

Electronic Supporting Information

for

Multi-functional MOF-derived Magnetic Carbon Sponge

*Kun-Yi Andrew Lin**, *Hsuan-Ang Chang* and *Bo-Jau Chen*

Department of Environmental Engineering, National Chung Hsing University,

250 Kuo-Kuang Road, Taichung, Taiwan

*Corresponding Author. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw (Kun-Yi Andrew Lin)

S1. Preparation and characterization of MCS:

The cobalt-based ZIF-67 nanocrystals were first synthesized based on the reported protocol with modification^{S1}. On the other hand, a piece of commercial melamine-formaldehyde sponge (*e.g.*, 1 cm × 1 cm × 2 cm) was washed with ethanol and water, and dried in a conventional oven at 60 °C. The sponge was then compressed and immersed in a glass vial containing 20 ml of surfactant solution (SDBS = 4000 mg L⁻¹). The dip-coating process of sponge in the surfactant solution allowed the deposition of surfactant molecules on the surface of sponge skeletons. To facilitate deposition of surfactant on sponge, the vial was placed on an orbital shaker at 300 rpm for 30 min. Subsequently, the sponge was washed thoroughly with DI water and ethanol, and dried at 60 °C to obtain the surfactant-modified sponge.

Next, a MOF suspension was prepared by adding 50 mg of ZIF-67 to 20 ml of DI water and the mixture was sonicated for 30 min to disperse ZIF-67 nanocrystals in DI water. The surfactant-modified sponge was then added to the ZIF-67 suspension and stirred on the orbital shaker at 300 rpm for 3 hours to allow the self-assembling process of ZIF-67 and the surfactant-modified sponge to proceed and a layer of ZIF-67 was formed on the sponge surface as illustrated in Fig. 3. Subsequently, the sponge was withdrawn from the suspension and washed repeatedly with DI water and ethanol, and dried at 90 °C under reduced pressure for 12 hours to obtain the self-assembled MOF-sponge. The resultant MOF-sponge was then carbonized in N₂ atmosphere at 600 °C for 6 hours to form a black sponge which was washed with ethanol thoroughly and dried at 65 °C to obtain the final product, MCS.

Morphologies of MCS and its precursors were characterized using electronic microscopies (SEM (JEOL JSM-6700, Japan) equipped with a Energy-Dispersive X-ray spectroscopy (EDX) and TEM (JEOL JEM-2010, Japan)). Crystalline structures of MCS and its precursors were determined by an X-ray diffractometer (Bruker D8, USA). Raman spectra of MCS and its precursor were measured by a Raman spectrometer (Tokyo Instruments Inc. Nanofinder, Japan). Surface chemistry of MCS was analyzed using X-ray photoelectron

spectroscopy (XPS) (PHI 5000, Japan). Saturation magnetization of MCS was measured by a vibrating sample magnetometer (Quantum Design MPMS, USA) at ambient temperature.

Surface areas and total pore volumes of MCS and its precursors were determined using a gas adsorption analyzer (Quantachrome Auto-IQ, USA). Mercury porosimetry of MCS and its precursor were measured using a mercury porosimeter (Micromeritics AutoPore® IV 9520, USA).

S2. Methods for analyzing oil adsorption behaviors

S2.1 Kinetics of oil droplets adsorbed to MCS

During the separation of O/W emulsions, the kinetics of oil droplets adsorbed to MCS was analyzed by the pseudo first order and second order equations using the following equations:

The pseudo-first-order rate law: $q_t = q_e (1 - e^{-k_1 t})$

where q_t and q_e denote the adsorption capacity (g g^{-1}) at a given time t (min) and at equilibrium, respectively. k_1 (min^{-1}) is the rate constant for the pseudo first order rate law.

The pseudo first order equation is adopted to model adsorption behaviors in solid-liquid systems, in which oil droplets are considered to be adsorbed to single sorption sites on the surface of MCS.

The pseudo-second-order equation: $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$

where k_2 ($\text{g g}^{-1} \text{min}^{-1}$) denotes the rate constant for the pseudo second order rate law. In the pseudo second order rate law, oil droplet is considered to be adsorbed to two sorption sites on the surface of MCS.

S2.2 Adsorption isotherm of oil droplets adsorbed to MCS

To estimate the saturated adsorption capacity of MCS for oil droplets, an adsorption isotherm model was employed to estimate fraction of oil droplets partitioned between MCS and the solution phase at equilibrium. The Langmuir isotherm, one of the most widely-used models, was adopted for analysis as follows:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$$

where q_{\max} denotes the maximal adsorption capacity, K_L is the Langmuir isotherm constant and C_e is the concentration of oil droplets at the equilibrium. In the Langmuir isotherm, adsorption is considered to occur as a monolayer on a uniform surface which consists of a limited amount of adsorption sites. When an adsorption site has been occupied by adsorbate, it cannot be used for adsorption anymore.

Reference:

[S1] J. Shao, Z. Wan, H. Liu, H. Zheng, T. Gao, M. Shen, Q. Qu, H. Zheng, J. Mater. Chem. A 2014, 2, 12194.

Table S1. Kinetic parameters for adsorption of oil droplets to MCS (MCS = 250 mg L⁻¹, oil droplets = 400 mg L⁻¹).

Conditions	Pseudo-first-order		Pseudo-second-order	
Temp. (°C)	k_1 (min ⁻¹)	R_1^2	$k_2 \times 10^3$ (g mg ⁻¹ min ⁻¹)	R_2^2
30	0.012	0.997	1.82	0.98
40	0.026	0.997	8.34	0.98
50	0.039	0.999	16.72	0.96

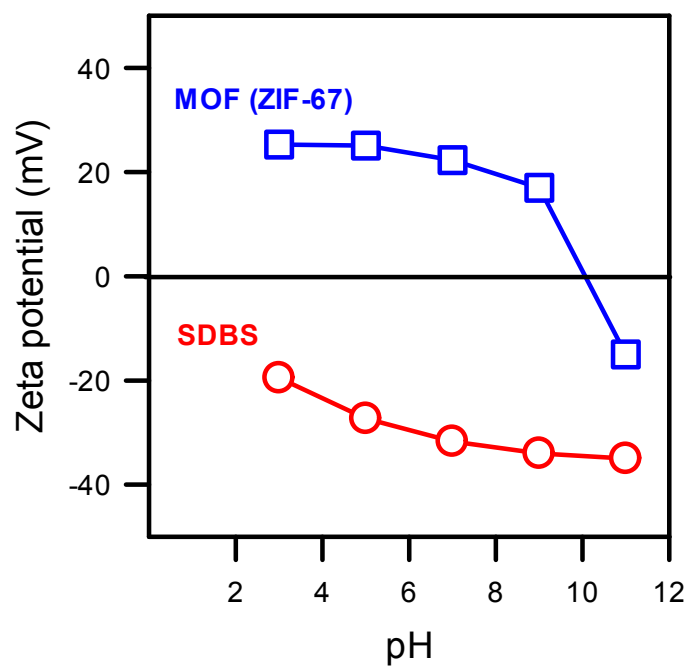


Fig. S1. Zeta potentials of ZIF-67 and SDBS under various pH values at 25 °C.

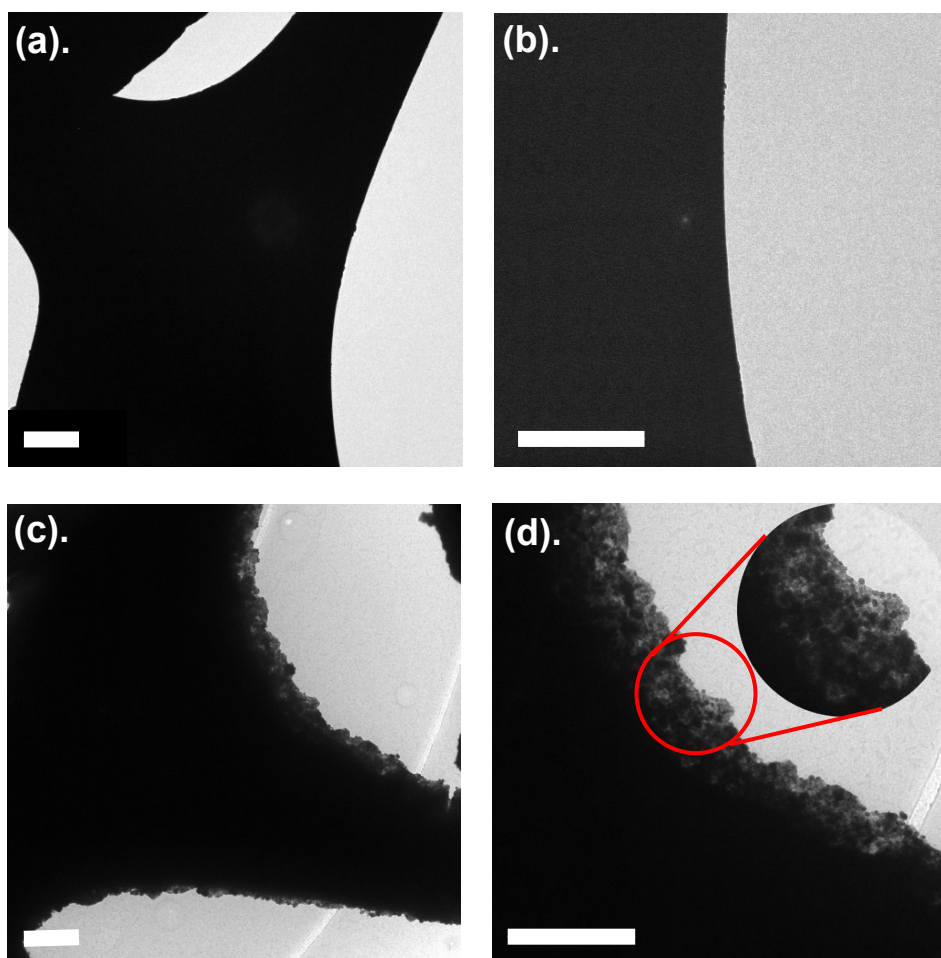
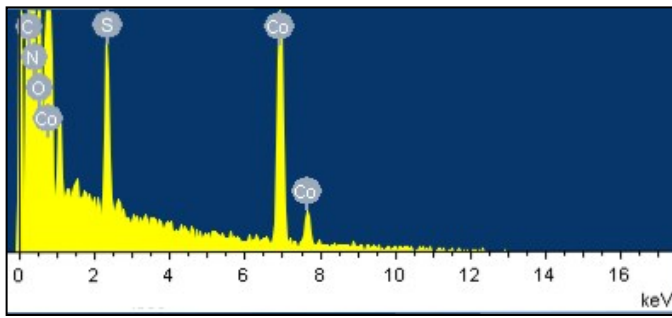


Fig. S2. TEM images of (a),(b) carbon sponge, and (c),(d) MCS at different magnifications. The scale bar is 2 μm .



Element	Weight %	Atomic %
C K	47.46	62.71
N K	13.96	15.81
O K	12.86	12.74
S K	8.07	3.99
Co L	17.65	4.75
Total	100	100

Fig.S3. Energy-dispersive spectroscopic analysis of MCS and the fractions of major constituents of MCS.

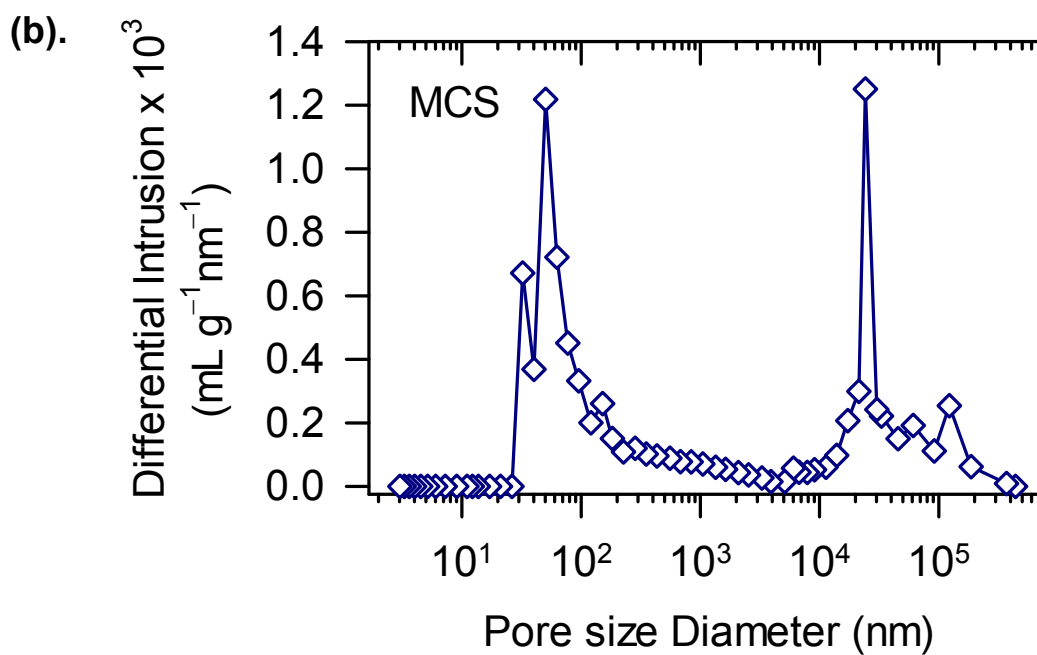
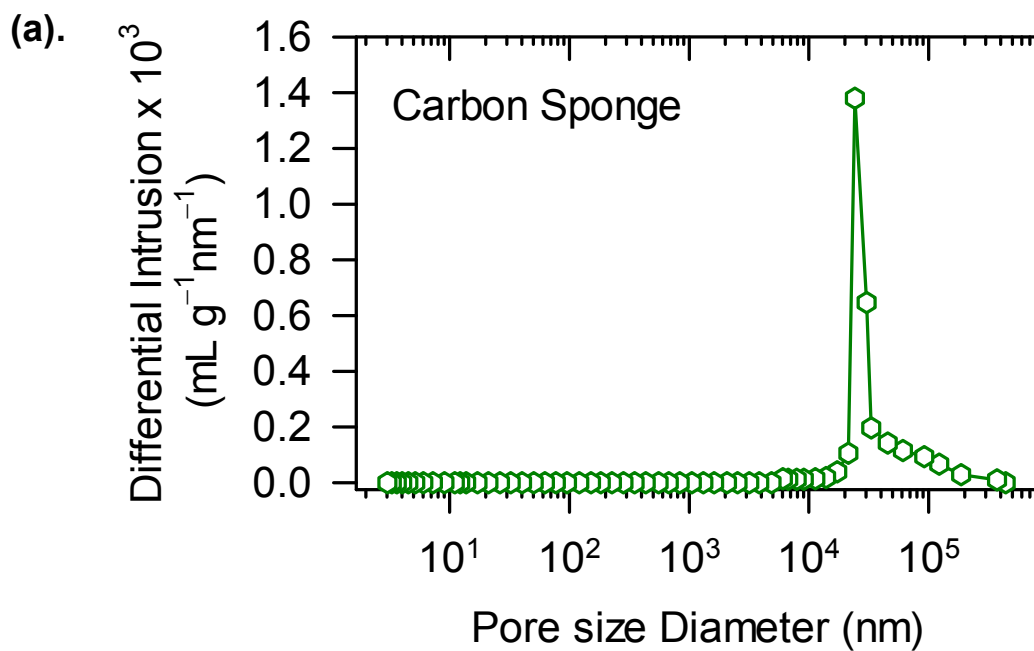


Fig. S4. Incremental intrusions obtained by mercury porosimetry: (a). carbon sponge, (b). MCS.

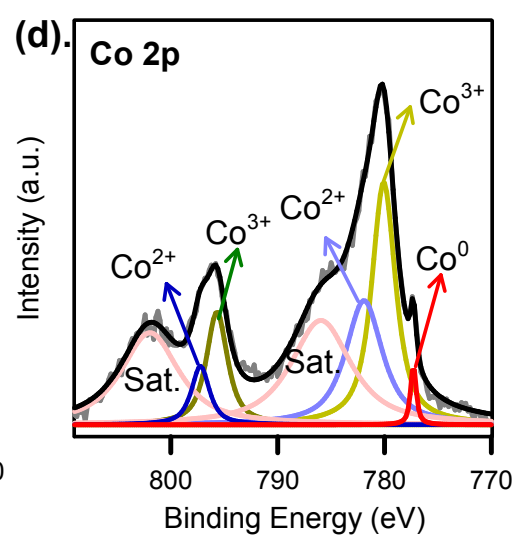
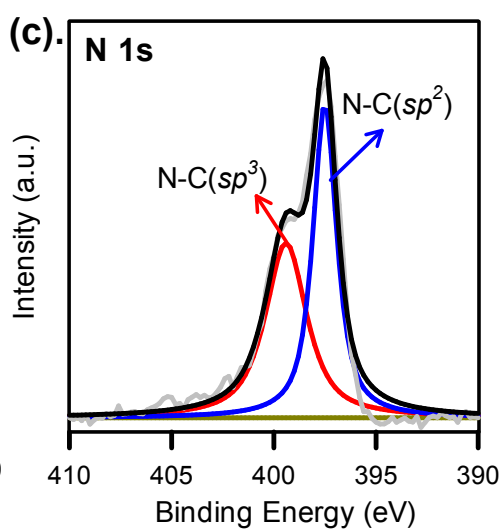
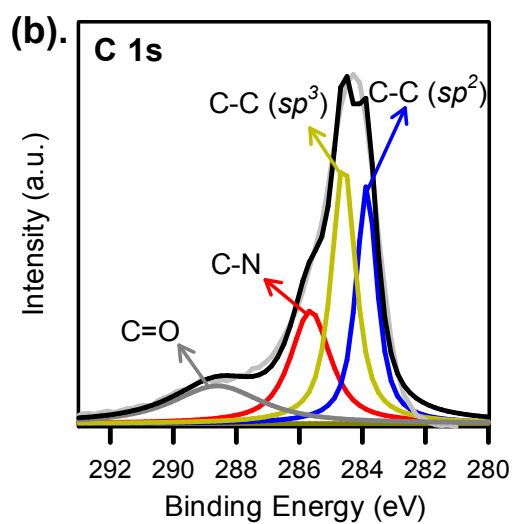
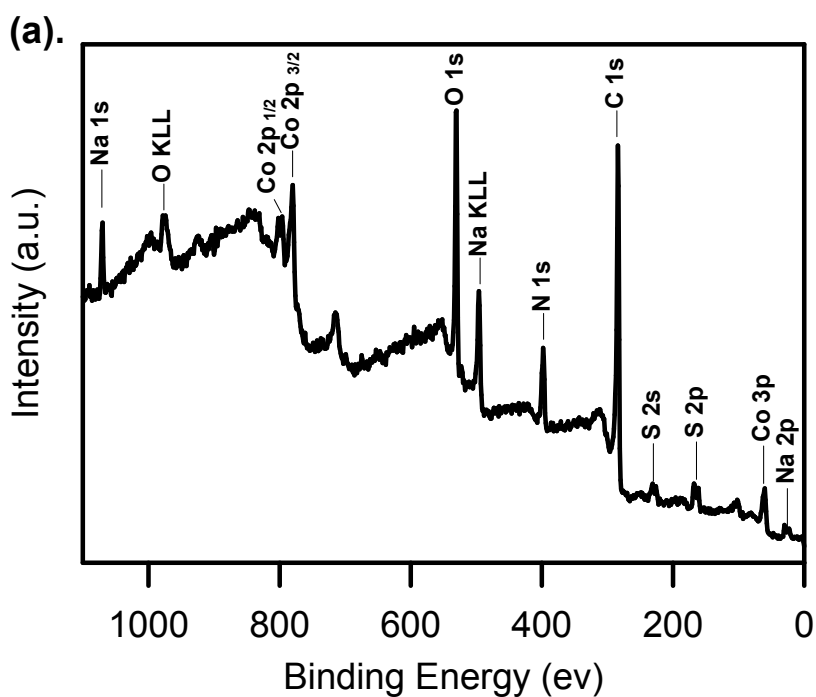


Fig. S5. XPS spectra of MCS: (a). Full survey, (b). C 1s core-level, (c). N 1s core-level (d). Co 2p core-level.

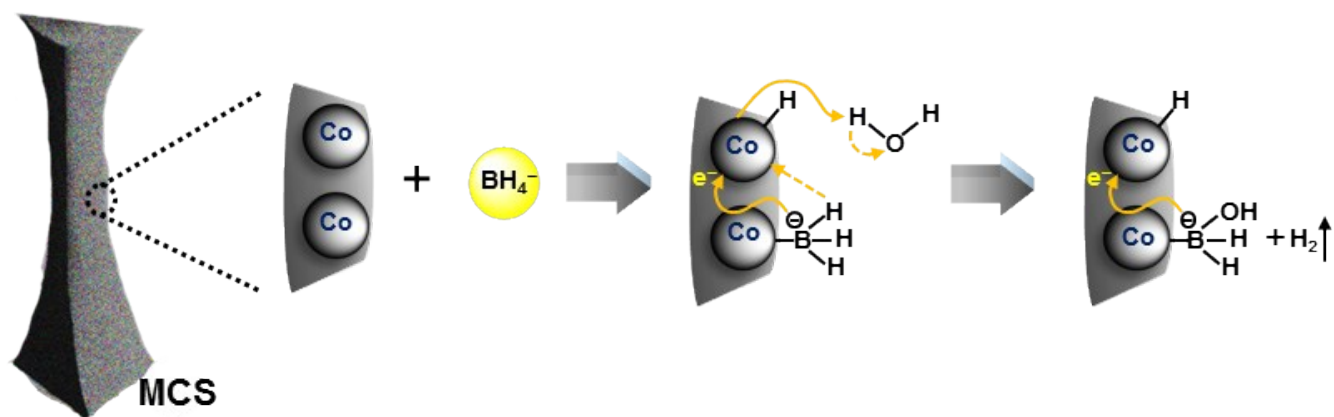


Fig. S6. The proposed mechanism for the catalytic hydrolysis of NaBH_4 for H_2 production using MCS as a heterogeneous catalyst.

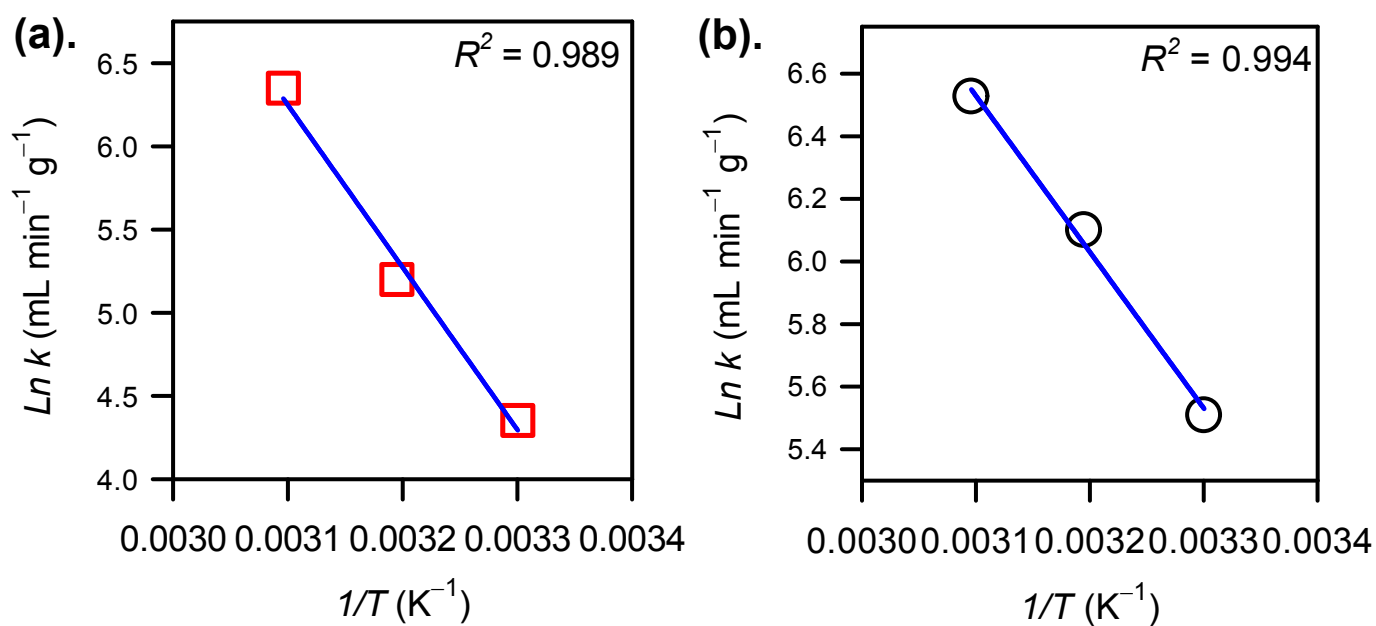


Fig. S7. (a) An Arrhenius plot for H_2 production using MCS without NaOH . ($E_a = 81 \text{ kJ mol}^{-1}$ based on the bulk material of MCS); (b) an Arrhenius plot for H_2 production using MCS without NaOH . ($E_a = 41 \text{ kJ mol}^{-1}$ based on the bulk material of MCS)