halogenated anilines are an important class of intermediates and raw materials for the synthesis of fine chemicals, which were traditionally synthesized by hydrogenation of halogenated nitrobenzenes, catalyzed by noble metal-based catalysts, while dehalogenation inevitably occurred.<sup>12-14</sup> Even though great effort has been paid to developing non-noble metal-based catalysts, low activity and selectivity have heavily frustrated their practical applications.<sup>15</sup> It is interesting that PMS-11 exhibited high catalytic activity and selectivity in hydrogenation of *p*-chloronitrobenzene (*p*-CNB) to produce halogenated aniline *p*-chloroaniline (*p*-CAN) with >99%conversion and >99% selectivity. Detailed experiments revealed that every metal species and porous silicate matrix played very important roles in the catalytic properties (Fig. S12, ESI<sup>+</sup>). The p-CNB conversion catalyzed by PMS-11 (CoGd) is very low, while a significant amount of p-CNB was dehalogenated catalyzed by PMS-11 (NiGd) under catalytic conditions. The Gd species also played very important roles in the catalytic reaction, which resulted in decreased conversion and selectivity in the absence of the Gd<sup>III</sup> species. Without the protecting silicate matrix, the p-CNB conversion decreased to 9.1%, due to the easy aggregation nature of metallic species. The annealing temperature also played important roles in the catalytic results, lower and higher temperature results in low catalytic activity, and even low selectivity (Table S3, ESI<sup>+</sup>). The catalytic properties of PMS-11 are much superior to those of most transition metal-based catalysts, even noble-metal-based catalysts, in the literature (Tables S4 and S5, ESI<sup>+</sup>).

To understand the catalytic properties of PMS-11, we studied the kinetic behaviors in the hydrogenation reaction. The reaction was conducted at 100-130 °C for the calculation of rational apparent activation energies  $(E_a)$ , resulting in different  $E_a$ values in the order of PMS-11 (34.1 kJ mol<sup>-1</sup>) < PMS-11 (NiCo)  $(49.8 \text{ kJ mol}^{-1}) < PMS-11 (NiGd) (65.3 \text{ kJ mol}^{-1}) < PMS-11$ (CoGd) (89.8 kJ mol<sup>-1</sup>) (Fig. 3 and Fig. S13–S15, ESI<sup>†</sup>). These results clearly demonstrate the correlation between the catalytic activity and the redox-active centers. It is worth noting that the  $E_{\rm a}$  value for PMS-11 is very close to those of Pt (42.7 kJ mol<sup>-1</sup>) and Au-based catalysts (24.9–94.6 kJ  $mol^{-1}$ ), indicating the high catalytic activity of PMS-11.16 PMS-11 with Ni: Co ratio of 1:1 also demonstrates the highest turnover frequency (TOF) of 394.9 h<sup>-1</sup>, compared with the control catalysts with different Ni:Co ratios, indicating that the Ni:Co ratio is one of the important factors to improve the catalytic properties by synergistically activating different reactant molecules (Fig. S16 and Table S3, ESI<sup>†</sup>). PMS-11 also demonstrates general applicability, which could hydrogenate various halogenated nitrobenzenes (Scheme 2). o-, m- and p-CNB and o-, m- and p-fluoronitrobenzenes were completely converted into the corresponding chloroanilines, despite the fact that there exists steric hindrance between -NO2 and -X in o-CNB and o-fluoronitrobenzene. o-, m- and p-bromonitrobenzene and o-, m- and p-iodonitrobenzenes, containing C-Br and C-I bonds, which are more easily dehalogenated, were also transferred into the corresponding halogenated anilines without dehalogenation. These results are interesting, because the



Fig. 3 Reaction rates for selective hydrogenation of *p*-CNB catalyzed by different catalysts (the inset shows the apparent activation energies for different catalysts). Reaction conditions: *p*-CNB (5 mmol), catalyst (0.05 mol% based on Ni and Co),  $H_2O$  (2.5 mL) and ethanol (7.5 mL), 1 MPa  $H_2$ .



Scheme 2 Hydrogenation of various halogenated nitrobenzenes to produce halogenated anilines catalyzed by PMS-11. Reaction conditions: halogenated nitrobenzene (0.5 mmol), PMS-11 (1.0 mol% based on Ni and Co),  $H_2O$  (1.5 mL) and ethanol (4.5 mL).

selectivity for catalytic hydrogenation of iodonitrobenzenes is difficultly improved in the literature.<sup>17</sup>

PMS-11 exhibited excellent stability and reusability, which could be simply recovered by centrifugation, and reused in the next run for ten cycles with > 99% *p*-CNB conversion and > 99% *p*-CAN selectivity (Fig. S17, ESI†). The PXRD pattern and TEM image of recovered PMS-11 are almost identical to those of the as-synthesized one, indicating that PMS-11 is stable and the metal species were not aggregated when catalyzing the hydrogenation reaction (Fig. S18 and S19, ESI†).

To comprehensively understand the contribution of different metal species in catalyzing the hydrogenation reaction, we synthesized a series of control catalysts that consist of different metal species by directly pyrolyzing the corresponding coordination complexes in the absence of protecting silicate matrix, denoted as [Ni], [Co], [NiCo], [NiGd], [CoGd] and [NiCoGd<sub>2</sub>] based on the metal species. Considering that iodonitrobenzene is more easily dehalogenated, we selected hydrogenation of o-iodonitrobenzene as a model reaction to more evidently illustrate the effect of different metal species on the catalytic results (Table S6, ESI<sup>+</sup>). The substrate conversion and product selectivity are 5.5 and 74% catalyzed by [Ni], which are different to 1.7 and >99% catalyzed by [Co], respectively, indicating that Ni and Co metallic species played different roles in improving the catalytic efficiency and selectivity, respectively. The conversion (7.1%) and selectivity (85%) were apparently improved when a physical mixture of [Ni] and [Co] was used as the catalyst, indicating that there occurred synergistic work between Ni and Co redox-active species by activation of different reactant molecules. When [NiCo] was used as a catalyst, the conversion and selectivity were further improved to 8.2 and 93%, respectively, due to the closed contact between Ni and Co redox-active sites. Gd<sup>III</sup> species could further improve the catalytic properties, as demonstrated by the catalytic results by  $[NiCoGd_2]$  with 8.5% conversion and >99% selectivity.

According to the catalytic results and the literature, we proposed a plausible mechanism for hydrogenation of halogenated nitrobenzenes catalyzed by PMS-11 (Scheme S1, ESI<sup>+</sup>). Initially, halogenated nitrobenzene and hydrogen molecules were chemically adsorbed on the Co<sup>0</sup> and Ni<sup>0</sup> active sites in PMS-11, respectively. The dihydrogen molecule was subsequently dissociated to form hydrogen (H<sup>•</sup>) active species on the Ni<sup>0</sup> site, which could react with the adsorbed nitro group in halogenated nitrobenzene to form a nitroso compound intermediate. The nitroso compound is highly reactive, which further reacted with hydrogen (H•) to produce phenylhydroxylamine, and finally arylamine compound.<sup>18,19</sup> The electronegatively charged Co site, as revealed by XPS spectra, could generate electrostatic repulsion interaction with the electronenriched C-X moiety, which would prevent the dehalogenation reaction to improve the selectivity.<sup>15,20,21</sup> The electrophilic Gd<sup>III</sup> species could also decrease the electron density of Ni species, which would improve the binding connectivity between Ni<sup>0</sup> and  $\mathrm{H}_2$  and subsequent dissociation rate of  $\mathrm{H}_2$  to improve the catalytic activity.22

In summary, we developed a practically applicable strategy for the synthesis of porous metal silicate material PMS-11, consisting of *in situ* generated multi-metal sites with controllable constituents, structures and properties inside the active site-adaptive pores. Attributed to the synergistic effect between Lewis acid Gd<sup>III</sup> sites and redox-active metallic Ni<sup>0</sup> and Co<sup>0</sup> species, PMS-11 demonstrates high catalytic activity, selectivity and stability in hydrogenation of halogenated nitrobenzenes to produce halogenated anilines with high conversion (>99%) and selectivity (>99%), and is ready for practical applications. We are grateful for the financial support of the National Natural Science Foundation of China (grant no. 21525312 and 21872122).

## Conflicts of interest

There are no conflicts to declare.

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