## Mesoporous Materials

## Mesoporous Bubble-like Manganese Silicate as a Versatile Platform for Design and Synthesis of Nanostructured Catalysts

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**Abstract:** Manganese silicate in bubble-like morphology was used as a versatile platform to prepare a new class of yolk–shell hybrids. The mesoporosity of the shell was generated from the interbubble space and the bubble structure of manganese silica was used to hold and support nanoparticles (e.g., Au, Ag, Pt, Co, Ni, Au–Pd alloy,  $MoO_2$ ,  $Fe_3O_4$ , carbon nanotubes and their combinations). We also used heterogeneous catalysis reactions to demonstrate the workability of these catalysts in both liquid and gas phases.

Hollow-structured mesoporous materials consisting of a cavity or void within a mesoporous shell have been attracting a great deal of attention across various fields.<sup>[1]</sup> Usually, the mesopore channels are generated by using self-assembled surfactant micelles as structural directors, similar to the preparation of MCM-41 type mesopores,<sup>[2]</sup> and the templating surfactants are removed by thermal treatment or solvent extraction.<sup>[3]</sup> However, these methods are not necessarily very cost-effective at an industrial scale and it is difficult to remove surfactants completely. A concept of a "surfactant-free process" may be realised if the mesopore channels can be created by the stacking of nano-building blocks (e.g., sheets and crystallites).<sup>[4]</sup> Unfortunately, the uniformity of pores arising from the interparticle space is usually low due to disordered aggregation and polydispersity of the building blocks. Therefore, the control of mesoporous nanostructures without using surfactants is particularly challenging.

Herein we report a facile surfactant-free approach for fabricating sophisticated yolk-shell nanocatalysts with mesoporous channels in the shell. Manganese silicate (MS) was used as the shell framework, since manganese has been explored as an essential component in numerous catalytic materials, especially important in electron-transfer reactions.<sup>[5]</sup> In order to pursue multifunctional catalysis or synergetic effects between the different active species, various catalytic nanoparticles (NPs) were encapsulated/or immobilised into hollow cavities or on the sur-

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 Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405697. faces of mesoporous MS, including Au, Ag, Pt, Ni, Co, Au–Pd alloy,  $MoO_2$ ,  $Fe_3O_4$ , carbon nanotubes (CNTs) and their combinations. We demonstrate their enhanced catalysis for both liquid- (e.g., 4-nitrophenol reduction) and gas-phase reactions (e.g.  $CO_2$  hydrogenation). MS also allows doping of rare-earth ions into its silicate framework;<sup>60</sup> therefore, catalytic properties brought in by the dopants could be further tuned.

We started with introducing Au NPs into the framework of MS, in view of their excellent catalytic activity.<sup>[7]</sup> Shown in Figure 1a, the Au@SiO<sub>2</sub> core–shell structure was first synthesised.



**Figure 1.** TEM images of a) Au@SiO<sub>2</sub> core–shell; b) and c) Au@MS yolk–shell; d) FESEM image of Au@MS yolk–shell; e) XRD patterns of the "bubble catalysts"; f) the ideal crystallographic structure of MS: yellow, green, and blue represent 4-coordinated Si<sup>4+</sup> (tetrahedrons), 6-coordinated Mn<sup>3+</sup> (octahedrons) and 8-coordinated Mn<sup>2+</sup> (irregular polyhedron), respectively; and g) elemental mappings of the Au@MS yolk–shell.

This solid precursor has a highly uniform size (ca. 226 nm) and contains a single Au NP core (ca. 15 nm) at the centre. Then the solid precursor (80 mg) was mixed with an aqueous solution (20 mL) of MnSO<sub>4</sub> (6.8 gL<sup>-1</sup>) and sodium maleate (9 gL<sup>-1</sup>). The mixture was stirred vigorously for 10 min before a hydrothermal treatment (180 °C for 12 h, see the Supporting Information section SI-1). Interestingly, the transformations of structure (core–shell  $\rightarrow$  yolk–shell) and composition (silica $\rightarrow$ MS) could be achieved in this one-pot hydrothermal process. The as-prepared yolk–shell structure with a movable Au NP core inside the MS shell (denoted as Au@MS) are shown in Fig-

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ure 1 b, c. The TEM images reveal that the thickness of MS shell is about 22 nm, which was composed of numerous smaller hollow bubbles (ca. 7 nm, see Supporting Information, section SI-2), and the overall size of MS hollow spheres is about 215 nm. The size of the Au@MS yolkshell is very uniform (Figure 1d). Occasionally, mechanically fractured spheres (<3%) were also observed under large-area SEM screening (see Supporting Information, section SI-3), proving the existence of hollow interior. The bubble-like shell was produced owing to the presence of CO<sub>2</sub> bubbles (from maleate anion decomposition under hydrothermal conditions), which serve as soft templates for the deposition of manganese silicate (through the ion-exchange of Mn<sup>2+</sup> with H<sub>4</sub>SiO<sub>4</sub>).<sup>[6]</sup> Our X-ray diffraction (XRD) results (Figure 1 e) indicate the presence of both metallic phase aold and blythite (Mn<sub>3</sub><sup>+2</sup> Mn<sub>2</sub><sup>+3</sup>[SiO<sub>4</sub>]<sub>3</sub>, JCPDS no. 89-5709) in the Au@MS yolkshell catalyst, while the Stöber silica is in its amorphous state. The crystal structure of MS is similar to other garnet-group minerals with a general chemical formula of A<sub>3</sub>B<sub>2</sub>(XO<sub>4</sub>)<sub>3</sub> (Fig-



**Figure 2.** a) N<sub>2</sub> adsorption/desorption isotherms of the "bubble catalysts"; b) pore size distribution of the Au@MS yolk-shell spheres; c) time-dependent UV/Vis spectra of the reaction mixture of reduction of 4-nitrophenol by NaBH<sub>4</sub> using Au@MS yolk-shell as a catalyst; and d) preparation procedures of "bubble catalysts": 1) pristine catalytic NPs, **2**) NPs@SiO<sub>2</sub> core-shell, **3**) NPs@mSiO<sub>2</sub> core-shell, **4**) NPs@MS yolk-shell, **5**) silica bead, **6**) hollow MS sphere, **7**) MS@NPs, **8**) CNT@mSiO<sub>2</sub> core-shell, **9**) CNT@MS yolk-shell, **10**) CNT@NPs@mSiO<sub>2</sub> core-shell, and **11**) CNT@NPs@MS yolk-shell.

ure 1 f).<sup>[8]</sup> Furthermore, our energy-dispersive X-ray (EDX) mapping study also confirms the formation of the Au@MS yolk-shell structure (Figure 1 g).

As expected, N<sub>2</sub> physisorption measurements (Figure 2a) reveal the highly porous nature of Au@MS spheres. The "bubble catalysts" followed Langmuir type IV isotherm with a hysteresis loop at high  $P/P_0$  (which is characteristic of mesopores). The Brunauer-Emmett-Teller (BET) surface areas are 341  $m^2 q^{-1}$  for the pristine MS and 217  $m^2 q^{-1}$  for the Au@MS, both of which are much higher than that of 15 m<sup>2</sup>g<sup>-1</sup> for nonporous Stöber silica beads. Intriguingly, the Au@MS gives pore volume of  $0.20 \text{ cm}^3 \text{g}^{-1}$  and mesopores of 3.3 nm (Figure 2 b), similar to those obtained by using cetyltrimethylammonium bromide (CTAB) micelles as a soft-template.<sup>[9]</sup> Using the reduction of 4-nitrophenol as a testing example,<sup>[10]</sup> we confirmed that the mesoporous MS shell indeed allows a convenient access for the reactant (namely, 4-nitrophenol with a molecular size of 0.66 nm  $\times$  0.43 nm<sup>[11]</sup>) to travel into the central cavity in which the Au NP catalyst is located. As shown in Figure 2c, the intensity of the characteristic absorption peak at 400 nm (assigned to 4-nitrophenol) guickly decreased upon the addition of the catalyst. The reduction reaction was completely finished in 12 min, along with the colour change from bright yellow to colourless. This reaction can be considered as a pseudo-firstorder reaction, and the rate constant was determined to be  $0.18 \text{ min}^{-1}$  (see the Supporting Information, section SI-4), much higher than that using pristine MS as a catalyst (0.03 min<sup>-1</sup>).

We also demonstrated a broad scope of applications of this approach by introducing other catalytic metal species to diversify the functions of the MS-based nanocatalysts. As illustrated in Figure 2 d, we have developed various synthetic strategies to produce eleven more representative "bubble catalysts"; they are spherical Ag@MS, Au–Pd@MS, MoO<sub>2</sub>@MS, Fe<sub>3</sub>O<sub>4</sub>@MS, MS@Pt, MS@Au, MS@Ni and MS@Co, and tubular CNT@MS, CNT@Au–Pd@MS and Au–Pd@MS. Generally speaking, the controlled fabrication can be divided into three steps, 1) synthesis of the discrete NPs with a desirable size and shape, 2) deposition of silica shell on the as-synthesised NP cores to generate core–shell structures (NPs@SiO<sub>2</sub> or NPs@mSiO<sub>2</sub>, where SiO<sub>2</sub> = nonporous SiO<sub>2</sub> and  $mSiO_2$ =mesoporous SiO<sub>2</sub>) and 3) conversion of NPs@SiO<sub>2</sub> or NPs@mSiO<sub>2</sub> core–shell to NPs@MS yolk– shell (i.e., nanocatalysts). Likewise, using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (Fig-



Figure 3. TEM images of a)  $Fe_3O_4@SiO_2$  core-shell, b)  $Fe_3O_4@MS$  yolk-shell, c)  $Ag@SiO_2$  core-shell, d) Ag@MS yolk-shell, e)  $Au-Pd@SiO_2$  core-shell, f) Au-Pd@MS yolk-shell, g)  $MoO_2@MSiO_2$  core-shell, and h)  $MoO_2@MS$  yolkshell. i) XRD patterns of these studied structures.

ure 3 a) as a precursor, the yolk-shell structure of Fe<sub>3</sub>O<sub>4</sub>@MS was also successfully obtained (Figure 3b). The Fe<sub>3</sub>O<sub>4</sub>@MS exhibits strong magnetic property, as it can be collected easily with an external magnetic bar (within 7 s, see Supporting Information, section SI-5). Other yolk-shell structures with different compositions and shapes can be readily produced by replacing the core materials, such as Ag NPs, MoO<sub>2</sub> NPs and flowershaped Au-Pd alloy NPs. The synthetic conditions were also optimised (see the Supporting Information section SI-1) in order to deposit uniform silica coating on the cores (Figure 3 c, e, g). As evidenced in the yolk-shell structures of Ag@MS (Figure 3d and Supporting Information, section SI-6), Au-Pd@MS (Figure 3 f and Supporting Information, section SI-7) and MoO<sub>2</sub>@MS (Figure 3 h and Supporting Information, section SI-8), the silica layer could be converted completely to MS shells, while the preinstalled cores were kept intact. Moreover, the XRD patterns of Figure 3i and EDX elemental mapping (see Supporting Information, section SI-8) also elucidate the presence of the nanoparticles within the MS shells. These "designed" yolk-shell structures, which could also be viewed as nanoreactors, endow the trapped core materials with excellent anti-aggregation properties. In addition to the applications in solution phase, high thermal stability of MS shells is very suitable for reactions at high temperatures. Such MS-supported catalysts are expected to be workable at harsh conditions,<sup>[12]</sup> which will be explored below for CO<sub>2</sub> hydrogenation.

CNTs are generally recognised as one of the best and most easily available one-dimensional nanomaterials. In Figure 4a, we also extended the spherical MS to one-dimensional structure by using  $CNT@mSiO_2$  as a precursor for the same transformative synthesis (see Supporting Information, section SI-9). Fig-



Figure 4. TEM images of a)  $CNT@mSiO_2$  core-shell; b) and c) CNT@MS yolk-shell; d)  $CNT@Au-Pd@mSiO_2$  core-shell; e) and f) CNT@Au-Pd@MS yolk-shell; and g) and h) tubular Au-Pd@MS. i) XRD patterns of these studied structures.

ure 4b, c display the typical TEM images of the as-prepared CNT@MS. As expected, the product preserves the shape of the original CNT@mSiO<sub>2</sub> and the CNTs were encapsulated within the central cavity. Analogously, we also fabricated CNT@ Au-Pd@MS catalysts employing CNT@Au-Pd@mSiO<sub>2</sub> as a precursor (Figure 2d (10 and 11) and Figure 4e, d, f). TEM images (Figure 4e,f and Supporting Information, section SI-10) show that the Au-Pd alloy NPs (size: 1.4 to 3.3 nm) are located on the CNTs backbones inside the hollow cavity of the CNT@ Au-Pd@MS. The XRD results of Figure 4i affirm the presences of Au-Pd alloy, CNTs, and manganese silicate in this product. The CNT@Au-Pd@MS has a surface area of 388 m<sup>2</sup>g<sup>-1</sup> and a pore volume of  $0.59 \text{ cm}^3 \text{g}^{-1}$  (Figure 2a). In addition, the CNTs inside this structure could be removed thermally (e.g., at 500 °C), and the thus obtained tubular Au-Pd@MS was also characterised by TEM (Figure 4 g, h and Supporting Information, section SI-10).

The metal NPs not only can be encapsulated inside the MS, but also be dispersed on the external surface of MS (Figure 2 d, **5–7**). The MS@Pt catalyst was prepared under in situ hydro-thermal conditions with potassium tetrachloroplatinate. As revealed by TEM (Figure 5 a, b) and STEM (Figure 5 c and Supporting Information, section SI-11) techniques, Pt NPs with a uniform size of 3.3 nm were highly dispersed on the surfaces of the MS and the bubble feature of MS was well maintained after metal loading. A high-resolution TEM image in Figure 5 d shows that the lattice fringe of Pt NPs is approximately 2.3 Å, consistent with the  $d_{111}$  value of platinum. Furthermore, chemical states of the surface Mn and Pt were investigated by XPS method (Figure 5 e and Supporting Information, section SI-11), revealing that Pt existed mainly as Pt<sup>0</sup> (ca. 68%) and surface-



**Figure 5.** a)–d) TEM, STEM and HRTEM images of the MS@Pt catalyst; e) XPS spectra of Pt 4f regions recorded on the MS@Pt catalyst (top) and pristine MS sample (bottom); f) XRD patterns of the MS@Pt catalyst; and g) elemental mappings of the MS@Pt catalyst.

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means of a reverse water gas shift reaction (see Supporting Information, section SI-13).<sup>[14]</sup> A certain amount of methanol and methane were found as by-products. Using the MS@Pt, the conversion increased considerably with temperature and pressure due to the endothermic reaction (Figure 6a, b). It should be mentioned that the hydrogenation of CO<sub>2</sub> towards CO was favourable at a high temperature, but at a low pressure (Figure 6b). Under the same pressure (0.1 MPa), for example, the CO<sub>2</sub> conversion was achieved at 30% with selectivity to CO at 97% at 673 K, while the selectivity to methanol and methane was 11 and 8%, respectively, at 548 K. Under the optimal conditions, a high turnover frequency (TOF) of 0.51 s<sup>-1</sup> (or 1836 h<sup>-1</sup>) was achieved, which is significantly higher than some previous results (see Supporting Information, section SI-13). In addition, the apparent activation energy  $(E_a)$  of the process was determined. As shown in Arrhenius plots of Figure 6 c, E<sub>a</sub> values of the MS@Pt and CNT@Au-Pd@MS were 47 and 32 kJ mol<sup>-1</sup>, respectively, which are much lower than other literature data.<sup>[15]</sup> By contrast, very low activity was observed for Au@MS catalyst with only 1.7% CO2 conversion at 673 K and 0.1 MPa, largely due to the big size of Au NPs (ca. 15 nm; inac-

oxidised Pt<sup>II</sup> (ca. 32%). In agreement with the findings from both TEM and XPS analyses, the XRD patterns in Figure 5 f show that the MS@Pt catalyst was composed of platinum (at a size of 3.7 nm; Scherrer method), blythite-type manganese silicate and others (e.g.,  $Mn_2SiO_4$  and Mn<sub>3</sub>O<sub>4</sub>). Again, results from EDX elemental mapping shown in Figure 5 g confirm its structural configuration, and an N<sub>2</sub> physisorption study (Figure 2a) indicates that MS@Pt has a specific area of  $210 \text{ m}^2 \text{g}^{-1}$ , surface a pore volume of  $0.23 \text{ cm}^3 \text{g}^{-1}$ and an average mesopore size of 3.9 nm. Moreover, other types of NPs can also be immobilised on the external surface of MS, such as Ni, Co and Au NPs (see the Supporting Information, section SI-12).

We also carried out  $CO_2$  hydrogenation as a test reaction to verify the effectiveness of these hybrid nanocatalysts,<sup>[13]</sup> namely the MS@Pt, Au@MS and CNT@Au-Pd@MS, at 548 to 673 K and 0.1, 1, 2 and 3 MPa. Firstly, we found that the MS@Pt catalyst was very selective towards the CO formation by

35 CO selectivity CO selectivity Conversion (%) Conversion (%) 30 20 25 80 20 15 15 70 10 + CO<sub>2</sub> conversion 10 + CO<sub>2</sub> conversion -60 CO selectivity (% % 5 5 - CO selectivity 0+ 580 600 620 640 660 680 **Temperature (K)** Pressure (MPa) d С -1.0 CO selectivity -1.5 Conversion (%) 80 -2.0 MS@Pt 20 60 -2.5 L -3.0 10 -3.5 CO<sub>2</sub> conversion (% 5 CO selectivity -4.0 CNT@Au-Pd@MS -4.5 <del>+</del> 1.45 1.50 1.55 1.60 1.65 1.70 1.75 1.80 1.85 20 10 15 25 30  $1000/T (K^{-1})$ Time on stream (h) e 12 20 dopant-free MS@Pt Conversion (%) Nd SBA-15@Pt Conversion (%) 10 16 La Ni silicate@Pt Sm 8 12 Ce 573 598 Temperature (K) **Temperature (K)** 

**Figure 6.** a) Catalytic performance of the MS@Pt as a function of reaction temperature at a feed pressure of 0.1 MPa; b) catalytic performance of the MS@Pt as a function of pressure at 623 K; c) Arrhenius plots of ln(r) versus 1/T for  $CO_2$  hydrogenation with different catalysts; d) catalytic performance of the MS@Pt as a function of time-on-stream at 623 K and 0.1 MPa; e) comparison of catalytic performance of Pt catalysts over different supports at 0.1 MPa (feed pressure); and f) comparison of catalytic performance of the MS@Pt catalysts with different rare-earth-metal dopants at 0.1 MPa.

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tive surface sites) and the low metal loading (0.52 wt%). The operating stability of these catalysts is remarkable; Figure 6d illustrates the catalyst performance of the MS@Pt over a period of 24 h, showing that there was no significant decrease in both the activity and selectivity. Our TEM investigation on the three types of catalysts after reactions proves that there is no major change in particle size and morphology (see the Supporting Information, section SI-13).

In order to demonstrate the synergetic effect between the Pt and MS, we also studied the catalytic performance of Pt catalysts on other support materials (e.g., SBA-15 and Ni-silicate; see the Supporting Information, section SI-13). Encouragingly, our MS based Pt catalysts exhibited the highest conversion (Figure 6 e). Concerning the product selectivity, no alcohol products (only CO and methane) were detected with the SBA-15@Pt and Ni-silicate@Pt catalysts. Based on these results, it is believed that the production of methanol is due to the presence of manganese. Previous studies have shown that Mn can act as both electronic modifier and structural promoter for catalysts, which favours the hydrogenation of CO<sub>2</sub> into valueadded oxygenates or olefin over methane.<sup>[16]</sup> Furthermore, it has been reported that the catalytic performance for CO<sub>2</sub> hydrogenation can be enhanced by adding rare-earth promoters to the catalyst.<sup>[17]</sup> Herein, the MS shell of MS@Pt catalyst was doped with five different rare-earth elements (namely, Y, La, Ce, Nd and Sm).<sup>[6]</sup> The effect of the dopant is shown in Figure 6 f. In general, catalysts with rare-earth doped MS shell could bring about appreciable enhancement in activity. For example, the reaction rate of Y-doped MS@Pt catalyst is about two times higher than that of the pristine MS@Pt at 548 K. The apparent activation energy of CO<sub>2</sub> hydrogenation over the doped catalysts decreases in the order of Nd (50 kJ mol<sup>-1</sup>) >  $(44 \text{ kJ mol}^{-1}) > \text{La}$   $(43 \text{ kJ mol}^{-1}) > \text{Ce}$   $(38 \text{ kJ mol}^{-1}) > \text{Y}$ Sm (35 kJ mol<sup>-1</sup>). The enhanced activities could be ascribed to the change of surface basicity (or amount of oxygen vacancy) of the catalysts, which in turn promotes the adsorption and activation of CO<sub>2</sub>.<sup>[18]</sup>

In summary, pure or doped nanobubble-like manganese silicate can be used as a versatile platform for the design and synthesis of a range of spherical and tubular catalysts. In addition to the flexibility in structural architecture and compositional tailoring, the attained interbubble space can serve as a new form of mesoporosity for protecting and/or supporting catalytically active phases. Because of their high chemical and thermal stability, the "bubble catalysts" can also work effectively in both solution and gas environments.

## **Experimental Section**

Detailed information on the chemicals used, treatments, and characterisation of products can be found in the Supporting Information section SI-1. The following are brief experimental highlights.

**Synthesis of NP@SiO<sub>2</sub> core-shell**: The silica beads were prepared with a modified Stöber process through hydrolysis/condensation of tetraethyl orthosilicate (TEOS) in aqueous solutions containing ethanol (or isopropanol), ammonium (or triethanoamine), surfactants (e.g., CTAB, cetyl trimethylammonium chloride (CTAC) and

polyvinylpyrrolidone (PVP)) and core materials (e.g., Au, Ag, Au–Pd, MoO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, CNT and CNT@Au–Pd). To prepare the Au@SiO<sub>2</sub>, for example, PVP-stabilised Au NPs (3 mL) was dispersed into a mixture of isopropanol (25 mL) and H<sub>2</sub>O (5 mL) with ultrasonication for 0.5 h. Then ammonium (0.6 mL) and TEOS (1.2 mL) were added successively into the mixture. The mixture was further stirred for 16 h at room temperature before collecting the solid by centrifuging and washing with ethanol twice. Details on the preparation processes of other core–shell structures Ag@SiO<sub>2</sub>, Au–Pd@SiO<sub>2</sub>, MoO<sub>2</sub>@mSiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, CNT@mSiO<sub>2</sub> and CNT@Au–Pd@mSiO<sub>2</sub> can be found in the Supporting Information, section SI-1.

**Synthesis of NP@MS yolk-shell**: In a typical synthesis, the aboveprepared NPs@SiO<sub>2</sub> core-shell (10–50 mg) was dispersed in H<sub>2</sub>O (10 mL) with ultrasonication for 0.5 h. During this period, MnSO<sub>4</sub> (50–150 mg) and sodium malate (50–200 mg) were dissolved in H<sub>2</sub>O (10 mL). Afterwards, the solid suspension was poured into the MnSO<sub>4</sub> and sodium malate solution under vigorous stirring for 10 min. The mixture was then transferred to a Teflon-lined autoclave and hydrothermal treated at 180 °C for 12 h. After the reaction, the yolk-shell products were collected by centrifugation, followed by washing with ethanol (40 mL×2) and drying at 60 °C overnight. Information on the optimised parameters during the synthesis for different structures can be found in the Supporting Information, section SI-1.

**Synthesis of MS@Pt catalysts**: Briefly, SiO<sub>2</sub> beads (60 mg) were dispersed in H<sub>2</sub>O (10 mL) with ultrasonication for 0.5 h. During this period, of MnSO<sub>4</sub> (136.6 mg), sodium malate (180 mg) and K<sub>2</sub>PtCl<sub>4</sub> (0.6 mL, 75 mM) were dissolved in H<sub>2</sub>O (10 mL), into which the suspension of SiO<sub>2</sub> beads was poured under vigorous stirring for 10 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 12 h. The brown product was harvested by centrifugation, followed by washing with ethanol (40 mL × 2) and drying at 60 °C overnight. Rareearth-metal-doped MS@Pt catalysts were also prepared in a similar way, except that MnSO<sub>4</sub> (136.6 mg) was mixed together with rareearth metal salts (0.04 mmol) such as Y(NO<sub>3</sub>)<sub>3</sub>, La(NO<sub>3</sub>)<sub>3</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, Nd(NO<sub>3</sub>)<sub>3</sub>.

**Catalytic evaluation**: The CO<sub>2</sub> hydrogenation was carried out in a continuous flow fixed bed reactor made of stainless-steel by using 0.20 g of the catalyst. A feed mixture (H<sub>2</sub>/CO<sub>2</sub>=3) was introduced with the space velocity of 9600 mLg<sub>catalyst</sub><sup>-1</sup>h<sup>-1</sup>. The temperature was measured with a thermocouple located at the centre of the catalyst bed. Concentrations of reactants and products were measured online by a gas chromatographic system.

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**Keywords:** CO<sub>2</sub> hydrogenation • heterogeneous catalysis • hollow structures • manganese silicate • mesoporous materials

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