

Tailorable formation of hierarchical structure silica (HMS) and its application in hydrogen production

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Abstract: Relentless endeavors have been committed to seek simple structure directing agent for synthesizing hierarchical mesoporous silica (HMS) materials but remaining challenges. In this contribution, we offered an improved one-pot hydrothermal route to prepare HMS materials using single non-ionic triblock co-polymer (F127) structure directing agent under mild polycarboxylic (citric acid) mediated condition. Via studies of key synthetic parameters including acid concentration, crystallization temperature and aging time, it is found that citric acid medium presents an important bridging effect under the optimal concentration from 0.018 M (pH = 2.57) to 1.82 M (pH = 1.09), contributing to the self-assembly of partially protonated non-ionic triblock copolymer and tetraethyl orthosilicate (TEOS) into high-quality multistage structure of silica materials. The specific surface area (SSA) of HMS shows a volcanic trend and is closely associated with the concentration of citric acid while the highest SSA of 739.9 m²/g can be achieved at the citric concentration of 0.28 M. Moreover, the as-synthesized HMS-CTA supported Ni/CeO₂ catalysts indicate an excellent production of hydrogen through dry reforming of methane (DRM) reaction over 172 h stability. The improved, facile synthesis strategy under polycarboxylic medium displays an expanded perspective for synthesizing other mesoporous materials in a wide range of applications such as catalytic material carrier, drug inhibitor and so on.

Keywords: Hierarchical silica; Polycarboxylic; Protonation; Triblock copolymer; Catalytic support; Hydrogen

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1. Introduction

Hierarchical mesoporous silica (HMS) materials are prestigious porous materials. Their interconnected periodic substructure, high specific surface area as well as high loading capacity are particularly attractive of the wide applications including catalysis, adsorption, separation, life science, energy storage and so on [1-5]. The most common synthesis route to HMS is implemented via the combinative self-assembly of nonionic block copolymers and silicate molecules [6,7]. For instance, ABC (ie. PE-b-PEO-b-PCL), ABA (ie. PEO-a-PPO-b-PEO-a) types triblock copolymers have attracted great attentions owing to their biodegradability, nontoxicity, and excellent interfacial stability. They have been widely applied as structure-directing agents to induce the formation of abundant spatial structure with various morphology (Nanoparticles, fibers, rods), such as cubic mesophase and hexagonal mesophase [8-10].

Generally, the secondary surfactants or additives are always engaged to construct these hierarchical mesoporous silica (HMS) materials [11]. Esquena et al. reported that silica materials characterized with a dual pore size distribution was prepared under a highly concentrated co-templating emulsions conditions, where the co-templates consist of emulsions droplets (C₁₂(EO)₈/decane) and cubic liquid crystal of PEO-PPO-PEO block

copolymer nonionic surfactant. The emulsion droplets would induce the formation of macropores whereas nonionic surfactant would template the formation of the mesopores structure [12]. Zhou et al. synthesized a series of micro/mesoporous silica materials using non-ionic block copolymer Pluronic (P123) and triethylamine acetate (PIL) as co-templates. The sub-structure of silica was closely related to the content of PIL and hydrothermal conditions [13]. Liu et al. prepared hierarchical mesoporous silicas using the triblock copolymer PEO₁₀₆-PPO₇₀-PEO₁₀₆ (F127) and the diblock copolymer poly(ethylene oxide-*b*- ϵ -caprolactone) (PEO-*b*-PCL) as co-templates [14]. Moreover, Shi et al found that hierarchically porous materials can be obtained from the polyelectrolyte-surfactant complex templating strategy [9]. The combination between surfactant templates and hard templates is another important approach in the formation of the hierarchical pore structure, as Stein et al. reviewed [15]. However, the secondary template would undoubtedly increase the complexity of preparation process, i.e. reaction conditions and formation mechanisms. Therefore, it is urgent to develop an efficient process to prepare hierarchical silica materials using only one type of surfactant to better meet the practical convenience.

Zhao et al. firstly reported that ABC amphiphilic triblock copolymer of poly(ethylene oxide)-block-poly(methyl methacrylate)-block-polystyrene (PEO-*b*-PMMA-*b*-PS) was of great importance for fabricating mesoporous materials [16]. However, the interconnected hydrophobic parts (PMMA and PS) were only capable to induce single hydrophobic domain and produce the mesoporous material with single pore size. Li et al. found that the hierarchical mesoporous silicas featured with two kinds of mesoporous size were synthesized using different hydrophobic segments (poly ethylene and poly ϵ -caprolactone), separately grafted at the chain end of the poly ethylene oxide [17]. It can be concluded that the location of hydrophobic segments plays an important role in strategically forming the hierarchical mesoporous morphology. These two kinds of hydrophobic groups were separately located at the end of the PEO, which showed an advantage in regulating the multistage spatial structure. However, it is rarely reported that these hierarchical silica structures can be prepared using only one ABA type of structure directing agent (ABA, where the same hydrophobic groups are separately located at the end of the PEO) via a convenient evaporation-induced self-assembly (EISA) strategy [10]. In our previous study, we reported that polycarboxylic acids (citric acid) plays a key role in preparing high-quality mesoporous silica without the addition of mineral acid (HCl) [18]. In this contribution, we deeply investigate the interaction between the non-ionic triblock co-polymer and polycarboxylic acid and their influence on the pore structure formation of silica materials. Surprisingly, hierarchical mesoporous silica (HMS) was formed with tunable dual pore structure. Via detailed characterization, we believe that the self-assembly of partially protonated non-ionic triblock copolymer and tetraethyl orthosilicate (TEOS) plays a key role for the formation of high-quality multistage structure of silica materials.

Moreover, the hydrogen economy boom has drawn great attention because of the environmental and energy crisis [19-21]. The route of hydrogen production via dry reforming of methane (DRM) reaction has become a hot scientific topic, covering the research on active compositions, catalysts carriers as well as their additives [22]. Catalysts support, as one of the core components, is vital to command the interaction strength between the metal and support, dispersion of the active species and the exposure of active center [23]. Undoubtedly, the mesoporous silica is propitious due to its large specific surface area, thermal stability and easy availability [23]. However, the weak interaction between active species and silica carrier causes the sintering of large metal nanoparticles, and formation of carbon deposition, resulting the less formation of hydrogen, especially on Ni-based catalysts [24]. It is usually advocated that the introduction of promoter would favor the adjustment of the above drawbacks. For example, the CeO₂ could not only improve the dispersion of Ni nanoparticles, but also activate carbon dioxide into mobile oxygen species and promote the carbon removal owing to its unique redox properties ($Ce^{4+} \leftrightarrow Ce^{3+}$), thermal resistance and enhancement of the metal-support interaction [25,26]. In our recently study, we found that the ceria loading interval ranges from 10 wt.%

to 30 wt.% exhibited outstanding production of hydrogen with different carbon deposition resistance. The optimized ceria loading of 15 wt.% (5Ni/15CeO₂-SBA-15-CTA) catalyst yielded the best anti-coke performance with the lowest coke deposition rate of 13.5 wt.% during 170 h DRM reaction [27]. These above interesting scientific phenomena inspire us to develop novel HMS and to support Ni/CeO₂ catalysts for hydrogen formation via DRM strategy.

2. Results and discussions

2.1 Formation mechanism of HMS materials

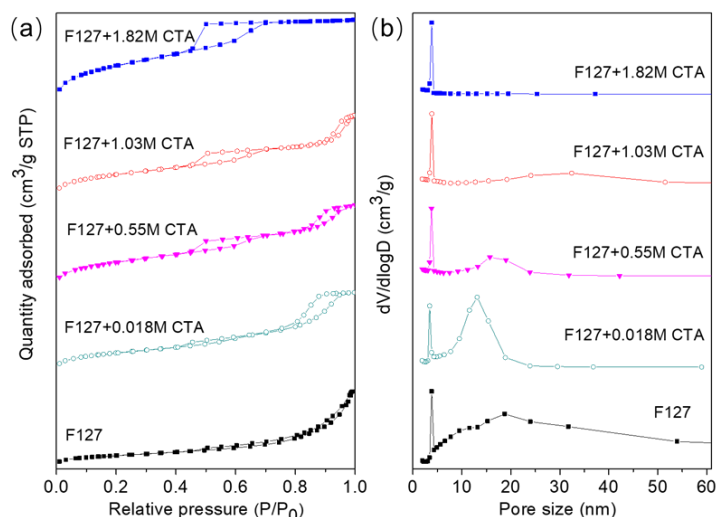


Figure 1. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) profiles of the calcined HMS samples.

Figure 1 depicted that hierarchical mesoporous silica synthesized using F127 as template under various citric acid concentration from zero to 0.018 mol/L (pH = 2.57) and 1.82 mol/L (pH = 1.09). Without citric acid, the silica indicates the typical nitrogen adsorption-desorption behavior as mesoporous material. While citric acid was added from 0.18 to 1.03 mol/L, their typical type-IV curves clearly highlights two overlapping hysteresis loops, indicating a hierarchical feature with two types of pores (Figure 1a). Figure 1b presented the pore size distribution curves of the prepared products, the adjustment of mesoporous size hinges on the concentration of citric acid (or pH). The high concentration (i.e. 1.82 mol/L) of acid or low pH would only cause a single mesoporous structure. On the contrary, the relatively low concentration of citric acid would facilitate the synthesis of HMS materials. Results suggest a controllable synthesis of silica materials with double mesoporous structure using a facile approach. Moreover, the specific surface area (SSA) of HMS was also closely associated with the concentration of citric acid. As displayed in Table 1, the SSA showed a volcanic trend with citric concentration for the HMS materials. The highest SSA of 739.9 m²/g (Entry 4) was achieved at the citric concentration of 0.28 mol/L. However, an even higher SSA can be obtained for a single mesoporous silica material at a high concentration of polycarboxylic acid at 1.82 mol/L, which is likely originated from the degree of well-ordered substructure.

Table 1. Preparation conditions and physicochemical properties of the synthesized hierarchical mesoporous silica.

Entry No.	F127 mass (g)	Citric concentration (mol/L)	Hydrothermal Temp./Time (°C, h)	pH value	S _{BET} (m ² /g)	Micropore Area (m ² /g)	Volume (cm ³ /g)	Pore size (nm)
1	2.5	0	100, 24	6.80	332.9	29.3	0.78	10.84

2	2.5	0.018	100, 24	2.57	651.1	88.8	0.95	6.80
3	2.5	0.055	100, 24	2.20	690.4	86.9	0.99	6.87
4	2.5	0.28	100, 24	1.82	739.9	86.4	0.75	4.78
5	2.5	0.55	100, 24	1.63	725.8	69.6	0.78	5.21
6	2.5	1.03	100, 24	1.40	703.2	74.2	0.88	5.76
7	2.5	1.82	100, 24	1.09	782.4	142.7	0.61	3.45
8	2.5	0.28	60, 24	1.82	443.2	181.6	0.29	3.18
9	2.5	0.28	140, 24	1.82	565.3	26.0	1.38	9.37
10	2.5	0.28	100, 4	1.82	502.3	167.1	0.36	3.44
11	2.5	0.28	100, 8	1.82	546.2	160.2	0.46	4.12
12	2.5	0.28	100, 16	1.82	702.6	104.2	0.69	4.67
13	2.5	0.28	100, 48	1.82	792.3	30.3	0.95	5.13
14	2.5	0.28	100, 72	1.82	729.7	18.2	0.96	5.39
15	2.5	0.28	100, 140	1.82	745.2	34.5	1.17	6.09
16	2.5	0.28	100, 480	1.82	629.7	55.7	1.16	8.28
17	0	1.03	100, 24	1.40	586.3	NA	1.23	7.65

According to the literatures, it is well known that the hydrothermal temperature would favor adjusting the pore substructure owing to the temperature sensitivity of polymerization between inorganic silicate and copolymer micelle [18,28]. Taking the hydrothermal temperature into consideration, it was found that a suitable temperature at 100 °C is necessary for preparing the well-ordered double-porous materials. Either higher or lower hydrothermal temperature can cause fatal defects, resulting the decrease of SSA (eg. 60 °C, 443.2 m²/g, Entry 8; 100 °C, 739.9 m²/g, Entry 8; 140 °C, 565.3 m²/g, Entry 9), as Figure 2a, 2b and Table 1 depicted.

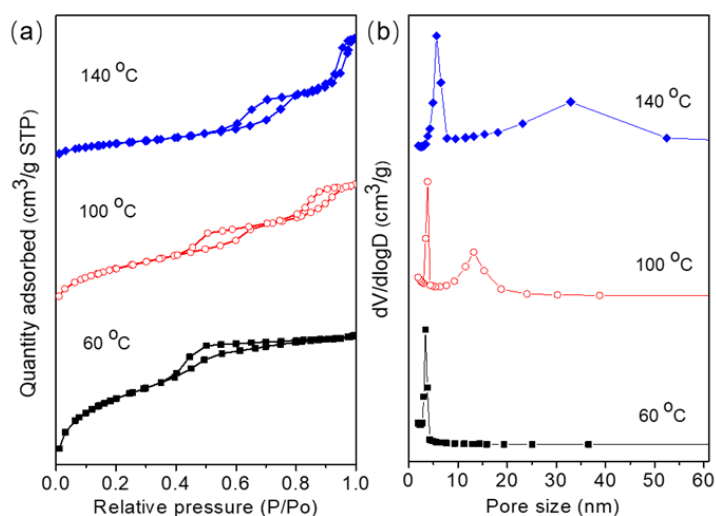


Figure 2. N₂-BET (a) and pore size distribution (b) curves of HMS materials (Entry No.4) synthesized under different hydrothermal temperature.

Moreover, the hydrothermal time dependence on mesoporous silica materials prepared under 0.28 mol/L citric acid was performed and showed in Figure 3. It was found that the hierarchical mesoporous silica with two typical hysteresis loops can only be formed while the duration time of hydrothermal was longer than 8 h (e.g. 16 h and 140 h) (Figure 3a). The hierarchical double pores were gradually formed and solidified during the extension of the hydrothermal treatment time (4 h - 8 h - 16 h -140 h-480 h). On the other hand, their pore size was positively increased along with the treatment time (Figure 3b and Table 1). Pore size ranges from 3.44 nm (Entry 10, 4h) to 6.09 nm (Entry 15, 140 h). The variation trend of specific surface area presents a volcanic shape, peaked at 792.3 m²/g (Entry 13). It may suggest that the extended hydrothermal time (>48h) would reduce the specific surface area of HMS materials with an enlarged pore size. Results are consistent

with the report using the hyper-protonation of PEO block [28], where a stronger affinity to the silicate (TEOS) than that of the hydrophobic PPO block was found under the enduring reaction time, inducing the deep penetration of PEO chains into the frameworks of silicate micelles, and subsequent pore size expansion after calcination. It is worth to be pointed out that the hierarchical merit with 629.7 m²/g SSA can be retained under the extended hydrothermal time of 480 h (20 day), indicating the hierarchical double pore structure is hydrothermally stable even with an excessive prolongation of the hydrothermal time up to 20 day (Figure 3a).

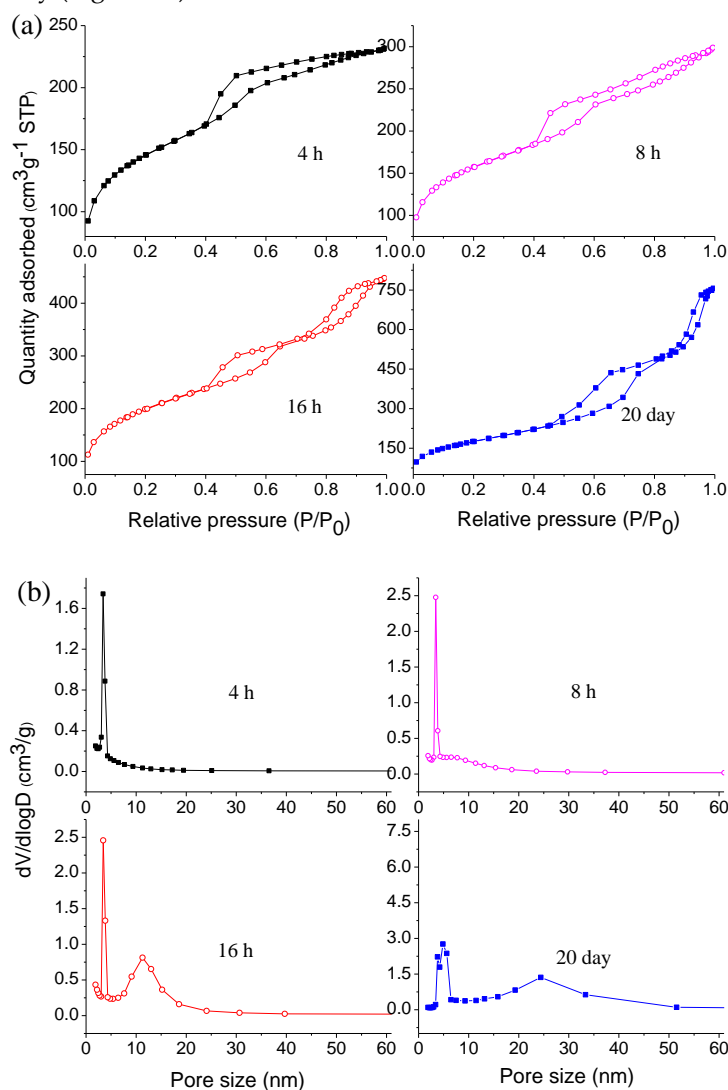


Figure 3. The curves of N₂-BET (a) and pore size distribution (b) for HMS samples were selected as the function of reaction time ranges from 4 h to 480 h.

From the data of SSA and pore structure, it was inferred that the merit of double-pore structure mainly depends on the mediated dose of citric acid amount and the optimized hydrothermal time (≥ 16 h). Small-angle ($2\theta = 0-6^\circ$) XRD patterns were recorded on a Bruker D8 Advance X-ray diffraction meter, to study the crystal phase or periodic structure of synthesized HMS materials. As shown in Figure 4, no periodic structure was formed only with F127 as surfactants. The mesoporous structure can only be formed with the coordination of F127 and citric acid, clearly indicating the importance of the mediation from citric acid. It was found that the high concentration of citric acid could benefit the formation of well-ordered cubic structure, as the Figure 4 indicated. An apparent diffraction intensity appears with a large d spacing of 115 Å (110), and another two weak

diffraction peaks reflect in the range of 1-1.4° with interplanar d spacing of 72.9 Å (200) and 64.0 Å (211), which should correspond to a cubic structure (*Im3m* space group, SBA-16) [7,29]. Thus, it was worthwhile noting that the silica materials with a periodic pore structure would not be easily synthesized under the low concentration citric modulator.

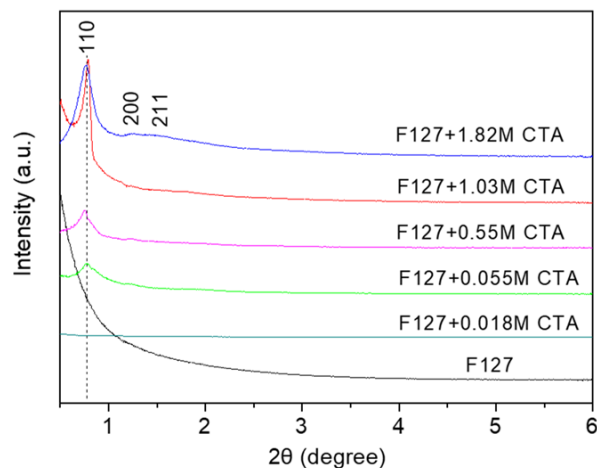


Figure 4. Small-angle XRD patterns of the calcined HMS samples.

In order to uncover the microstructure of the as-prepared HMS materials, we took the measurement of TEM observation of the typical HMS sample synthesized under the CTA concentration of 0.28 mol/L (pH =1.82) calcined at 550 °C. The TEM and HRTEM (inset) images displayed in Figure 5 exhibits the well-ordered arrays and reveals an antipant 3D cubic microstructure. Which well corresponds to the results of small angle XRD and BET measurements.

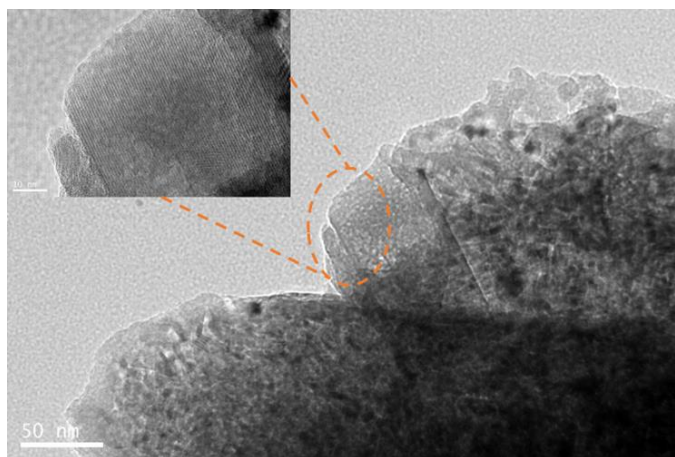
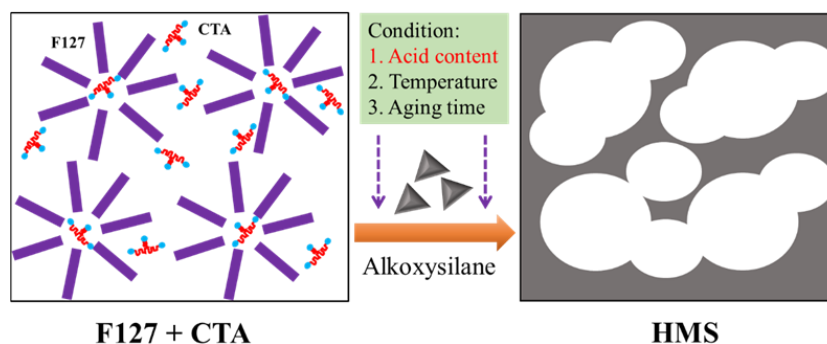


Figure 5. TEM images of HMS calcined at 550 °C.

According to the above characterization results, the microstructure of mesoporous silica is closely related to the synthesis conditions such as concentration of citric acid, hydrothermal temperature as well as hydrothermal time. The proposed formation mechanism was briefly proposed in Scheme 1. Optimal acid conditions (0.018 - 1.82 mol/L), hydrothermal temperature (100 °C) and hydrothermal time (16 h) were necessary for the synthesis. However, it was noting that the content of citric regulator is the key controlling parameter to synthesize HMS materials. Stronger acidity (above 1.82 mol/L) would promote a rapid hydrolysis/condensation of silicate species that would form a well-ordered cubic structure (SBA-16). The formation of HMS probably originated from the incomplete

condensation of silicate under the mild acid condition (Scheme 1). Moreover, it was accepted that the aging process would enhance the silicates condensation and the hydrothermal stability of the HMS materials. In this contribution, prolonged hydrothermal treatment should not be advocated due to the minor changes in structure, accompanied by the enlargement of the pore size.



Scheme 1. Formation mechanism of an inorganic network of HMS with different pore sizes by applying single non-ionic triblock co-polymer (F127) under citric acid condition.

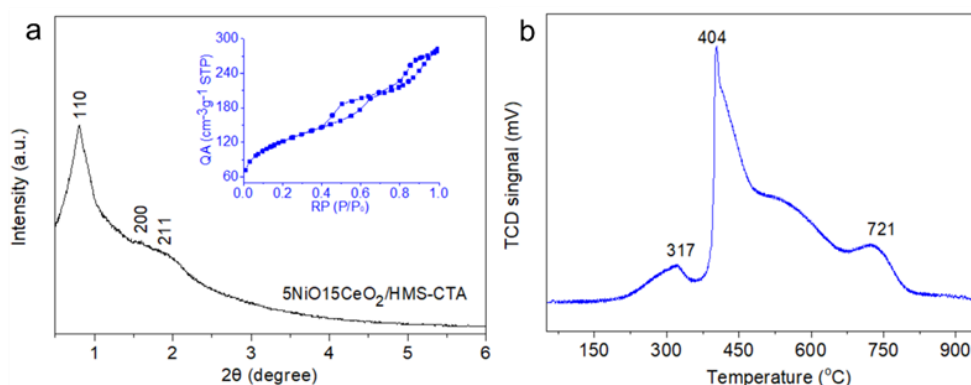


Figure 6. Small-angle XRD pattern (a) of the 5NiO15CeO₂/HMS-CTA catalyst and H₂-TPR (b) profile of 5NiO15CeO₂/HMS-CTA sample, the inserted image (left) correspond to its nitrogen adsorption-desorption isotherms curve.

2.2 Catalytic activity of Ni based catalysts in DRM reaction

These porous silica materials possess high surface areas and tunable pore dimensions (2–50 nm), where the relatively large pores would enhance mass transfer, while the high surface area facilitates the exposure of active centers per mass of catalysts, which are of great catalyst carrier candidate for heterogeneous catalysis, such as DRM [23,30,31]. In our previous contributions, high-quality SBA-15-CTA (CTA signifies citric acid) materials with typical 2D hexagonal pore structure have been successfully prepared under moderate polycarboxylic citric acid, being utilized to synthesize Ni/SBA-15-CTA and CeO₂ doped NiCeO₂/SBA-15-CTA hybrid catalysts [18,27]. The catalytic activity results showed that the addition of CeO₂ could significantly improve the sintering resistance properties of Ni and carbon elimination rate due to the strong interaction between Ni nanoparticles and CeO₂ additives [27]. In this contribution, we will secondly explore the relationship between the strong interaction of metal-support and its performance on the new hierarchical silica carrier, to evaluate their application prospects of our multi-porous silica materials. Figure 6a displayed the structural periodicity of the synthesized hierarchical materials loaded by active species of Ni (5 wt.%) and additive of CeO₂ (15 wt.%), it was found that the addition of active Ni nanoparticles and additive of CeO₂ would not damage the spatial microstructure of HMS materials. However, the SSA of 429.1 m²/g showed a

decreasing tendency compared to the SSA of 739.9 m²/g of HMS-CTA parent carrier as the channels are clogged with some nanoparticles (NiO and CeO₂) to some extent (inserted adsorption desorption curve of Figure 6a). Moreover, the first reduction peak (317 °C) of NiO nanoparticles and surface oxygen in ceria for 5NiO15CeO₂/HMS-CTA catalyst becomes narrower and shifted to the lower temperature (404 °C, Figure 6b) than the 5NiO15CeO₂/SBA-15-CTA (464 °C), revealing that CeO₂ could better promoted the dispersion of NiO nanoparticles on HMS carriers uniformly than that on 2D silica [27,32]. Nevertheless, the second reduction peaks of 404 °C and wide peak of 450 °C should be attributed to the reduction of NiO species with strong interaction with CeO₂ on HMS support, well corresponds to our previous study [33]. For the fourth reduction peak around 721 °C, which reflected the reduction of Ce⁴⁺ → Ce³⁺ species [34]. It's worth noting that CeO₂ indeed improves the dispersion of NiO species and strengthens the interaction between metal and carriers of HMS materials.

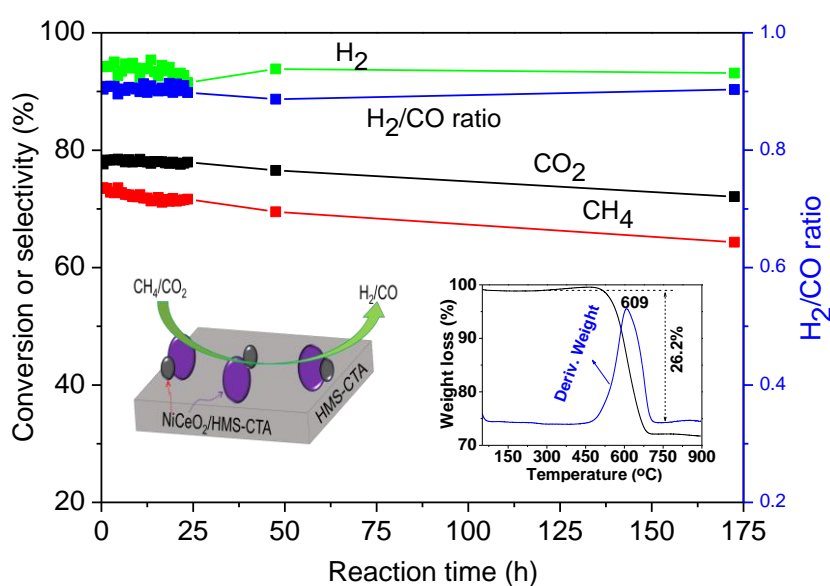


Figure 7. DRM activity results for the 5Ni15CeO₂/HMS-CTA catalyst, the left inserted image stands for the reaction mechanism, the right inserted image presents the weight loss curve of the used catalyst.

The catalytic activity of 5NiO15CeO₂/HMS-CTA catalyst was evaluated for 172 h at 700 °C in Figure 7. It was found that the initial conversion of CO₂ and CH₄ reached ca. 77.8% and 73.2%, with 93.2% H₂ selectivity and H₂/CO molar ratio of 0.91. Moreover, CO₂ conversion, CH₄ conversion, H₂ selectivity and H₂/CO molar ratio were maintained at ca. 71.5%, 64.1%, 91.8% and 0.90 after 172 h long term stability testing (Figure 7). The syngas production rate is substantially higher than that of reports on common amorphous silica supported Ni-based catalysts (<85%) [24,26]. Moreover, the weight loss curve on spent 5NiO15CeO₂/HMS-CTA catalyst was 26.2 wt.% for 172 h with a DTA peak of 609 °C (right inserted image in Figure 7) probably further confirm that the graphitic carbon was successfully hindered and the formed coke was more reactive over 5NiO15CeO₂/HMS-CTA catalyst [35]. Hence, the synthesized HMS materials present a great potential in heterogeneous catalysis field. In addition, it is noted that the CO₂ conversion was slightly superior to that of CH₄, which is mainly originated from the presence of side effect from reverse water gas shift reaction under high temperature condition [36,37]. According to previous studies, the optimal loading of ceria promoter should be located at ca. 15 wt.% for Ni-based catalysts supported on the mesoporous silica carriers such as SBA-15 and SBA-16 for DRM reaction [27,38]. The enhanced interaction between Ni nanoparticle and ceria over HMS could better improve the dispersion of active Ni species and achieve the high

syngas formation rate. Moreover, the optimized ceria content of 15 wt.% would favor the formation of high concentration of oxygen vacancy as well as Ce^{3+} , serving to the *in-situ* coke removal and promoting the carbon resistance [27,32].

3. Materials and Methods

3.1 Materials

All chemicals, including anhydrous citric acid, tetraethyl orthosilicate ($\geq 98\%$, TEOS), poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P127, $M = 12600 \text{ g mol}^{-1}$), anhydrous ethanol, cerium (III) nitrate hexahydrate and nickel nitrate hexahydrate were purchased from Sigma-Aldrich.

3.2 Materials preparation

HMS materials were synthesized via a self-assembly strategy in deionized water, using F127 as single template and TEOS as the silica precursor. Typically, TEOS (8.75 g) and a certain amount of citric acid were added to a premixed solution (125 mL water and 2.5 g copolymer template P127) and the mixture was stirred at $38 \text{ }^\circ\text{C}$ for 24 h. The resulting solution was poured into a Teflon autoclave and hydrothermally synthesized at various temperature ($60 \text{ }^\circ\text{C}$, $100 \text{ }^\circ\text{C}$ or $140 \text{ }^\circ\text{C}$) for different time range from 4 h to 20 day (Table 1). After that, the crystallized precursor was filtered, washed, and dried at $100 \text{ }^\circ\text{C}$ for 24 h. Finally, the white powder product was calcined at $550 \text{ }^\circ\text{C}$ for 6 h to gain hierarchical mesoporous silica.

The above-mentioned HMS materials (2 g) were impregnated with an aqueous solution of $\text{Ce}(\text{NO}_3)_3$ (0.073 mol/L) and $\text{Ni}(\text{NO}_3)_2$ ($2.5 \times 10^{-4} \text{ mol/L}$), then dried at $100 \text{ }^\circ\text{C}$ for 12 h. After that, the materials were calcined at $750 \text{ }^\circ\text{C}$ for 2 h to obtain catalyst. CeO_2 and Ni loadings were at 15 and 5 wt.%, separately, which was labeled as $5\text{Ni}15\text{CeO}_2/\text{HMS-CTA}$.

3.3. Catalytic activity testing

DRM reaction was investigated in a fixed-bed quartz reactor (ID: 7 mm) at ambient pressure. Specifically, catalysts (150 mg, 45-60 mesh) were uploaded in the central of quartz reactor tube with the hold of quartz wool. Before activity testing, catalysts were pretreated with a flow of $10\% \text{ H}_2/\text{He}$ (50 mL/min) at $700 \text{ }^\circ\text{C}$ with heating rate of $5 \text{ }^\circ\text{C/min}$ for 1 h. Then, the feed gas ($\text{CO}_2/\text{CH}_4/\text{Ar}/\text{N}_2 = 3:3:3:1$) was introduced to the catalysts bed at a total flow rate of 50 mL/min (GHSV of $20,000 \text{ mL}\cdot\text{gcat}^{-1}\cdot\text{h}^{-1}$). The exhausted products were studied using online Gas Chromatograph (Agilent GC-6890) equipped with a TCD detector (a Carbon-Plot coupled with a HP-Plot capillary column).

3.4 Materials characterization

Small-angle ($2\theta: 0-6^\circ$) and normal X-ray diffraction ($2\theta: 5-80^\circ$) XRD patterns were measured on a Bruker D8 Advance X-ray diffractometer with a $\text{Cu K}\alpha$ irradiation. N_2 adsorption-desorption isotherms curves were analyzed on a Micromeritics ASAP 2420 automatic analyzer and the temperature of pretreatment was settled at $200 \text{ }^\circ\text{C}$ under vacuum for 12 h. A FEI Tecnai G2 F20 Transmission electron microscopy (TEM) was employed to test the pore structure of the HMS synthesized materials. Hydrogen temperature programmed reduction (H_2 - TPR) experiment was carried out to study the reduction properties of $5\text{Ni}15\text{CeO}_2/\text{HMS-CTA}$ catalyst on a chemisorption (Thermo Scientific, Auto-ChemII 2920) instrument. The weight loss curve of the spent $5\text{Ni}15\text{CeO}_2/\text{HSM}$ was obtained on a Thermogravimetric analysis instrument (TGA Q500).

4. Conclusion

To sum, we advocated an improved, facile one-pot hydrothermal route to prepare hierarchical mesoporous silica (HMS) materials using single ABA type of non-ionic triblock co-polymer structure directing agent under novel polycarboxylic acid mediated

condition. The process parameters such as citric acid concentration, hydrothermal temperature and crystallization time had been systematically studied. Results revealed that the spatial structure of HMS highly hinges on the concentration interval of citric acid ranges from 0.018 M to 1.82 M owing to the incomplete protonation and bridging effect of citric acid, while the hydrothermal temperature and aging time could more impact the pore distribution and size due to the condensation reactions. Moreover, as-synthesized HMS-CTA supported Ni/CeO₂ catalysts displayed a long-term stability of 172 h during **DRM reaction**. The improved synthesis route for HMS under citric acid medium exhibits great potential for other hierarchical mesoporous materials synthesis and applications in heterogenous catalysis, environmental governance and nanomedicine and so on.

Author Contributions: Experiment, L.L., and Z.L., writing—original draft, L.L., and J.D., characterization, L.L., and Y. L., writing—review and editing, L.L., J.D., and Y.L., project administration, Y.L., and W. C. All authors have confirmed and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no competing interests.

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