Electronic Supplementary Information

# Photocatalytic reversible amination of α-keto acids on ZnS surface: Implications for the prebiotic metabolism

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## 1. Experimental details

### *1.1. Materials*

Amino acids （> 99%, Solarbio）and α-keto acids (>99, Aldrich) were used without further purification. All other chemicals (Sinopham) were obtained in analytical grade. Ultrapure water (Millipore) was deoxygenated with high purity argon gas (99.999%) by bubbling it through the water for 1 h before being used.

### *1.2. Preparation and Characterization of ZnS*

ZnS particles were prepared by two methods. In the first method, ZnS colloidal suspensions were freshly *in situ* precipitated with stirring by dropwise adding 20 mL of 0.1 M $Na_2S$ to 20 mL of 0.1 M $ZnSO_4$. In the second method, the newly-synthesized ZnS solid products were collected by filteration, washed with 15 mL deionized water five times, sucked as dry as possible and then calcined at 100-400 ℃ in a high purity nitrogen flow. Finally, the heat-treated ZnS was ground to 120 mesh and stored under argon atmosphere. According to both preparation methods, ZnS samples were labelled as $ZnS_{is}$, $ZnS_{100}$, $ZnS_{200}$, $ZnS_{300}$, and $ZnS_{400}$, respectively.

The phase stricture of the catalysts was measured by powder X-Ray diffraction (XRD) experiments on a Rigaku Ultrima IV diffactometer. The morphology and particle sizes were determined by field emission scanning electron microscopy (FESEM, Quanta 200FEG). Specific surface area (SSA) analysis was carried out on a Micromeritics ASAP 2420 surface area and porosity analyzer.

### *1.3. Photochemistry experiments*

All experiments were conducted in a 60-mL sealed quartz conical flask under flowing argon atmosphere at controlled temperature (Fig. S1). In a typical run, the flask was charged with 2 mmol ZnS, 1 mmol amino acids (or 1 mmol keto acids and

100 mmol $NH_4Cl$). $Na_2SO_3$ (10 mmol) was added as the hole scavenger when required. The final volume of the reaction solutions is 50 mL by surcharging water. The pH was adjusted to 9 using NaOH. A 500 W mercury-xenon lamp set in a closed box was used as an external light source. The light was collimated by a planoconvex lens (Φ25.4 mm, $f$ = 50 mm) and then ushered into the flask to trigger photoreaction (Fig. S1). The ZnS suspension was kept stirring (500 rpm) during the reaction.

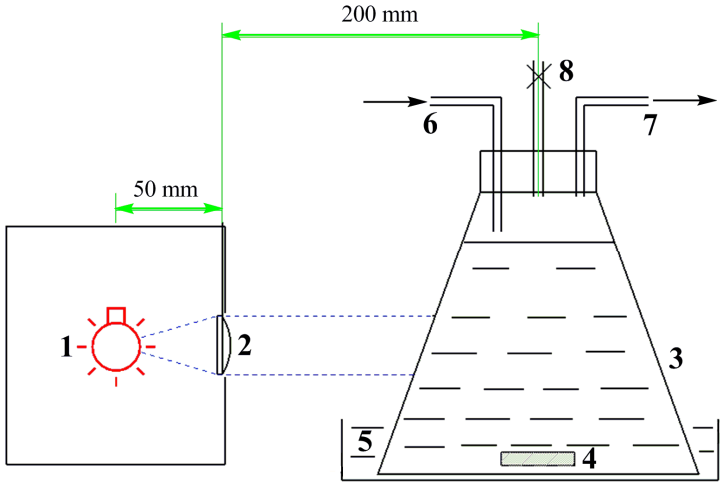


**Figure S1** Schematic diagram of the photochemical reaction apparatus (not drawn to scale). 1. 500 W mercury-xenon lamp; 2. Planoconvex lens (Φ25.4 mm, focal length $f$ = 50 mm); 3. Conical flask made of quartz; 4. Magnetic stirring bar; 5. Water bath; 6. Argon gas inlet (10 mL/min); 7. Argon gas outlet; 8. Sampling aperture.

### *1.4. Chemical products analysis*

After irradiation for a selected time period, 1.0 mL of the suspension was withdrawn from the flask through a sampling aperture (Fig. S1) and then forced through a 0.22 μm microvoid filter film. HPLC was used to determine the concentrations of keto acids[1] and amino acids[2] with a C18 column (Phenomenex, Luna, 5 μm, 250 × 4.6 mm).

## References

[1] M. Petrarulo, O. Bianco, D. Cosseddu, M. Marangella, S. Pellegrino, F. Linari, *J. Chromatogr. B* 1990, **532**, 130-134.

[2] Y. Fu, G. Yang, D. Gong, S. Yuan, D. Shi, G. Huang, W. Wang, *Chin. J. Pharm. Anal.* 2005, **25**, 762-764.

## Experimental data

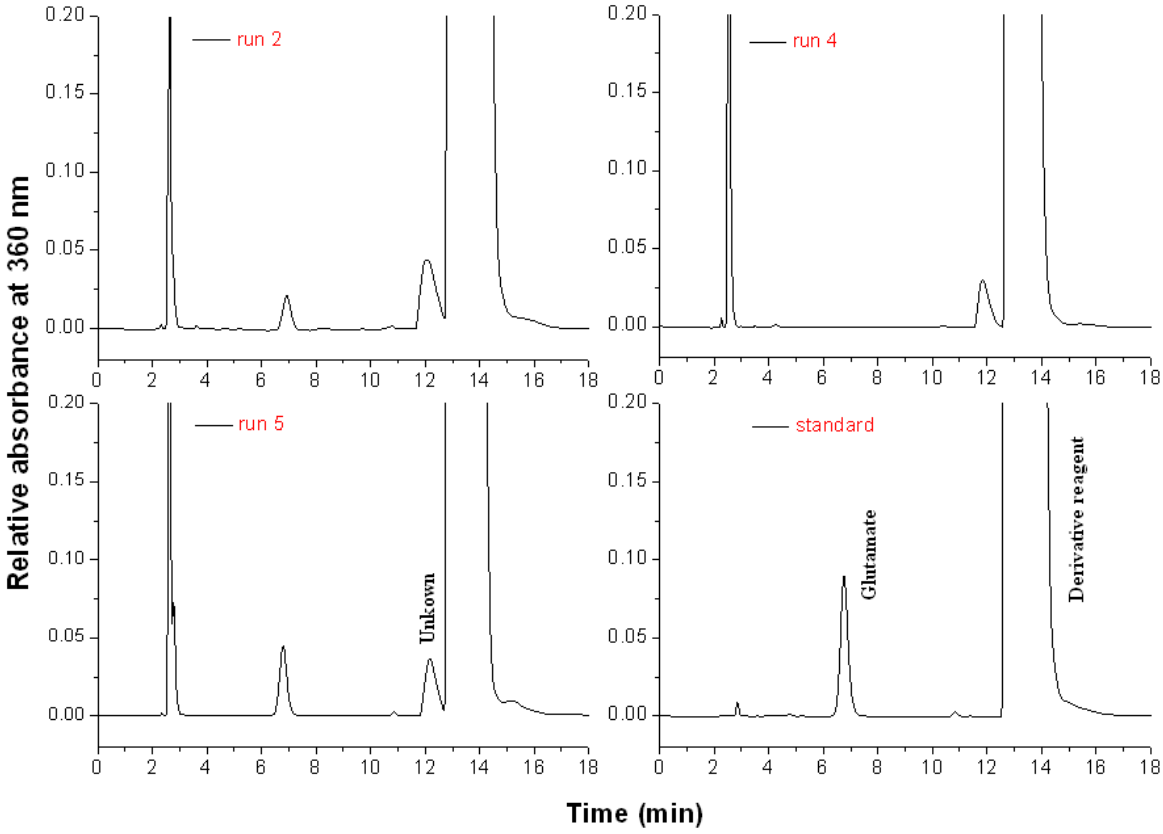


**Figure S2** HPLC analysis of glutamate from α-ketoglutarate (runs 2, 4, and 5 in Table 1). The bottom right separation profile shows the standard glutamate (5 mM).

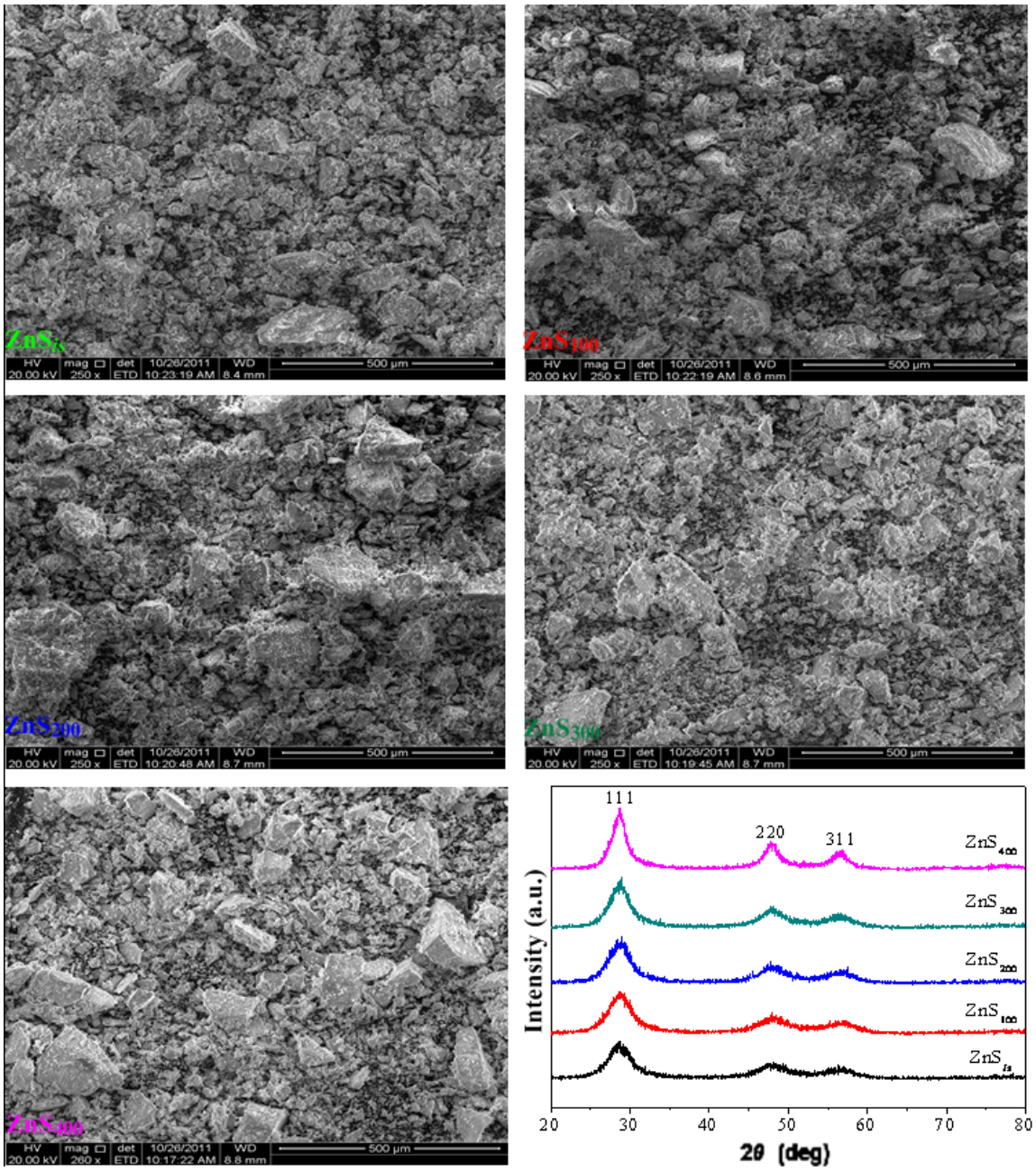


**Figure S3** SEM and XRD analyses of ZnS. It can be observed from the SEM micrographs that the samples prepared by different methods have similar particle size distributions. The XRD data show that the higher the thermal treatment temperature, the sharper the X-ray diffraction peaks and the higher the intensities of an XRD pattern, indicating the better crystallinity.

**Table S1** Comparison of the specific surface area of different ZnS samples and their catalytic efficiency in glutamate synthesis. It can be found that there exits no positive correlation between these two characteristics.

| Samples | Specific area ($m^2/g$) | Glutamate yields (%) |
|---|---|---|
| $ZnS_{is}$ | 106.19 | 2.9±0.3 |
| $ZnS_{100}$ | 165.09 | 7.4±0.7 |
| $ZnS_{200}$ | 199.39 | 6.8±0.6 |
| $ZnS_{300}$ | 143.46 | 0.6±0.1 |
| $ZnS_{400}$ | 132.22 | 1.5±0.1 |

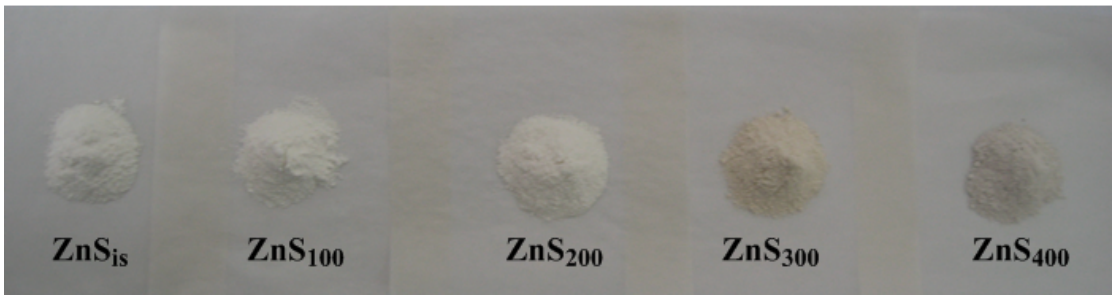


**Figure S4** Photographs of ZnS samples. It is clearly observed that higher temperature (> 300 ℃) gives rise to a visible alteration of the appearance of the samples. The dark color may act as an optical filter, reducing the photoelectron excitation from the valence band to the conduction band on ZnS surface.

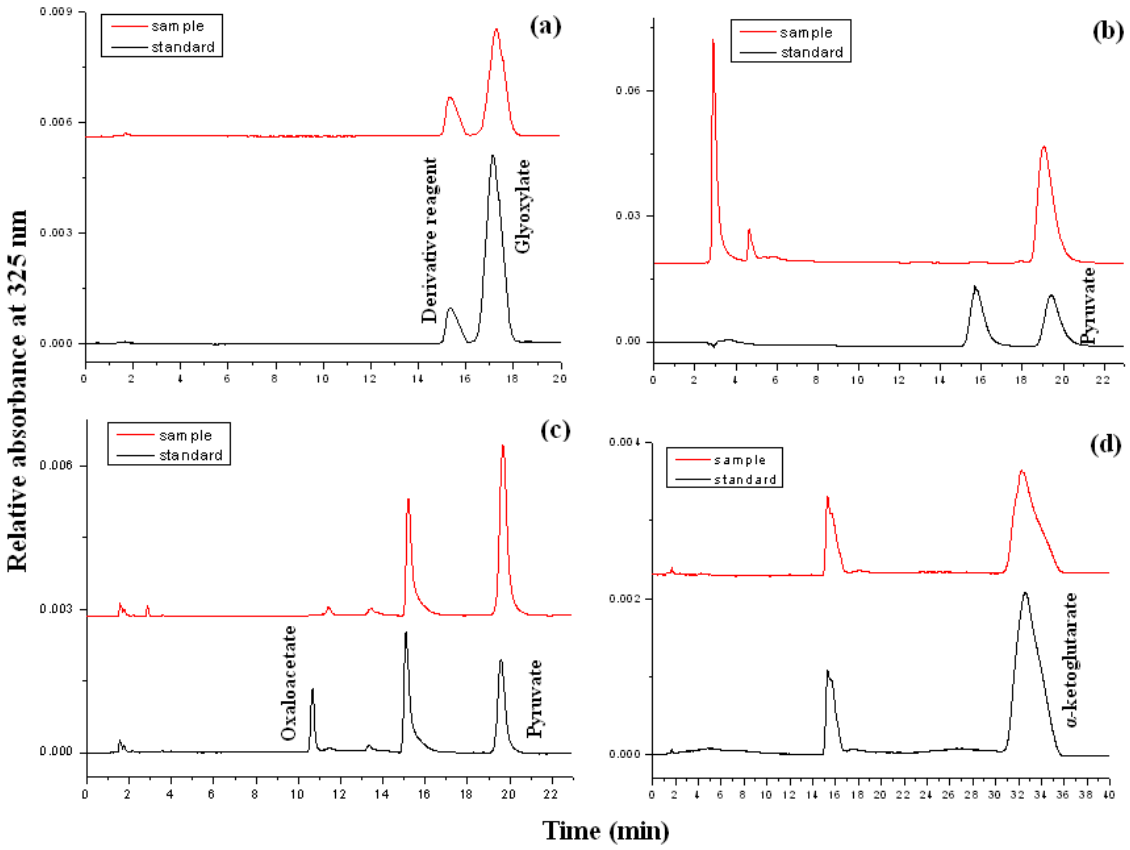


**Figure S5** HPLC profiles showing the formation of (a) glyoxylate, (b) pyruvate, (c) oxaloacetate, and (d) α-ketoglutarate due to the deamination of glycine, alanine, aspartate, and glutamate, respectively. Note that no oxaloacetate but pyruvate was formed in the aspartate sample. Reaction conditions: pH9, 30 ℃, 4 hours.

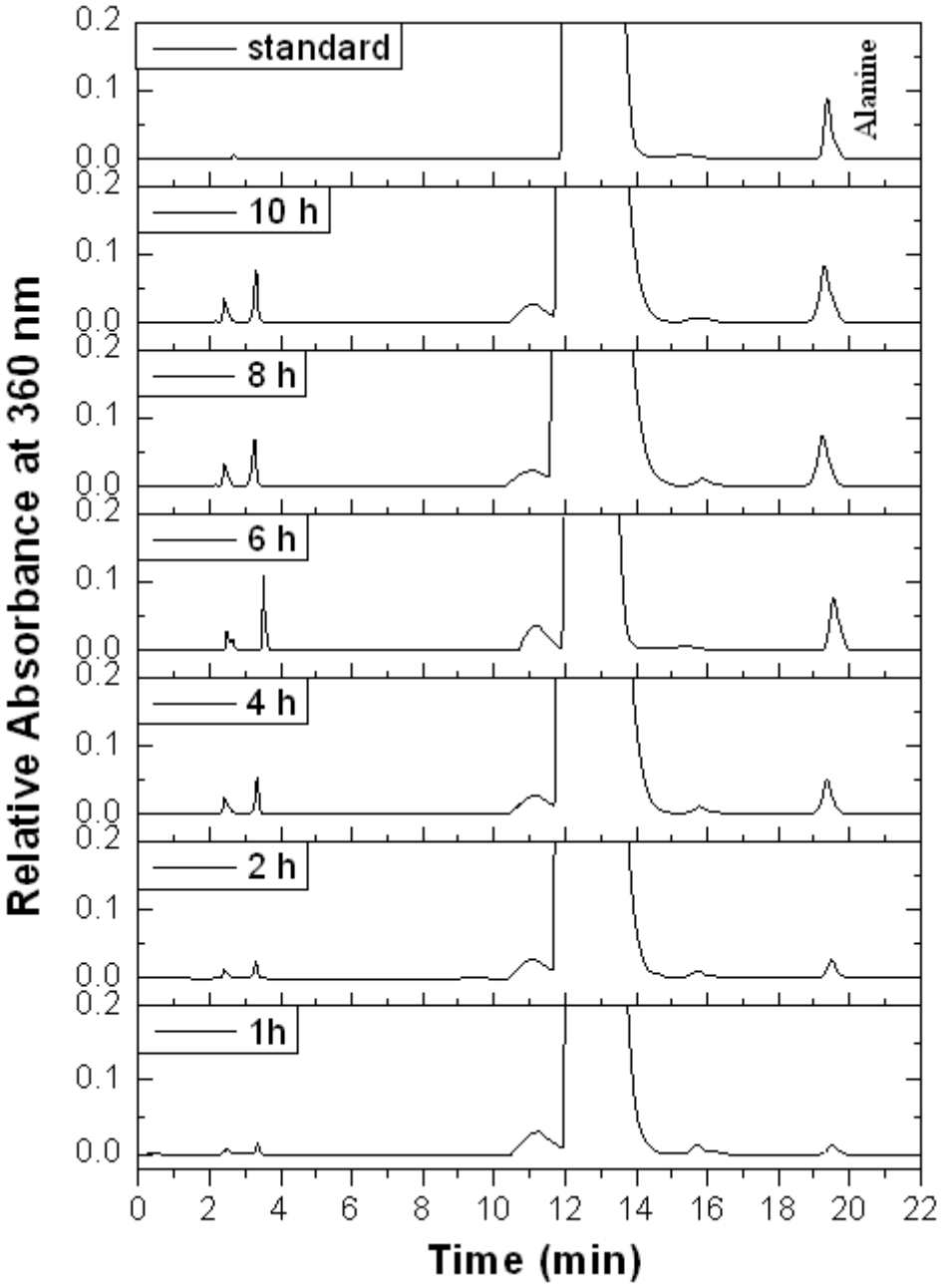


**Figure S6** HPLC analysis of alanine from pyruvate.

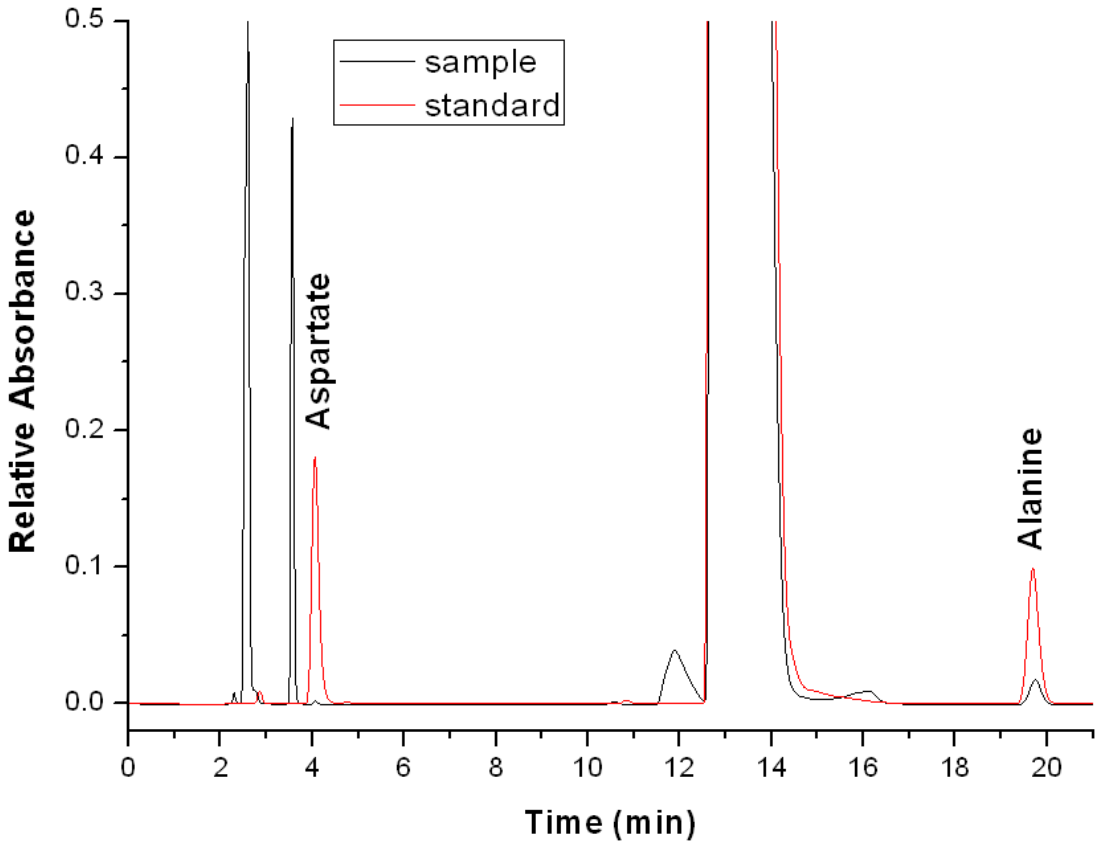


**Figure S7** HPLC analysis of aspartate and alanine from the amination of oxaloacetate. Please note that only trace of aspartate was formed. Reaction conditions: pH9, 30 ℃， 10 hours.

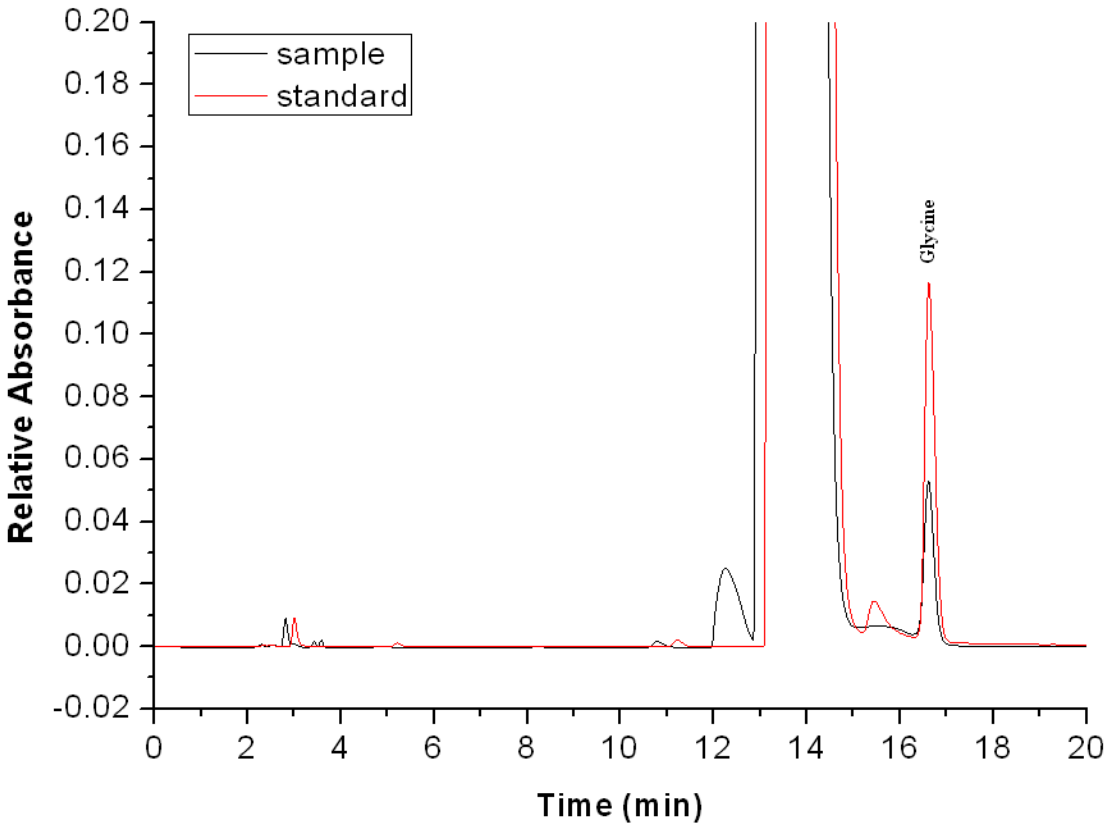


**Figure S8** HPLC profiles showing the formation of glycine from glyoxylate. Reaction conditions: pH9, 30 ℃， 10 hours.