Support Information

Microwave-accelerated direct synthesis of 3-picoline from glycerol through a liquid phase reaction pathway

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1. Characterizations

N_2-physisorption was conducted on a Quantachrome Autosorb-1 instrument at liquid-N_2 temperature. Before measurement, the specimen was in situ outgassed in the instrument at 300 °C for 12 h under a vacuum of 10^{-8} Torr. The Brunauer−Emmett−Teller (BET) method was employed to calculate the specific surface area, with the correlation coefficient being above 0.9999. The total pore volume was calculated at a relative pressure of P/P_0 = 0.99, assuming full surface coverage with nitrogen. The "t-plot" method was used to estimate the micropore area and volume.

Ammonia temperature-programmed desorption (NH_3-TPD) profile was recorded by a Micromeritics AutoChem II 2920 analyzer equipped with a TCD detector. The specimen (170 mg) was first heated by a rate of 10 °C·min^{-1} from room temperature to 400 °C in a stream of helium (99.99%, 60 mL·min^{-1}) and pretreated at that temperature and atmosphere for 0.5 h. Then, the specimen was cooled to 100 °C and subjected to ammonia-saturation in a stream of 5% NH_3/He with a flow rate of 50 mL·min^{-1}. After the sample was purged with helium at 100 °C for 1 h, ammonia was desorbed by heating the specimen to 800 °C at a rate of 10 °C·min^{-1}.

Figure S1

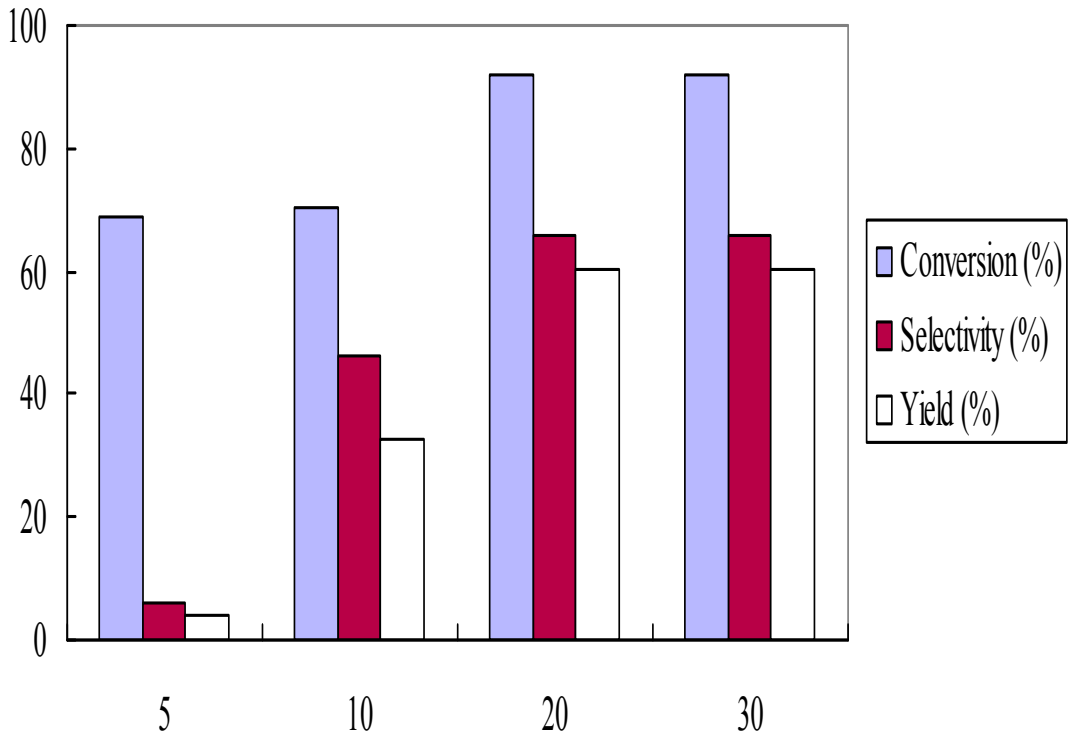

Fig. S1. Effect of reaction time (min) on the production of 3-picoline under microwave irradiation. (Reaction conditions: reaction temperature = 373 K, and molar ratio of glycerol / ammonium acetate / HAc = 1 / 3.58 / 15.4).

Figure S2

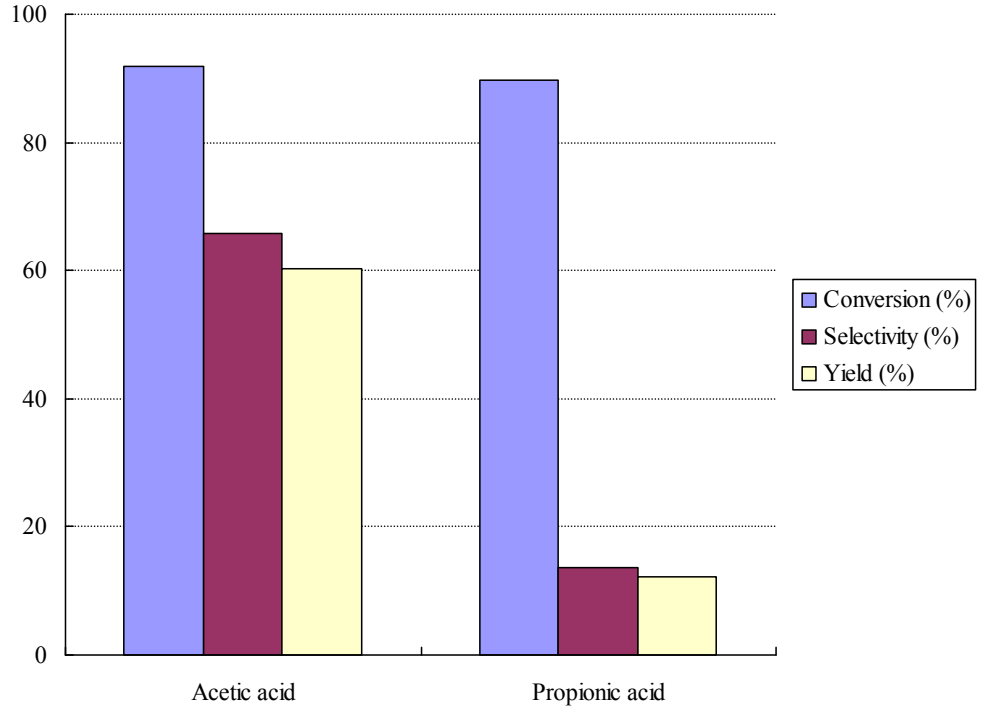

Fig. S2. Comparison between the production of 3-picoline using acetic acid and propionic acid as both the solvent and catalyst under microwave irradiation, respectively. (Reaction conditions: reaction temperature = 373 K, reaction time = 20 min, and molar ratio of glycerol / ammonium acetate / (acetic acid or propionic acid) = 1 / 3.58 / 15.4).

Figure S3

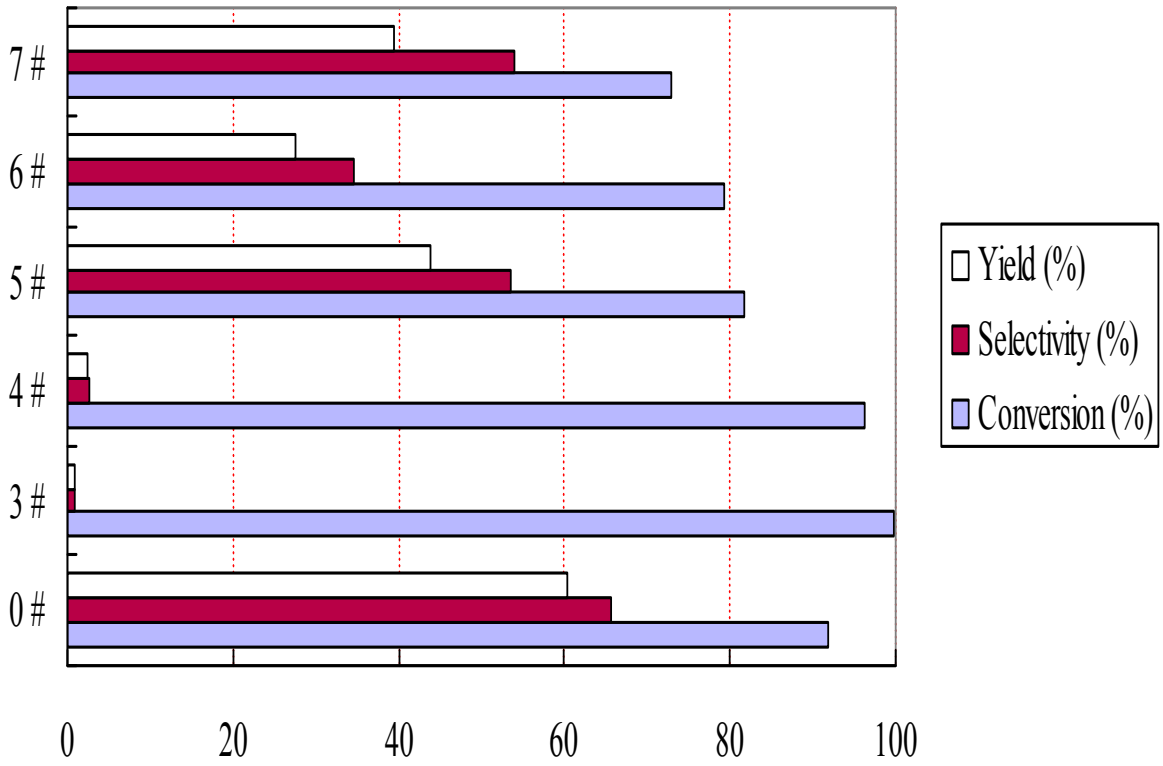

Fig. S3. Effect of various organic acid solid catalysts on the production of 3-picoline under microwave irradiation. 0 #: Blank, 3 #: stearic acid, 4 #: oxalic acid, 5 #: adipic acid, 6 #: sulfosalicylic acid, 7 #: edetic acid. (Reaction conditions: reaction temperature = 373 K, reaction time = 20 min, and mass ratio of glycerol/ammonium acetate/acetic acid/solid catalyst = 1/3/10/0.2).

Figure S4

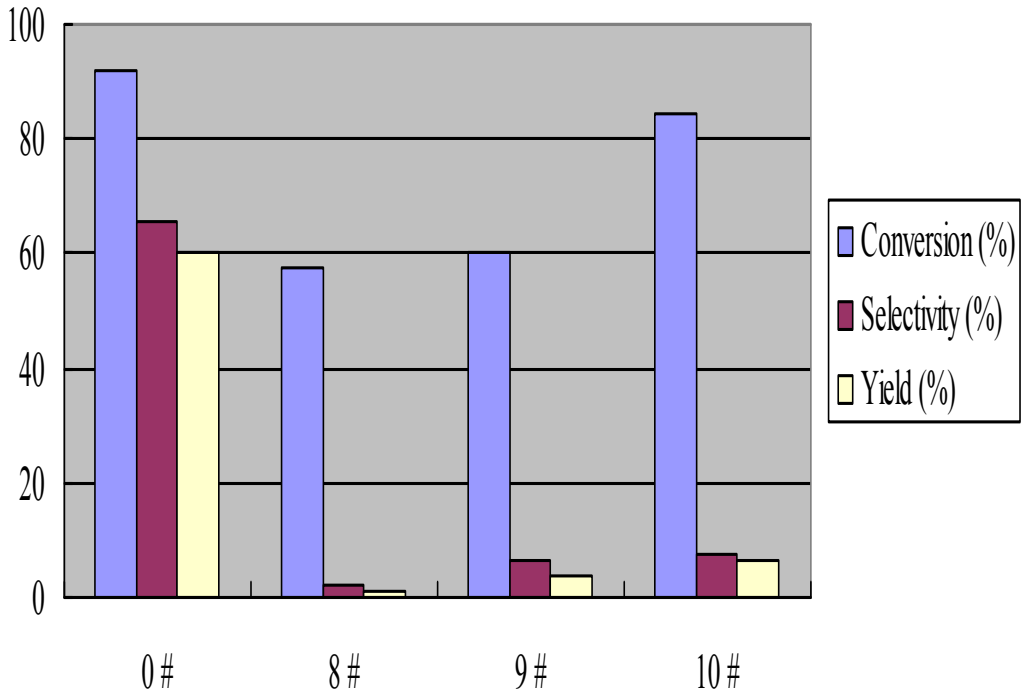

Fig. S4. Effect of various ion-exchanged resin on the production of 3-picoline under microwave irradiation. 0 #: Blank, 8 #: D 402 Na, 9 #: D 113 III, 10 #: D 001 H. (Reaction conditions: reaction temperature = 373 K, reaction time = 20 min, and mass ratio of glycerol/ammonium acetate/acetic acid/solid catalyst = 1/3/10/0.2).

Figure S5

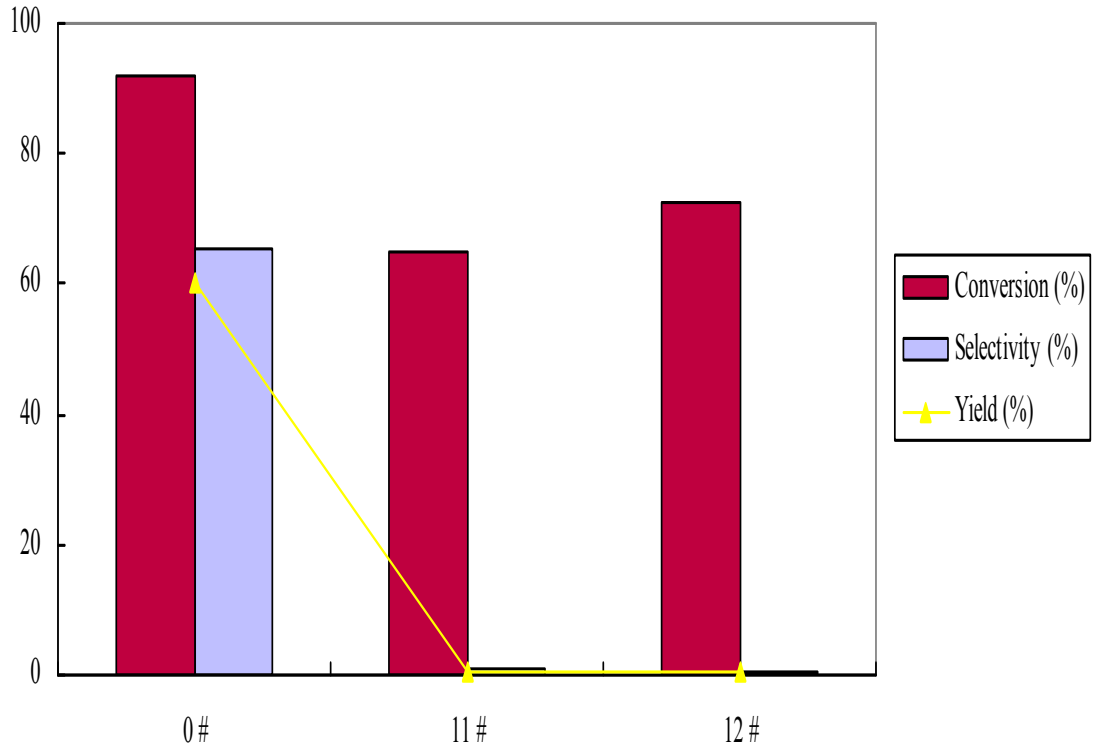

Fig. S5. Effect of KF and MgF_2 on the production of 3-picoline under microwave irradiation. 0 #: Blank, 11 #: KF, 12 #: MgF_2. (Reaction conditions: reaction temperature = 373 K, reaction time = 20 min, and mass ratio of glycerol/ammonium acetate/acetic acid/solid catalyst = 1/3/10/0.2).

Tables

Table S1

The textural and acid properties of various catalysts*

Catalysts	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	$T_{m,i}$ [a] and A_i [b] for various desorption peaks				
				$T_{m,1}$ (℃)	A_1 (mmol/g)	$T_{m,2}$ (℃)	A_2 (mmol/g)	A_{total} [c] (mmol/g)
HZSM-5	336	304	32	165	0.84	360	1.03	1.87

*S_{BET}, S_{micro} and S_{ext} refer to specific surface area, micropore surface area and external surface area, respectively, and $S_{BET} = S_{micro} + S_{ext}$.

[a] $T_{m,i}$ refers to the temperature at the maximum of desorption peak i;

[b] A_i refers to the integral area of desorption peak i and it means also the concentration of acid site corresponding to desorption peak i;

[c] $A_{total} = \Sigma A_i$.