

Supporting Information

Sea-urchin-like Hollow CuMoO₄-CoMoO₄ Hybrid Microspheres, a Noble-Metal-Like Robust Catalyst for the Fast Hydrogen Production from Ammonia Borane

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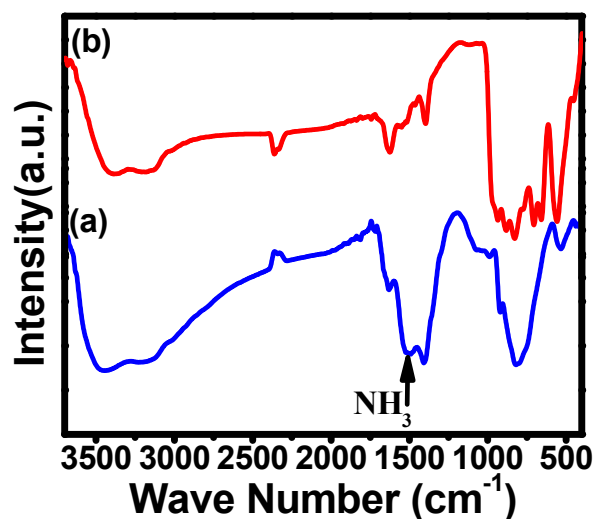


Figure S1. FT-IR spectra of the precursor (a) and $\text{CuMoO}_4\text{-CoMoO}_4$ (b).

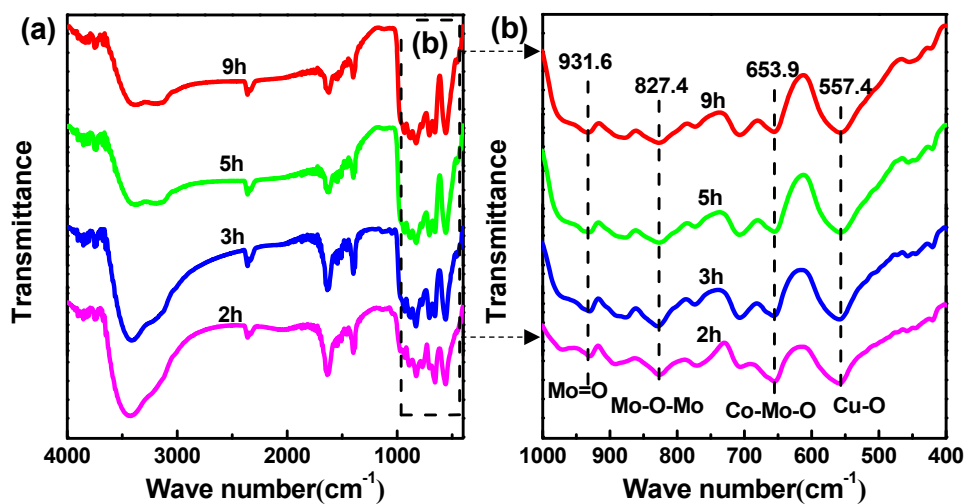


Figure S2. FT-IR spectra of $\text{CuMoO}_4\text{-CoMoO}_4$ samples obtained at different hydrothermal reaction time (a) and the enlargement zone ranging from 1000 – 400 cm^{-1} (b).

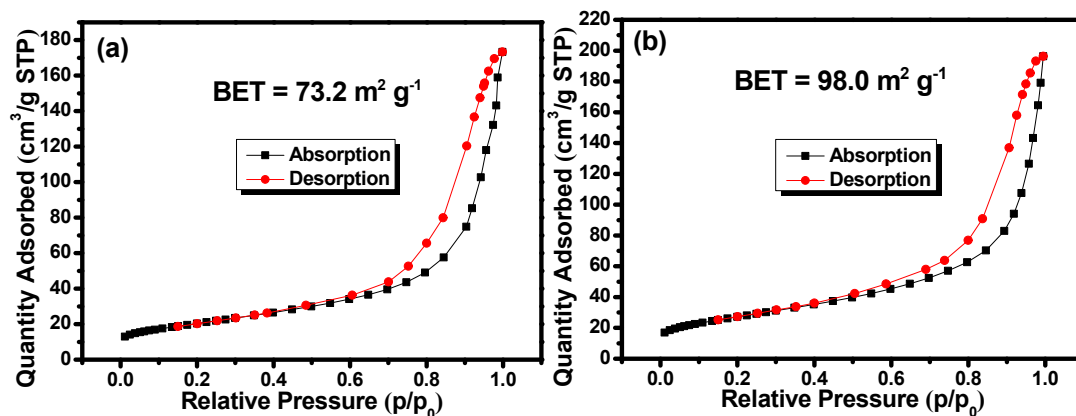


Figure S3. N_2 absorption-desorption isotherms of the precursor (a) and $\text{CuMoO}_4\text{-CoMoO}_4$ (b).

CoMoO₄ (b).

Illustration S1 Calculation of TOF values

The TOF value can be calculated by the following equation:

$$\text{TOF} = M_{\text{H}_2} / (t \cdot M_{\text{Cu+Co}})$$

M_{H_2} demotes the mole number of generated hydrogen (mole), t denotes the corresponding hydrolysis time (min) and $M_{\text{Cu+Co}}$ denotes the total mole number of Cu and Co used in the catalytic testing (mole), respectively. Note that the values of M_{H_2} and t can only be taken from the linear part of the plots in Figure 8a. The ICP-MS result indicates that molar ratio of Co:Cu:Mo in CuMoO₄-CoMoO₄ is around 0.5:0.5:1. Thus, CuMoO₄-CoMoO₄ can also be expressed as Cu_{0.5}Co_{0.5}MoO₄ with the average relative molecular mass of 221.2. When CuMoO₄-CoMoO₄ with dosage of 5.0 mg are used as catalysts, 2.366 mmol hydrogen can be produced at hydrolytic reaction time of 60 s. The TOF value is calculated by the following way:

$$\text{TOF} = \frac{2.366 \times 10^{-3}(\text{mol})}{\frac{60}{60}(\text{min}) \times \frac{5 \times 10^{-3}}{221.2}(\text{mol})} = 104.7 \text{mol}_{\text{H}_2} \text{min}^{-1} \text{mol}_{\text{cat}}^{-1}$$

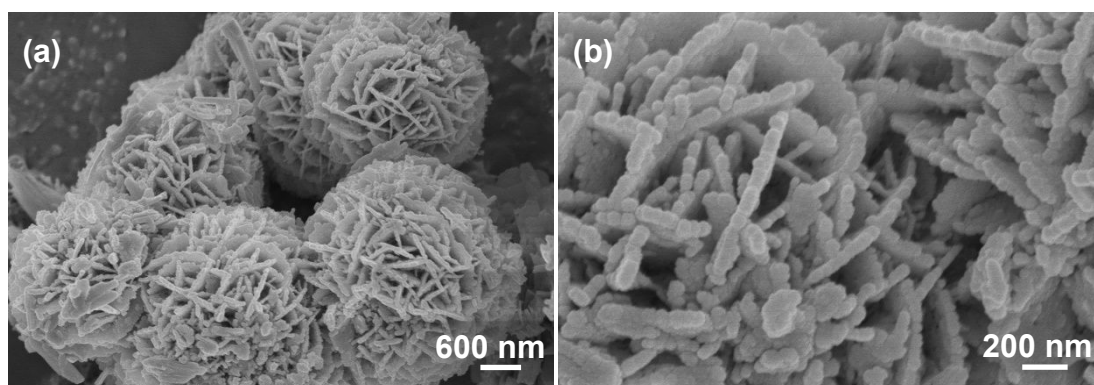


Figure S4. Low (a) and high (b) magnification SEM images of the CuMoO₄-CoMoO₄ sample prepared without natrium salicylicum.

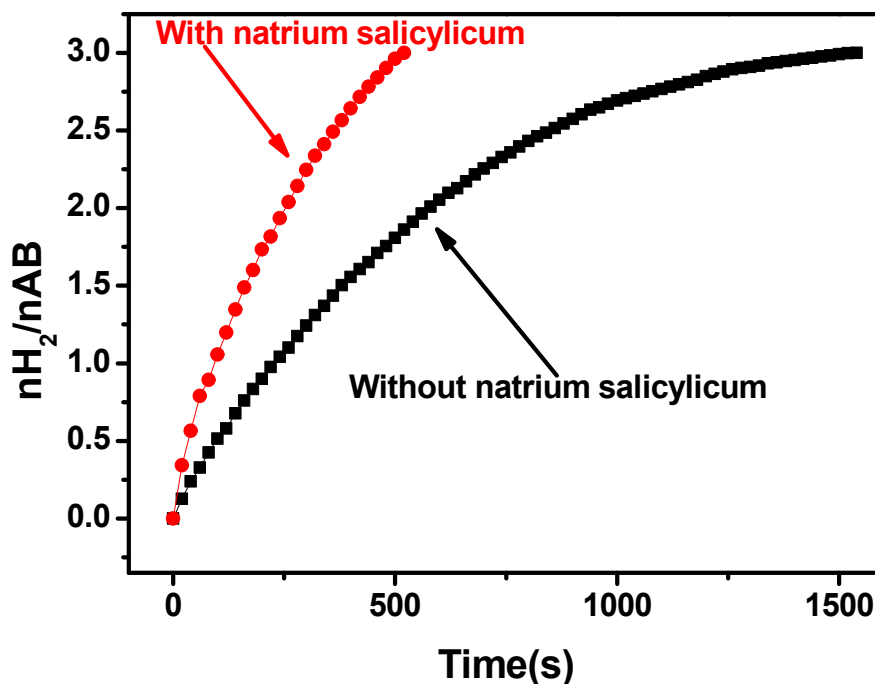


Figure S5. Catalytic activity of the CuMoO₄-CoMoO₄ samples prepared with and without natrium salicylicum in the synthesis.

Computational details

In this work, all the density functional theory (DFT) calculations were performed by using Vienna *Ab-initio* Simulation Package (VASP) [S1, S2]. The Projected Augmented Wave (PAW) method was adopted to describe the interaction between the ionic cores and valence electrons [S3]. The Perdew-Burke-Ernzerhof version of the generalized gradient approximation (GGA-PBE), including van der Waals corrections (DFT-D3 method), was used to describe the exchange and correlation effects [S4-S6]. For all the calculations, the cutoff energy was set to be 500 eV. To avoid the interaction between the neighboring periodic structures, we applied periodic boundary conditions with a vacuum slab of 15 Å. In addition, a 3×3×1 Monkhorst-Pack grids was carry out for all the calculations [S7]. During the structure optimizations, the bottom five layers were kept fixed while the top layers were allowed to be fully relaxed. The convergence threshold for the geometry optimizations was set to be 10⁻⁵ eV in energy and 0.02 eV Å⁻¹ in force. In order to reduce the calculation time, the convergence threshold for the transition state searching calculations was set to be 0.05 eV Å⁻¹ in force. The climbing image nudged elastic band (CI-NEB) method was taken to search the minimum energy pathway (MEP) involved in the bond-cleaving and -forming processes [S8].

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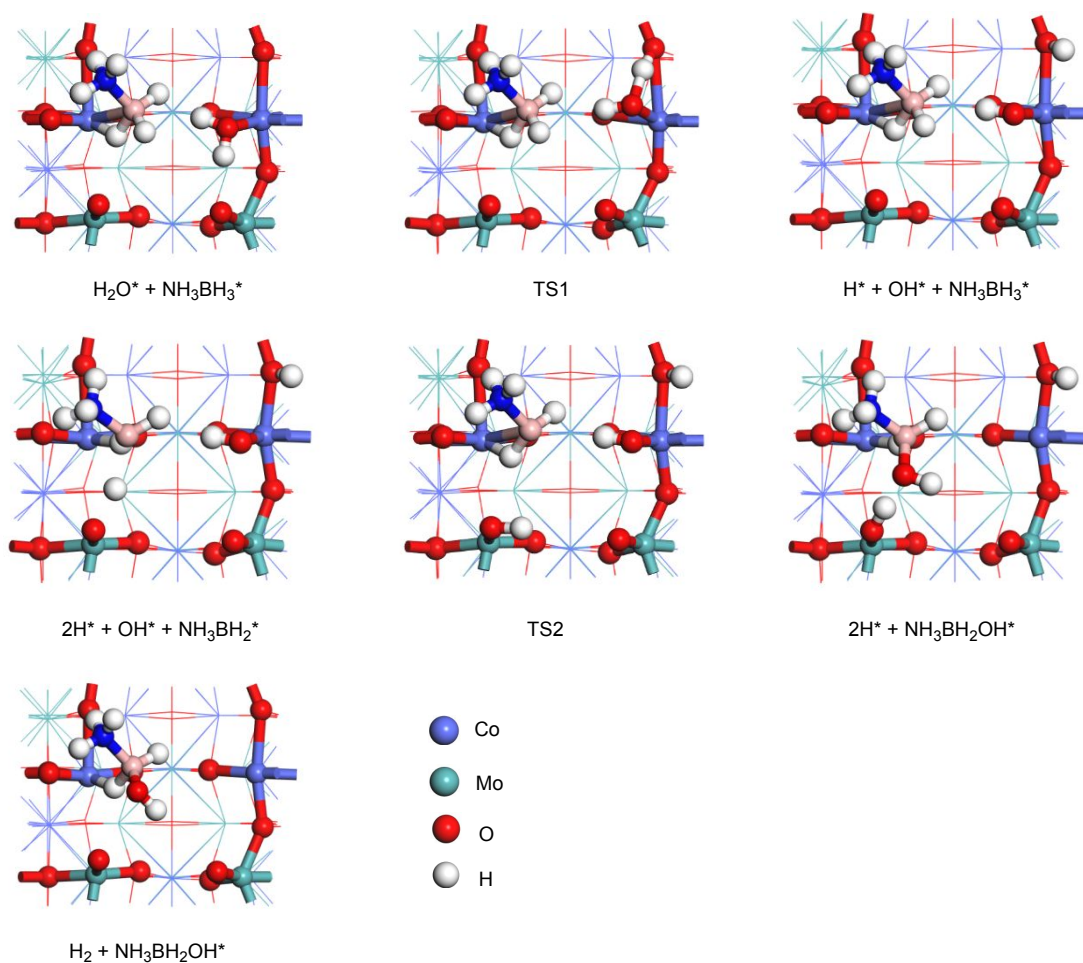


Figure S6. The crucial species of CoMoO₄ catalyzed AB hydrolysis.

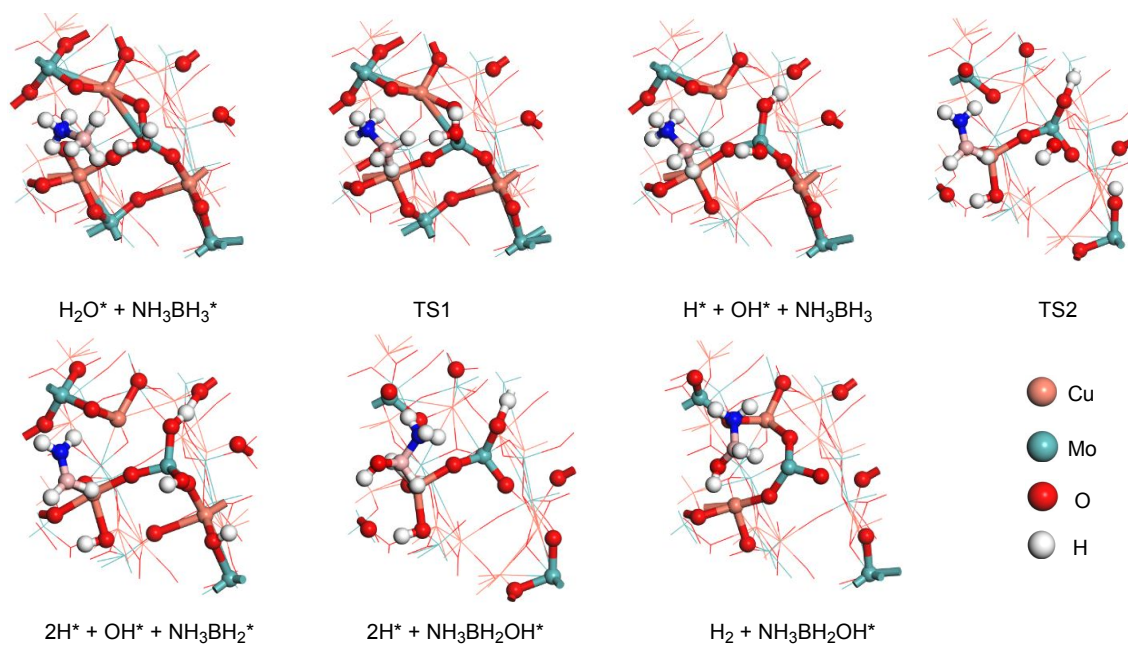


Figure S7. The crucial species of CuMoO₄ catalyzed AB hydrolysis.

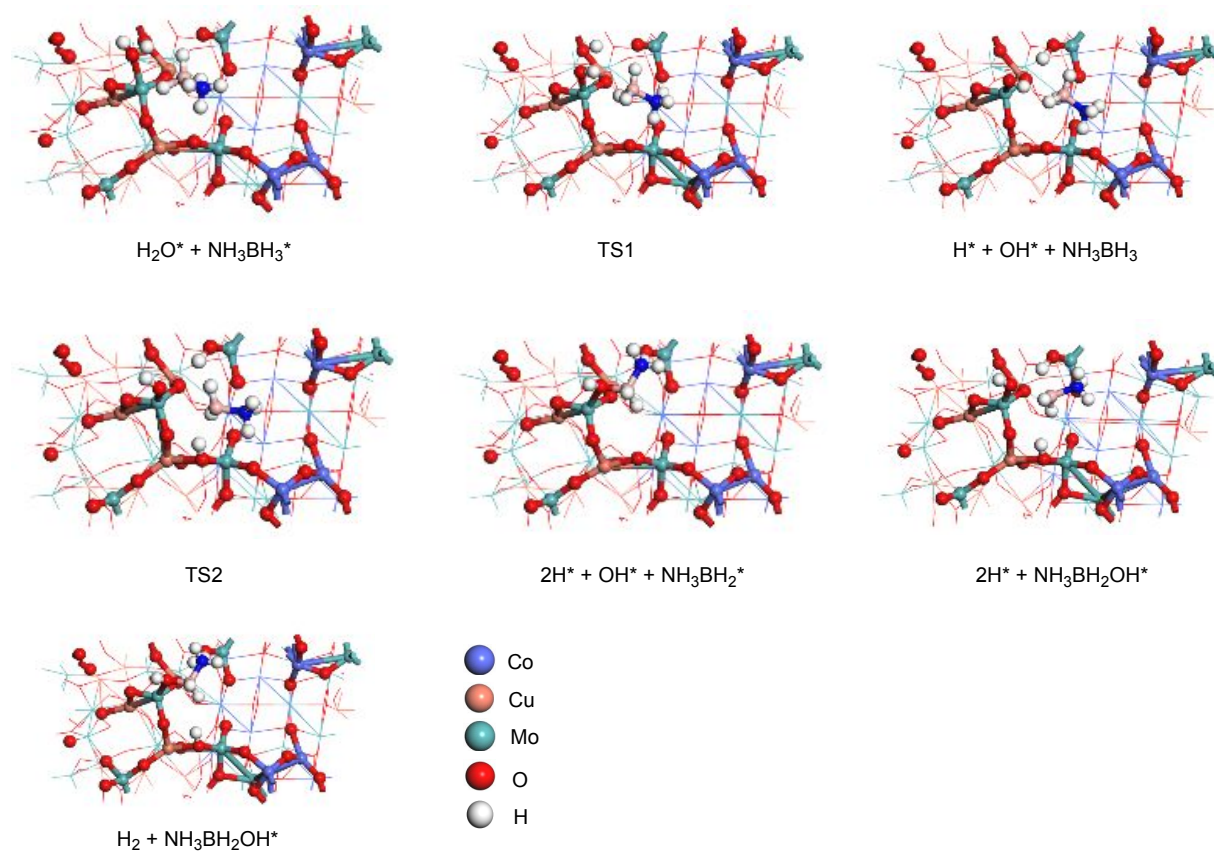


Figure S8. The crucial species of $\text{CuMoO}_4\text{-CoMoO}_4$ catalyzed AB hydrolysis.

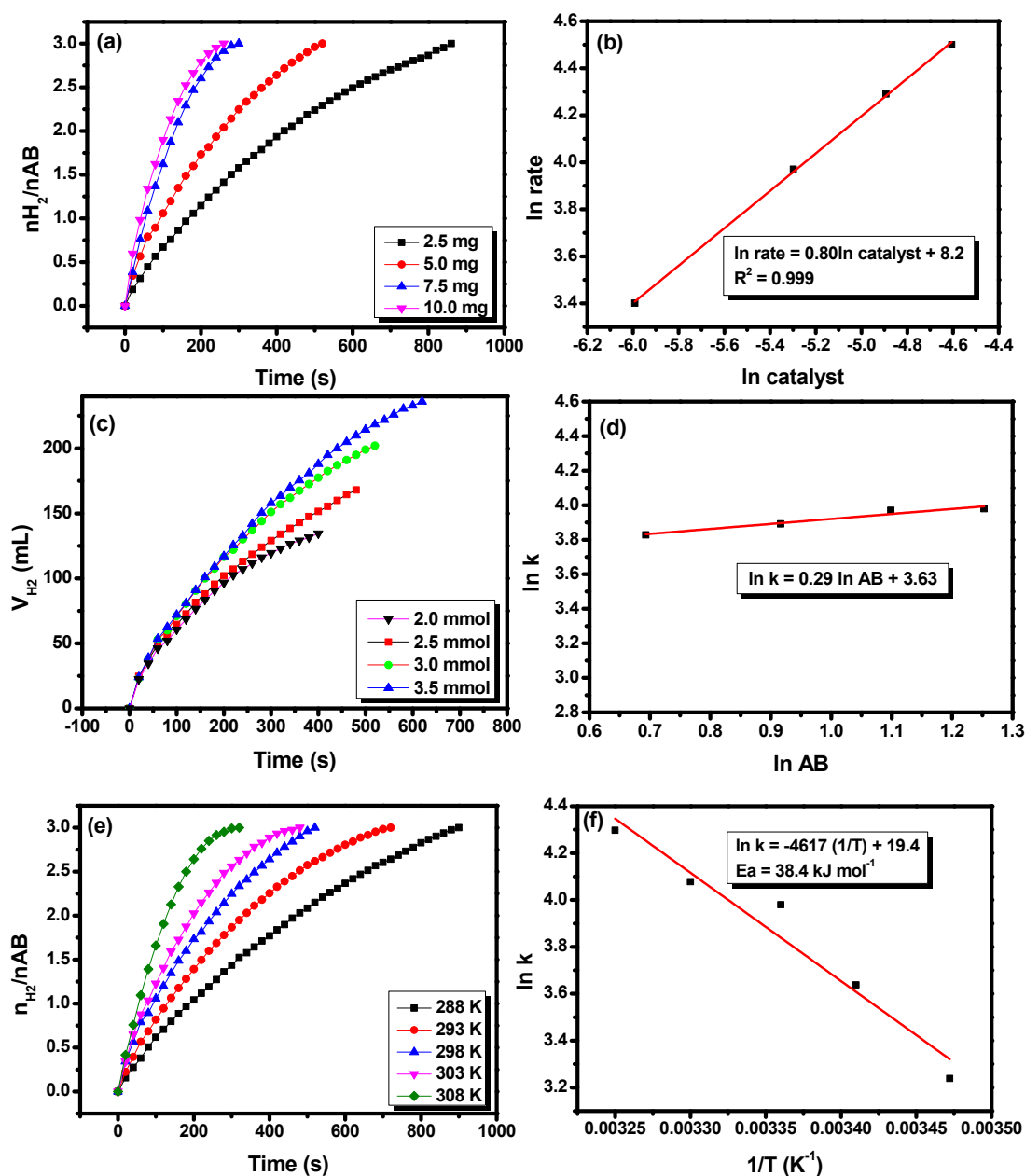


Figure S9. (a) Effect of catalyst amount on hydrogen evolution; (b) logarithmic value of the hydrogen evolution rate vs. logarithmic value of catalyst amount; (c) effect of AB amount on hydrogen evolution; (d) logarithmic value of the hydrogen evolution rate constant vs. logarithmic value of AB amount; (e) effect of reaction temperature on hydrogen evolution; (f) logarithmic value of the hydrogen evolution rate constant vs. reciprocal of reaction temperature.