Nanostructured $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$ material prepared by colloidal crystal templated sol-gel method for chemical looping with hydrogen storage

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ABSTRACT

Chemical looping is a novel process in clean energy conversion with inherent CO_2 sequestration. For successfully operating the chemical looping, the cyclic material must meet a variety of criteria, such as high dispersion of the cyclic phase on the support, large external surface area, and small crystallite size, *etc.* in attempt to better activity and stability. In this paper, we applied a colloidal crystal templated sol-gel synthesis route to produce materials for chemical looping with hydrogen storage. To understand the role of template in the sol-gel process, two samples prepared with or without template were investigated by various characterization techniques. The results showed the template could not only promote the homogeneity of the metallic precursors, but also efficiently control the material morphology. The resulting high dispersion and confinement effects endowed this material better activity and stability in chemical looping multicycles. Our current experiments demonstrated this strategy can be used as a platform for convenient incorporation of a variety of structural features, and we anticipated it can be extended to synthesis more chemical looping materials.

22 *Keywords:* Sol-gel; Iron oxides; Chemical looping; Hydrogen storage

23 **1. Introduction**

24 The stochastic nature of the wind or solar energy input makes the large-scale energy storage
25 technology an inevitable requirement. Using H₂ as a storage medium can be employed as a
26 promising method to address this problem, in that the hydrogen can be easily produced from the
27 excessive electricity through water splitting in an efficient and low cost way. However, if using this
28 strategy, the hydrogen storage material must be environmental compatibility, handling safety, and
29 more importantly, with relatively high storage capacity and low costs, in order to make this method
30 technically and commercially feasible.

31 Currently, a great number of hydrogen carriers, ranging from metal hydrides, metal alloys, metal
32 organic frameworks (MOFs) to carbon nanotubes and among others, have been designed,
33 synthesized, and tested [1-8]. Despite the researchers continuously struggle for improving the
34 storage capacity of these materials, there still lacks of a good candidate that can meet all
35 requirements in the large-scale hydrogen storage unit. An alternative hydrogen storage material is
36 iron oxides (IO). Thanks to the source abundant and readily available of these natural ores, it has
37 drawn rising interests recently. The first use of IO to store hydrogen was proposed by Otsuka et. al
38 [9,10]. They employed pure hydrogen as fuels in steam-iron process and successfully created the
39 hydrogen storage and release cycles within the chemical looping of magnetite.

40 Hydrogen charge:

42 Hydrogen discharge:

44 Theoretically, the proposed method can provide a storage capacity of 4.8 wt% of Fe in mass basis,

45 prevailing over 70% metal alloys. An additional noteworthy point is that the feedstock is only H₂O,
46 Fe₃O₄, which are readily available, environmentally friendly and with low costs. Therefore, this
47 technology is expected to be applicable for the industrial hydrogen storage unit, such as the energy
48 storage power plant. However, it has been demonstrated that IO particles suffer from severe
49 sintering caused by the high operation temperature (typically at up to 800 °C); this implies that the
50 practical hydrogen storage capacity will decay along with the cyclic numbers. In order to limit the
51 sintering, cyclic IO needs to be deposited on refractory materials [11-21], for example Al₂O₃, CeO₂,
52 ZrO₂, TiO₂, yttria-stabilized zirconia (YSZ), MgAl₂O₄, *etc.* In this case, a critical issue is the degree
53 of dispersion of IO phase on the supports, which determines the stability of the produced materials.
54 Conventional methods, such as mechanical mixing or impregnation, are difficult to give the high
55 dispersion of IO at high loadings, and thus the resistance to sintering of the resulting materials is
56 significantly compromised. Another issue is to produce small IO particles in order to expose large
57 active surface area to the redox environment, based on a fact that the bulk oxygen transfer is
58 considered the rate-limiting step in the chemical looping [22,23]. scheffe et al [24] produced
59 Co_xFe_{3-x}O₄ ALD films by atomic layer deposition and found peak hydrogen production rate was
60 determined by the gas-film interface. Similar behaviors were confirmed by Weidenkaff et al. [25].
61 They observed the particle size of FeO was highly dependent on H₂O splitting, and ascribed this to
62 bulk diffusion limitations. Finally, the resulting materials must be in porous architecture to facilitate
63 the mass transport of fuels and products; this not only promotes the reactions kinetically but also
64 drags the reactions to the products side thermodynamically. However, the redox cycles need to be
65 operated in high temperatures, which present great challenges in producing this nanostructured IO
66 particle.

67 In this work, we proposed a novel route of preparing IO from colloidal crystal templated (CCT)

sol-gel precursors. By virtue of the homogeneous mixing of metallic precursors in the sol solutions, the resulting iron oxides can be well dispersed on the supports. The conventional sol-gel methods, however, fail to give satisfactory porous architecture after the thermal treatment, since the capillary pressures of the aqueous solution can lead to large shrinkages or even destruction of the incipient network [26,27]. Comparatively, we modified the sol solutions with CCT template in this synthesis route, which acts as sacrifice material with high voids left after calcination. In addition, the template introduces the confinement effects to the metal oxides precursors, resulting in nanoscale IO particles with high reactivity. In the chemical looping multicycle tests, the resulting materials show both good reactivity and stability, and our current experiments demonstrated this strategy can be used as a platform for convenient incorporation of a variety of structural features in synthesizing more chemical looping materials.

2. Experiments

2.1. Template synthesis

Within the aqueous system, non-crosslinked and monodisperse PMMA microspheres were prepared with the use of an emulsifier-free emulsion polymerization (EFEP) technique [28]. All the used water was distilled and deionized to a resistivity of over 16 M Ω . cm. Methyl methacrylate (MMA, 100 ml) was washed three times with 50 ml of 1 M NaOH and five times with water, respectively. The MMA was refined through the reduced pressure distillation at 70 °C. A 500 ml round-bottomed flask was filled with 100 ml solution containing 10 g refined monomers and 0.15 g sodium chloride (NaCl), and deaerated 20 min by N₂. Afterward, 0.075 g potassium persulfate (KPS, water-phase initiator) was added in the solution with vigorous stir, whilst the flask was heated to 70 °C in oil bath. The polymerization was kept overnight and the resulting PMMA spheres were collected by membrane filter and dried in ambient atmosphere. In the present studies, the average

diameters of the obtained microspheres were 300–500 nm estimated by scanning electron microscopy (SEM) (Figure S1). The solid content of the prepared emulsion polymer was ca. 15%.

2.2. Porous IO synthesis

Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were employed as the Fe, Al, Mg sources, respectively. The stoichiometric amount of mixed metal nitrates precursors were dissolved in water, where the $\text{Fe}^{3+} : \text{Mg}^{2+} : \text{Al}^{3+}$ molar ratio was controlled at 1.77:1:2, corresponding to 50% Fe_2O_3 mass content in the final MgAl_2O_4 supported IO materials. For completely chelating the metal ions in the sols, the citric acid (CA) : total metal ion (TMI) molar ratio was set at 1.1, slightly over the stoichiometric value. Polyethylene glycol (PEG, $M_w=400$) was added to link those individual chelates together via a thermally activated polyesterification. Hereafter, the sol solution was kept 20 min at 50 °C with magnetic stir.

The precursor solutions were infiltrated into CCTs and heat-treated at 95 °C for 48 h in tightly sealed glass vials, transforming the precursor to a hard gel within the template. The produced gel was calcined in a muffle furnace under the air atmosphere at 450 °C and 950 °C (2 °C.min⁻¹ ramp, 2 h dwell time at each temperature). After the template removal, the red brown powders (sample B) can be obtained, subsequently crushed and sieved the size range of 0.075-0.125 mm. Additionally, control samples (sample A) prepared from the conventional sol-gel precursors (without a template) were treated following the same procedure, that is, sol, gelled, and calcined.

2.3. IO characterization

A V-sorb X800 Surface Area and Porosimetry Analyzer was used in the nitrogen adsorption-desorption analysis. In each measurement, 300 mg IO were evacuated at 250 °C for 5 hours prior to the measurement under 10 μPa of vacuum. The specific surface area of the samples

114 was calculated following BET equation. The morphology of the materials was examined using
115 scanning electron microscopy (SEM). Materials, as-produced, were sputter-coated with a thin layer
116 of gold and then imaged with a Hitachi SU3500 electron microscope. The same instrument is used
117 for elemental analysis of the samples using energy dispersive Xray spectroscopy (EDS) technique.
118 The surface of the samples is examined by EDX mapping analysis to evaluate the dispersion of the
119 active phase on the support. The STEM, HRTEM analysis were performed by Titan 80-300
120 transmission electron microscope. The particles were crushed into powders before characterizations,
121 and dispersed in isopropanol by ultra-sonication, dipped on the carbon-filmed copper grid and dried
122 in ambient atmosphere. The crystalline phases was recognized using Powder X ray diffraction
123 (XRD) method on a Ultima IV diffractometer, where Cu, Ka radiation was generated at 30 mA and
124 40 kV, and the scanning scope (2theta) was in a range of 5° to 85°.

125 *2.4. Cyclic performance in a fixed bed reactor*

126 The cyclic tests were conducted in a stainless steel-made fixed-bed reactor that was 12mm in
127 inner diameter with a total length of 400 mm. A porous distributor was installed at 180 mm from the
128 bottom of the reactor in order to support the bed material. The heat was provided by an electric
129 furnace and the reaction temperature was controlled and monitored by two thermocouples, one (T_1)
130 located between the tube and the furnace, and the other (T_2), inserted into the IO bed material. By
131 adjusting T_1 , the desired T_2 could be reached, that is also considered as the reaction temperature.

132 The flow rates of H_2 , N_2 , (99.99% purity) were measured by the mass flow controllers (MFC,
133 Beijing Sevenstar Co. Ltd). The distilled water was introduced by a high performance liquid Longer
134 Pump (LSP01-2A, $0.166\mu\text{l}.\text{min}^{-1}$ - $10.831\text{ml}.\text{min}^{-1}$) and evaporated by a steam generator operating at
135 250 °C. The carrying N_2 used in the experiments was to introduce the steam vapor smoothly and the
136 inlet and outlet heat taps were kept at 250 °C. The schematic layout of the experimental setup is

137 shown in Fig. S2.

138 Prior to each experiment, 15 ml sand particles with a size range of 0.6-1.0 mm was placed on the
139 porous distributor to prevent the IO particles from dropping through the distributor. A batch of 5 g
140 IO particles (0.075-0.125 mm) was subsequently loaded on the sand bed, after which the reactor
141 was heated under the N₂ atmosphere. When the desired temperatures (900 °C) reached, the samples
142 were alternatively exposed to a reducing (200 ml.min⁻¹ H₂ + 100 ml.min⁻¹ N₂, STP) and oxidization
143 (0.5 ml.min⁻¹ water + 100 ml.min⁻¹ N₂, STP) atmosphere with 5 min N₂ purging (300 ml.min⁻¹, STP)
144 between each gas switching. The redox step was terminated when the evolved gas composition
145 stabilized.

146 The outlet gas was mixed with the diluting N₂ to accommodate the limited range of the Emerson
147 multi-component gas analyzer. The gas analyzer has a detection range of CO₂ (0~100%, 0.01%
148 uncertain), CH₄ (0-10%, 0.01% uncertain), CO (0-100%, 0.01% uncertain), O₂ (0-25%, 0.01%
149 uncertain), and H₂ (0-50%, 0.1% uncertain).

150 2.5. Data evaluation

151 (1) Volumetric flow rate of outlet hydrogen

152 The volumetric flow rate of outlet hydrogen was calculated based on a N₂ mass balance method:

$$V_{H_2} = \int_{t_1}^{t_2} V_{out} x_{H_2} dt \quad (3)$$

153 With

$$V_{out} = V_{N_2,in} / x_{N_2,out} = V_{N_2,in} / (1 - x_{H_2}) \quad (4)$$

154 Where x_{N_2} and x_{H_2} are the detected concentration of N₂ and H₂ in the gas stream, V_{in} and V_{out}
155 are the total inlet and outlet volumetric gas flow rate, respectively.

156 (2) Relative weight

157 The relative weight (R_x) for the IO was calculated by:

$$R_t = \frac{m_t}{m_i} \quad (5)$$

Where m_i is the initial weight of the sample and m_t are the weights of the sample at time t .

(3) Hydrogen storage capacity

Hydrogen storage capacity (δ) is denoted as:

$$\delta = \frac{\int_{t_1}^{t_2} V_{\text{in,H}_2} - V_{\text{out}} x_{\text{H}_2} dt}{11200 m_{\text{Fe}}} \quad (6)$$

Where $V_{\text{in,H}_2}$ is the inlet H_2 volumetric flow rate, t_1 and t_2 are the starting and ending points in a charge process, m_{Fe} is the weight of metallic iron in the sample.

3. Results

3.1. The role of CCT in material synthesis

Fig. 1 illustrates the XRD patterns of the prepared two samples calcined in air at different temperatures from 350 °C to 950 °C. Clearly, sample A displayed good crystallinity at lower temperatures, whereas sample B was semi-crystallite or amorphous before 550 °C. For both two samples, the peaks near 33° were correlated with the $\alpha\text{-Fe}_2\text{O}_3$ phase (hematite, PDF: 33-0064), and the corresponding intensity was sequentially intensified with the increase in the calcination temperatures. The major characteristic peak of MgAl_2O_4 (spinel, PDF: 21-1152) support were detected at ca. 36°, whilst no reflections of Al_2O_3 and MgO were observed in all the experiments. Compared with the standard lattice constant of cubic MgAl_2O_4 (0.8083nm), we also found the expansion in the MgAl_2O_4 matrix (Table 1). Considering the larger size of the Fe^{3+} cation (0.055 nm) compared with Al^{3+} (0.0535), this deformation indicated that some Fe^{3+} ions were incorporated into the MgAl_2O_4 matrix to form Mg-Fe-Al solid solutions.

The crystallite size of Fe_2O_3 and MgAl_2O_4 was deduced from XRD line broadening using the Scherrer equation. As listed in Table 1, the IO crystallites of two samples continued to grow along

180 with the increase of the calcination temperature; this can be easily ascribed to the crystallite growth
181 during the sintering. The crystallite size of Fe_2O_3 of sample A reached 75.8 nm after 950 °C
182 calcination. When the material was produced with CCT, completely dissimilar, the corresponding
183 size was much smaller, at 49.3 nm. Considering the physical nature of the template, we can deduce
184 that CCT embedded in the material precursor spatially limited the crystallite growth. BET analysis
185 further illustrated the effects of template played in the material structure evolutions. From the last
186 volume in Table 1, the BET surface area of sample B sharply increased at 550 °C, well
187 corresponding to the melting temperature of the template. As to sample A, the surface area
188 decreased continuously. This confirmed the different mechanisms during the formation of the
189 material network in two samples, that is, the network was build-up from the dynamic solvent space
190 between the aggregated particles, and when materials are prepared in the presence of CCT, pores
191 can also be generated from the template space in the precursors. SEM imaging verified the pore
192 forming effects of the CCT in the sol-gel synthesis. As shown in Fig. 2, the conventional sol-gel
193 process resulted in a porous matrix with irregular micron-scale pores distribution; this result can be
194 attributed to the dynamic characteristics of the incipiently produced network in sol precursors [29].
195 In contrast, the sample obtained by CCT method possessed the three dimensionally ordered (3DOM)
196 structure with homogenous pore configuration, where the architecture was made up of various small
197 cubic cavities, and on the surface of which six hemispheroidal pore windows were separately
198 arranged. The pore sizes estimated from the SEM images are about 200–300 nm, which
199 corresponded to a half shrinkage compared with the initial sizes of PMMA template. This shrinkage
200 can be attributed to the stress produced during the template etching and the subsequent calculation
201 process [26]. Nevertheless, owing to the good strength of the networks having been achieved before
202 the melting point of the template reached, the long-range order in the material was sustained in spite

203 of this drastic structural shrinkage. Above, we can conclude that the CCT modified sol-gel method
204 can be employed to produce highly porous material.

205 The role of CCT in material synthesis was further investigated by SEM-EDS and HRTEM
206 method. In this synthesis, we start with a sol-gel process, where the chelation of the metallic ions by
207 the CA can lead to homogenous dispersion of the IO. EDS mapping of sample A confirmed the
208 good dispersion of the cyclic phase (Fig.3). Nevertheless, we also detected the partial agglomeration
209 of IO marked in the dotted cycles; frequently, these are attributed to localized incomplete chelation
210 in the sol precursors. Completely different, the local non-uniform dispersion was not observed when
211 CCT was present, and the HRTEM of sample B again verified the homogenous dispersion of Fe_2O_3
212 on MgAl_2O_4 support (Fig. 4). During the template synthesis, we employed an emulsifier-free
213 emulsion polymerization route depends on the use of water-soluble initiators. These initiators
214 produce negative charged functional groups on the surface of the PMMA spheres. In the sol
215 solutions, the electrostatic attraction between the negative charged template surface and positive
216 charge chelates maybe occur, which promoted the homogeneity of the metallic precursors.

217 3.2. Charge and discharge behavior

218 The charge and discharge behavior of the two prepared samples was evaluated during isothermal
219 redox cycling in TGA. In each test, samples of 30 mg was loaded in a platinum pallet and heated to
220 900 °C (20 °C.min⁻¹ ramp) under the N₂ atmosphere. When the desired temperatures reached, the
221 samples were alternatively exposed to a cyclic reduction and oxidation atmospheres using H₂ as
222 gaseous fuel (H₂ 50% + N₂ 50% vol %, total flow rates 120 ml. min⁻¹, STP), and CO₂ (CO₂ 50% +
223 N₂ 50% vol %, total flow rates 120 ml. min⁻¹, STP) as oxidizing gas. Herein, the reason for not
224 directly using steam as oxidizing gas was due to the technical forbids in presenting water in our
225 TGA equipment, while the redox potential of CO₂ is almost identical to that of steam. For fresh and

226 20 cycled samples, the changes of the charge and discharge kinetics were also studied using the
227 H₂-TPR and CO₂-TPO method.

228 Fig. 5 compares performance of two samples over 20 cycles. Clearly, sample B showed relatively
229 stable operation, characterized by reproducible sample weights in successive reduced and oxidized
230 states, although the initial decay in the first five cycles. In contrast to that, sample A showed
231 stronger deactivation with incomplete re-oxidation to Fe₃O₄ (as indicated by the dotted lines
232 representing the thermodynamic charge and discharge limits). This deactivation suggested sintering
233 or agglomeration during the cycles, where the increasing particle size led to greater resistance in the
234 bulk oxygen transfer.

235 The charge behavior of these materials was evaluated further through conventional H₂-TPR
236 experiments. Fig. 6 represents reduction profiles of the two prepared samples. For sample A, the
237 first peak of hydrogen consumption is at 439.6 °C, corresponding to the transformation of hematite
238 to magnetite. Further reduction of magnetite to wustite started at 500 °C, with a local peak around
239 597.7 °C, which was however overlapping with the onset of complete reduction to metallic iron
240 with a major peak at 768.1°C. After 20 cycles, the profile of sample A presented only the peak at
241 higher temperature; this was not surprisingly resulted from the inability of CO₂ to oxidize the IO to
242 the hematite. As for sample B, the profiles were similar, but it is noticeable that the shift of the
243 reduction peaks to lower temperature was present. As shown in Fig. 2, the pore wall of sample B
244 was about 30~40 nm in thickness, whereas the pore wall thickness of sample A was over 500 nm in
245 average. The pore wall of the sample introduced the confinement effects and limited the crystallite
246 growth, therefore, the better activity was observed for sample B.

247 Samples freshly prepared and cycled were also tested by CO₂-TPO. As shown in Fig. 6c-d, the
248 discharge kinetics was much faster than that of charge process, indicating the chemical looping for

hydrogen storage was limited by the hydrogen charge reactions. In these two samples, we found sample B had better charge kinetics owing to the highly porous nanostructure; the charge temperature, however, was still much higher than the discharge process, especially when high storage capacity was required. Therefore, further attentions should be focused on the enhancement of the charge performance, not just on the morphology control to facilitate the mass transfer, but also on altering its charge thermodynamics, for example, doping the Fe_3O_4 with Co, Mn, Ce, *etc.* [30,31].

3.4. Cyclic test in fixed bed reactor.

The above experiments in TGA simulated the hydrogen charge and discharge process using H_2 and CO_2 as redox agent. In the real conditions, however, the steam must be introduced to release the H_2 ; this change in the oxidizing agent would affect the stability of the material, because of a fact that water could significantly accelerate the sintering rate of the particles. The results in Fig. 7 show the cyclic performance of two samples in the real steam oxidization conditions. Obviously, the stability in this case was much lower than that in TGA, with the results showing that the hydrogen capacity decreased to 3.57% for sample B. Comparatively, poorer stability of sample A was observed. SEM image (Fig. 8) and BET analysis (Table 2) indicated the sintering occurred during the cycling. By comparing the material before and after cycles, we can observe pronounced shrinkage in porosity; this led to the loss of external surface. In the material characterizations, we found sample B had higher dispersion of the active phase on the support, therefore, the better stability was observed.

Apart from the sintering, the solid-solid interaction between the cyclic phase and the support was considered as another import factor causing the IO deactivation. For the freshly-prepared samples, some Fe^{3+} ions were incorporated into the MgAl_2O_4 matrix (Table 1). After 20 cycles, we observed

the expansion of the MgAl_2O_4 lattice was intensified, indicating more Fe^{3+} substituted the Al^{3+} in the Mg-Al spinel crystals. Since the formed Mg-Al-Fe spinel possessed high thermal stability in hydrogen atmosphere, this incorporation would adversely affect the storage capacity. By comparing the lattice constant of the two samples, this result also suggested more Fe^{3+} incorporated in Mg-Al matrix for sample A.

4. Discussions

4.1. CCT assisted sol-gel prepared material for clean energy applications

Similar to the chemical looping for hydrogen storage, many other novel processes for energy applications are highly dependent on the redox cycles of materials. Examples are steam iron for hydrogen production [32], chemical looping combustion and gasification [15,33], calcium looping [34], and solar hydrogen production [35].

One of the major challenges involved in these processes is the lack of a material with good activity because the conventional preparation methods, such as mechanical mixing, co-precipitation and impregnation, fail to produce materials with satisfactory porosity after high temperature calcination. According to our current research, CCT assisted sol-gel method can provide a convenient access to the 3DOM pore structure of material with high BET surface area. More importantly, the electrostatic attraction between the negative charged template surface and positive charge chelates promoted the homogeneity of the metallic precursors. This leads to the high dispersion of the cyclic phase, and resulted in better ability to resist the sintering. For other clean energy applications, we expect this strategy to be employed to produce more materials for the high temperature redox cycles.

4.2. IO chemical looping cycles for renewable energy conversion and storage.

To reduce the dependence of petroleum, bio-oil, a source abundant and renewable liquid fuel,

stimulates particular interest in recent decades [36-38]. Unfortunately, due to the high oxygen content, high viscosity and acidity [39], the utilization of these promising energy carriers has always been a great problem to be addressed. Producing hydrogen from these materials is a major solution [40]. However, the freshly-prepared oil is required to be processed immediately because of the instability of the physical and chemical properties of the oil [41], *e.g.* the viscosity will increase along with the oil storage time, and thus causes the difficulties in the feeding system.

The IO chemical looping cycles employed in this contribution provides a novel method in bio-oil conversion and storage. Similar to the hydrogen charge process, the reduction of IO can be achieved with the gaseous fuels from bio-oil:

Oil inert gasification:

IO reduction (CO as a representative):

Steam oxidization:

Through the reduction, the chemical energy oil is transferred to iron, a material possessing high chemical and physical stability. In addition, if using iron as an energy carrier in the hydrogen-based system, the associated transportation costs will be reduced owing to the high storage capacity of hydrogen. By virtue of the good fuel flexibility, this strategy can be also extended to other hydrogen-based energy conversion and storage system.

5. Conclusions

In this paper, we applied a colloidal crystal templated sol-gel synthesis route to produce materials for chemical looping with hydrogen storage. To understand the role of template in the sol-gel

315 process, two samples prepared with or without template were investigated by various
316 characterization techniques. The results showed the sample obtained by CCT method possessed the
317 three dimensionally ordered structure with higher BET surface area, whereas the controlled sample
318 present irregular porous networks. In the presence of the template, we also found the crystallite size
319 was significantly limited and the dispersion of the cyclic phase was great promoted. In the
320 multicycle tests, these preferred structural properties made the material better activity and stability.

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430 **Figure captions**

431 Fig.1. XRD patterns of the samples calcined under different temperatures. (a) Sample A; (b) Sample
432 B.

433 Fig.2. The SEM imaging of the prepared two samples. (a-b) Sample A; (c-d) Sample B.

434 Fig.3. EDS mapping of the prepared two samples. (a) Sample A; (b) Sample B.

435 Fig.4. HRTEM micrograph of sample B.

436 Fig.5. Cyclic performance in TGA. (a) sample A; (b) sample B.

437 Fig.6. H₂-TPR and CO₂-TPO study of the two samples before and after 20 cycles. (a-b) H₂-TPR;
438 (c-d) CO₂-TPO.

439 Fig.7. Cyclic performance in a fixed bed reactor.

440 Fig.8. SEM imaging of the samples after 20 cycles. (a-b) Sample A; (b) sample B.

441 Fig.9. XRD patterns of the samples after 20 cycles.

442 Fig. S1. SEM imaging of the prepared PMMA template.

443 Fig. S2. Schematic diagram of the experimental setup.

444 **Table captions**

445 Table. 1. Structure properties of the prepared samples.

446 Table. 2. Structure properties of the samples after 20 cycles.

447

448

Table. 1.
Structure properties of the prepared samples.

IO	Calcination temperature (°C)	Crystalline size (Fe ₂ O ₃ ,nm) ^a	Crystalline size (MgAl ₂ O ₄ ,nm) ^a	Lattice constant (MgAl ₂ O ₄ ,nm) ^a	BET surface area (m ² .g ⁻¹)
Sample A	350	64.8	37.6	0.8139	47.54
	450	67.1	35.6	0.8132	41.21
	550	68.4	33.3	0.8149	37.64
	650	69.7	32.1	0.8148	31.25
	750	71.6	34.7	0.8136	19.53
	850	73.6	35.4	0.8143	10.78
	950	75.8	40.4	0.8137	4.21
Sample B	350	-	-	-	23.74
	450	-	-	-	29.21
	550	-	-	-	62.74
	650	-	9.1	-	58.36
	750	32.2	12.9	0.8139	45.37
	850	45.6	15.8	0.8161	31.65
	950	49.3	19.1	0.8153	22.47

a: Calculated on the basis of the X-ray diffraction peaks.

Table. 2.
Structure properties of the samples after 20 cycles.

IO	Lattice constant (MgAl ₂ O ₄ ,nm) ^a	BET surface area (m ² .g ⁻¹)
Sample A	0.8195	2.67
Sample B	0.8171	15.87

a: Calculated on the basis of the X-ray diffraction peaks.

Fig.1. XRD patterns of the samples calcined under different temperatures. (a) Sample A; (b) Sample B.

Fig.2. The SEM imaging of the prepared two samples. (a-b) Sample A; (c-d) Sample B.

Fig.3. EDS mapping of the prepared two samples. (a) Sample A; (b) Sample B.

Fig.4. HRTEM micrograph of sample B.

Fig.5. Cyclic performance in TGA. (a) sample A; (b) sample B.

Fig.6. H₂-TPR and CO₂-TPO study of the two samples before and after 20 cycles. (a-b)

H₂-TPR; (c-d) CO₂-TPO.

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