Supplementary Information for

Rational design of stainless steel self-catalytic reactors for CO_2 methanation: Extending from metal powder to 3D-printed reactor

Hyo-Jin Kim,[a] Kohsuke Mori,*[a,b,c] Takayoshi Nakano,[a,b] Hiromi Yamashita [b,c]

[a]Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

E-mail: mori@mat.eng.osaka-u.ac.jp

[b]Anisotropic Design & Additive Manufacturing Research Center, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

[c]Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan.

Supplementary Methods

Materials and chemicals. Sodium hydroxide (NaOH, 97 %), and ammonia solution (NH_4OH, 28 %) were purchased from Nacalai Tesque Inc. Ni alloy (Ni-21Cr-18Fe-8Mo at. %) was prepared as a reference sample by a gas-atomization process from EOS GmbH.

Preparation of STS powder and STS 3D SCRs. STS 316L powder (EOS, Krailling, Germany) was prepared by a gas-atomization process and used as a starting material of fabrication of STS 3D SCRs. The chemical composition and SEM images of STS 316L powder are shown in **Table S1** and **Fig. S1a**, respectively. EOS M 290 (EOS, Krailling, Germany) was used for the laser powder bed fusion (LPBF), and a cylinder-shaped STS 3D SCRs with 23 mm in diameter and 70 mm long was designed by 3D AutoCAD (**Fig. S1b**). The details of fabrication conditions are in Table. S2. The building platform was heated to 80 °C, and the O_2 concentration was maintained at under 100 ppm by Ar gas flow. The energy density (E) in Table. S2 is calculated as follows:

$$E = \frac{P}{v \times t \times h} \left(J\ mm^{-3}\right)$$

where P refers to the laser power (W); v to the scan speed (mm s^{-1}), t to the layer thickness (mm), and h to the hatch spacing (mm).

Two-step surface functionalization method. In the case of powder sample, 50 wt.% NaOH electrolyte solution (50 g) was added to a 45 mL Teflon liner with 0.3 g of STS powder. Subsequently, the solution was sealed in a stainless-steel autoclave and hydrothermally treated at 220 °C for 24 h. The solution was cooled to room temperature and centrifugated two times with 50 wt.% of NaOH and sufficient water until the pH

reach 7. After washing, the hydrothermal treated STS powder (STS-H220) was dried overnight in vacuum. As a second step, 30 mL of 28 % NH_4OH was added to a 45 mL Teflon liner with 0.3 g of STS-H220 and sealed in a stainless-steel autoclave for hydrothermally treatment at 80 °C for 24 h. The solution was cooled to room temperature and centrifugated with sufficient water until the pH reach 7. After that, the NH_4OH treated STS powder (STS-H220-NH80) was dried overnight in vacuum.

In the case of STS 3D SCRs, same two step surface functionalization method were applied using 500 mL Teflon liner and autoclave with the variation of the solution amount to 500 g of 50 wt.% NaOH at first step and 350 mL of 28 % NH_4OH at second step.

Characterization methods. FE-SEM and EDS analysis were performed with JSM-6500F (JEOL, Tokyo, Japan) and Ultima® Max (Oxford Instruments, Abingdon-on-Thames, UK) microscopes. All results were collected with an accelerating voltage of 20 kV. XRD spectra were acquired using a Rigaku Ultima IV diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation (λ = 1.5406 Å). Japan Information Center of Science and Technology (JICST) database was used to identify peaks in the analysed XRD spectra. XPS spectra were collected by ESCA 3400 (Shimadzu, Kyoto, Japan) with a Mg Kα radiation source. The binding energies were calibrated by setting the C-C peak at 284.8 eV. Data analysis was performed using CasaXPS.

Evaluation of CO_2 methanation performance. The CO_2 methanation performance was evaluated using a fixed-bed reactor system. 100 mg of powder samples were placed into a U-shaped quartz cell with an internal diameter of 10 mm between quartz wool and then placed in an electric oven. In the case of the SCRs, STS 3D SCRs was placed at the center of a quartz cell enclosed by a ribbon heaters. Both of powder and

3D SCRs, raw (As-printed) and first hydrothermal treated sample (STS-H220) was pretreated with H_2 gas (40 mL min^{-1}) at 400 °C for 2 h, whereas NH_4OH treated samples were directly evaluated without any pretreatment. The CO_2 methanation reaction was carried out with a mixed feed gas ($H_2/CO_2/N_2$ = 64:16:20), where nitrogen (N_2) was used as an inert gas to dilute the reactants, control exothermic heat generation, and minimize hot spot formation, at a total flow rate of 20 mL min^{-1}. The gas products were analysed with an online gas chromatograph (Shimadzu GC-14B) equipped with an active carbon column connected to a flame ionization detector combined with a methanizer. The conversion and selectivity were calculated as follows:

$$CO_{2conversion}\,(\%) = \frac{CO_{2in} - CO_{2out}}{CO_{2in}} \times 100\%$$

$$CH_{4selectivity}\,(\%) = \frac{CH_{4out}}{CO_{2in} - CO_{2out}} \times 100\%$$

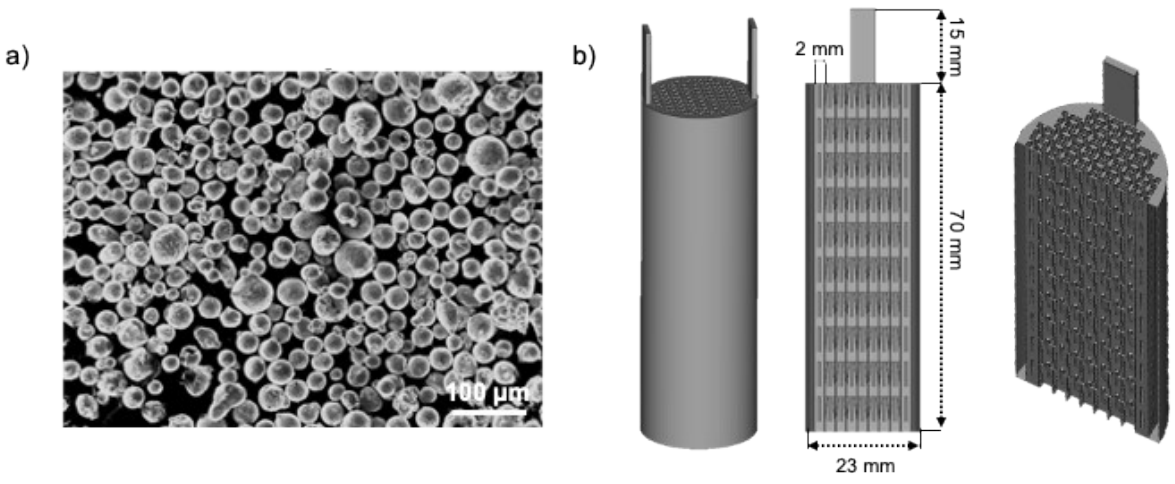

Fig.S1. a) SEM image of STS powder. b) 3D illustration of STS 3D SCRs

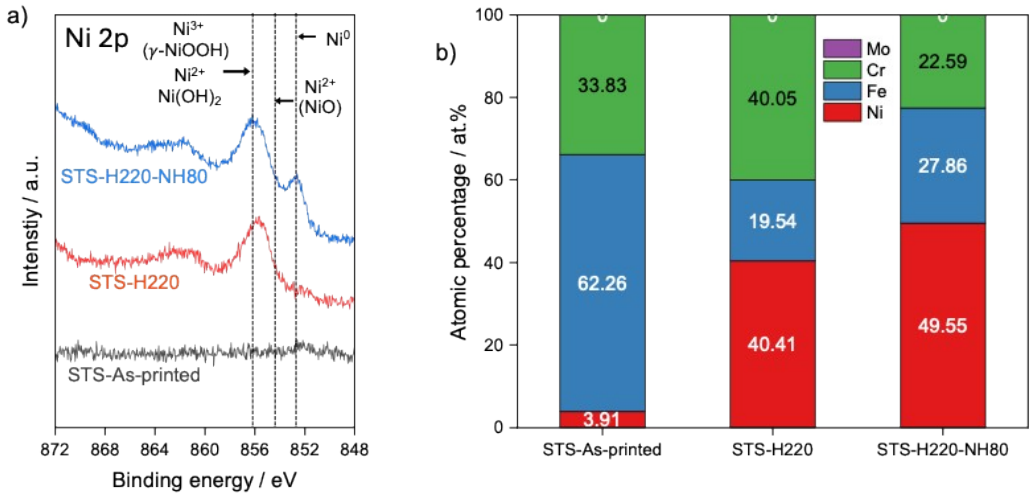

Fig.S2. a) Ni 2p XPS spectra before and after each step. b) quantification results obtained from XPS spectra.

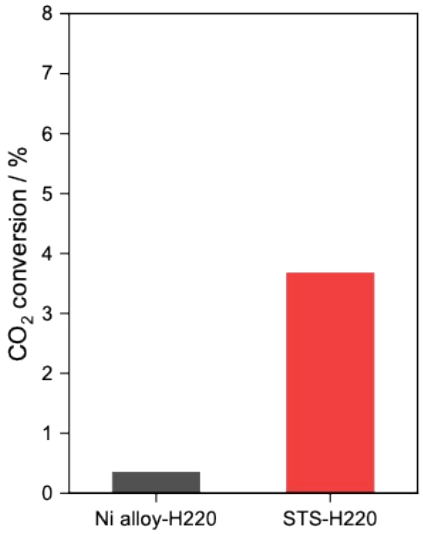

Fig.S3. Comparison of CO_2 hydrogenation performance between Ni alloy (Ni-21Cr-18Fe-8Mo at. %) and STS after hydrothermal treatment in 50 wt.% of NaOH. Reaction conditions: T = 300 °C, P = 1 bar, Flow rate = 20 mL min^{-1}, Reaction gas = $H_2/CO_2/N_2$ = 64/16/20

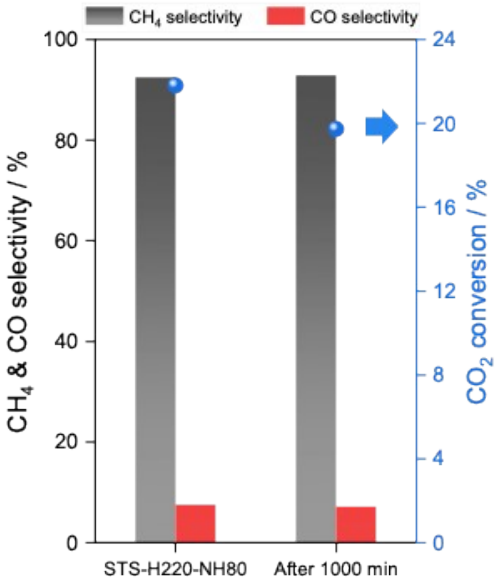

Fig.S4. Long term stability test (1000 min) of STS-H220-NH80 (Powder). Reaction conditions: T = 300 °C, P = 1 bar, Flow rate = 20 mL min^{-1}, Reaction gas = $H_2/CO_2/N_2$ = 64/16/20

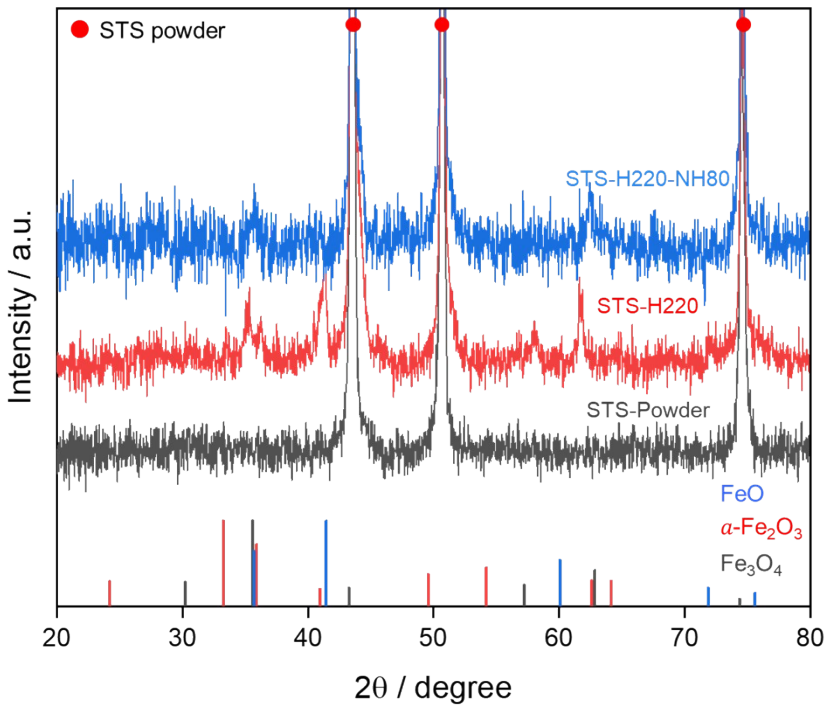

Fig.S5. XRD profiles of STS powder before and after each step.

Table S1. Chemical composition of gas atomized STS powder measured by ICP-combustion method.

	Fe	Cr	Ni	Cu	Mn	Si	Mo	C	S	P	N
wt.%	Bal	17.85	14.44	<0.01	1.59	0.26	2.71	0.006	<0.005	0.017	0.07

Table S2. Building condition of STS 3D SCRs.

Power (*P,* W)	Layer thickness (*t*, mm)	Hatching space (*h*, mm)	Scan speed (*v*, mm s^{-1})	Energy density (J mm^{-3})
240	0.06	0.1	800	50
			1200	33.3

Table S3. BET surface area (S_{BET}, m^2 g^{-1}) and total pore volume (V_{total}, cm^3 g^{-1}) of STS-RAW, STS-H220, STS-H220-NH80, and STS-H220-NH80-Used powder samples.

	STS-RAW[a)]	STS-H220	STS-H220-NH80	STS-H220-NH80-Used [b)]
Surface area (m^2 g^{-1})	-	0.48836	3.3244	2.1176
Total pore volume (cm^3 g^{-1})	-	0.1122	0.7638	0.4865

a) Unable to obtain BET result due to low surface area of STS-RAW.

b) After 2 h of reaction at 300 °C.