Supporting Information

Highly efficient conversion of fatty acids into fatty alcohols with Zn over Ni catalyst in water

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(8 Pages)

1. **General information.**

Palmitic acid (AR, Sinopharm Chemical Reagent Co., Ltd) was used as reagent and 1-hexadecanol (≥99.5%, GC) was purchased from Aladdin Industrial Corporation for the qualitative analysis of the products in the liquid samples. Lauric acid, dodecanal and dodecanol were purchased from Aladdin Industrial Corporation to investigate the universality of this research. Ethyl acetate (AR, Shanghai Lingfeng Chemical Reagent Co., Ltd) was used as an extraction agent. As preliminary tests, various active metals including Zn, Fe, Mn (200 mesh AR, Sinopharm Chemical Reagent Co., Ltd) were used as reductants in powder form. Other metals and metallic compounds including Cu, Ni (200 mesh), Mo, CuO, Cu_2O, TiO_2, Fe_2O_3, MnO_2 and WC (AR, Sinopharm Chemical Reagent Co., Ltd) were used as catalysts in powder form. $CuFe_2O_4$ and $AgSiO_2$ were synthesized by our group, Ru/C (5 wt.%) was purchased from Aladdin Industrial Corporation, Pd/C (5 wt.%) was ordered from Sigma-Aldrich. All reagents were used as test materials without further purification.

2. **Product analysis.**

After reaction, the liquid samples were analyzed with a GC-FID (Agilent 7890A) equipped with a HP-5 capillary column with dimensions of 30 m × 0.32 mm × 0.25 μm for the quantification of hexadecanol. The liquid sample analysis was confirmed by GC-MS (Aglient GC7890A-MS5975C) equipped with an HP-5 capillary column with dimensions of 30 m × 250 μm × 0.25 μm. The solid samples were characterized by X-ray diffraction (XRD) (Shimadzu XRD-6100) to determine the composition and phase purity.

3. **General procedure for the synthesis of hexadecanol from palmitic acid.**

All experiments were conducted in a tube reactor (3/8 in. diameter, 1 mm wall thickness, and 120 mm length) made of SUS-316 alloys with an internal volume of 5.7 mL. In a typical procedure, the mixture of tested materials was added into the reactor, and then the sealed reactor was put into the salt bath that had been preheated to the desired temperature. The salt bath can offer a fast heat-up time of about 15 s from 20 ^{o}C to 300 ^{o}C. The reactor was shaken horizontally in the salt bath until the desired reaction time was completed. After the reaction, the reactor was taken out of the salt bath and put into a cold water bath to quench the reaction. The reaction time was defined as the time that the reactor was kept in the salt bath. Water filling was defined as the ratio of the volume of the deionized water put into the reactor to the

inner volume (5.7 mL) of the reactor. After cooling off, the extraction was processed in a volumetric flask with ethyl acetate, which was used to wash the reactor continuously until all the target products were extracted from the liquid sample. And then, the solution was kept standing for at least 30 min. After standing, the supernatant liquid was filtered with 0.45μm syringe filter. Solid sample was collected and washed with acetic ether several times and dried in air for analysis.

4. Definitions

The yield of hexadecanol is calculated as the percentage of hexadecanol to the initial palmitic acid on the carbon basis. The yields are mean value of three times experiments and relative errors of these data are less than 5%.

$$Yield,mmol\ \% = \frac{C\ in\ hexadecanol,\ mmol}{C\ in\ the\ initial\ palmitic\ acid,\ mmol} 100\%$$

$$\text{Water filling \%} = \frac{\text{Volume of water}}{\text{Volume of sus316 tube}}\ 100\%$$

5. GC-MS chromatograms of liquid products.

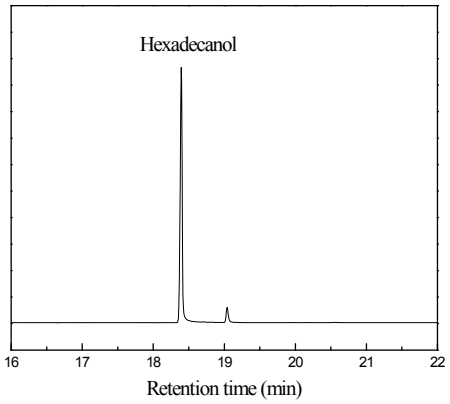


Fig. SI-1. GC-MS chromatogram of liquid products after palmitic acid reaction

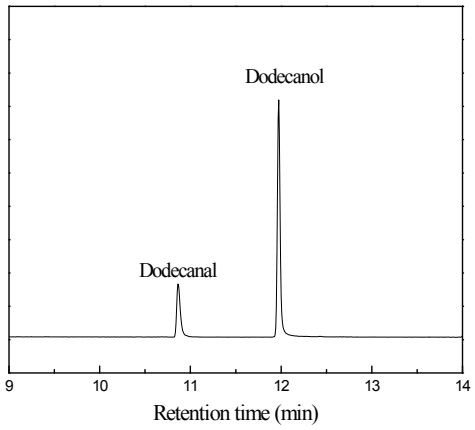


Fig. SI-2. GC-MS chromatogram of liquid products after lauric acid reaction

6. GC-FID chromatograms of liquid products.

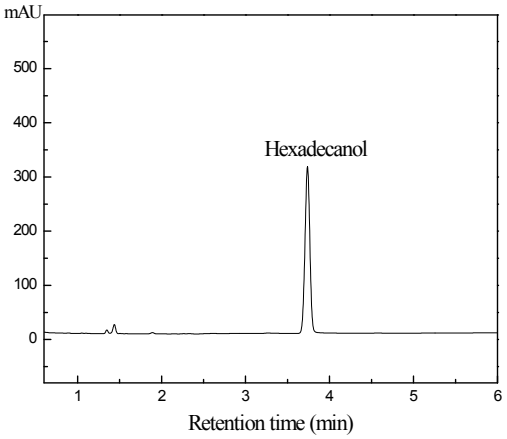


Fig. SI-3. GC-FID chromatogram of reagent hexadecanol in XRD pattern of solid products after the reaction with Zn over Ni catalyst.

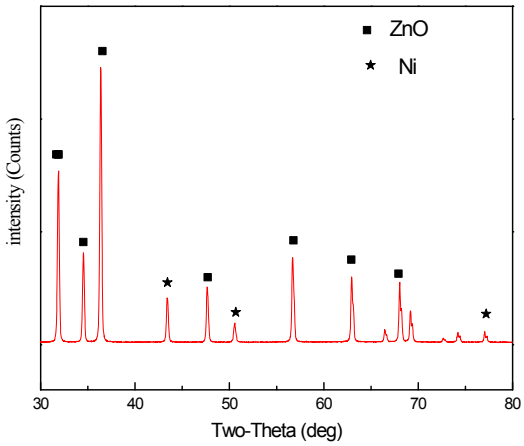


Fig.SI-4. XRD pattern of solid products after reaction (palmitic acid: 0.2 mmol, Zn: 6 mmol, water filling: 50%, temperature: 300 °C, time: 1 h).

7. Complementary reaction optimization data.

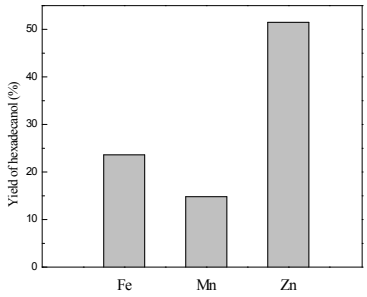


Fig. SI-5. Effects of different reductants on the conversion of palmitic acid into hexadecanol (palmitic acid: 0.2 mmol, Zn: 6.0 mmol, catalyst: 1.0 mmol, water filling: 40%, temperature: 300 °C, time: 1 h)

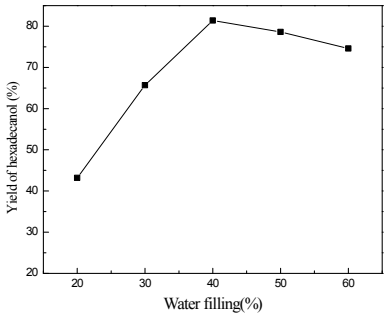
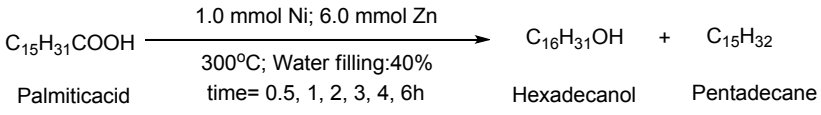


Fig. SI-6. Effect of water filling on the yield of hexadecanol (palmitic acid: 0.2 mmol, Zn: 5 mmol, Ni: 1mmol, water filling: 20~60%, temperature: 300 °C, time: 2h)

8. Conversion of palmitic acids into hexadecanol and pentadecane at different time.

In order to discriminate between these possibilities, we extended to 6 hours and the products were determined by GC-Mass. We have found that when the reaction time exceeded 3 h, production of pentadecane was obtained, and its yield increased with the time as the yield of hexadecanol decreasing. When the reaction time was extended to 3h、4h、6h, the Pentadecane could be obtained in same condition and the yield also increased along with the increase of reaction time. Following pictures were GC-Mass of reaction products at 1h、2h、6h.（Agilent 19091S-433: 2149.44829 HP-5MS 5% Phenyl Methyl Silox　325 °C: 30 m x 250 μm x 0.25 μm）



Scheme 2　Conversion of palmitic acids into hexadecanol and pentadecane

Table S1 Conversion of palmitic acids into hexadecanol and pentadecane at different time

Time	0.5h	1h	2h	3h	4h	6h
Hexadecanol %	30.3	51.5	**81.4**	78.1	69.7	42.5
Pentadecane %	-	5	12.5	23.4	30.6	38.6

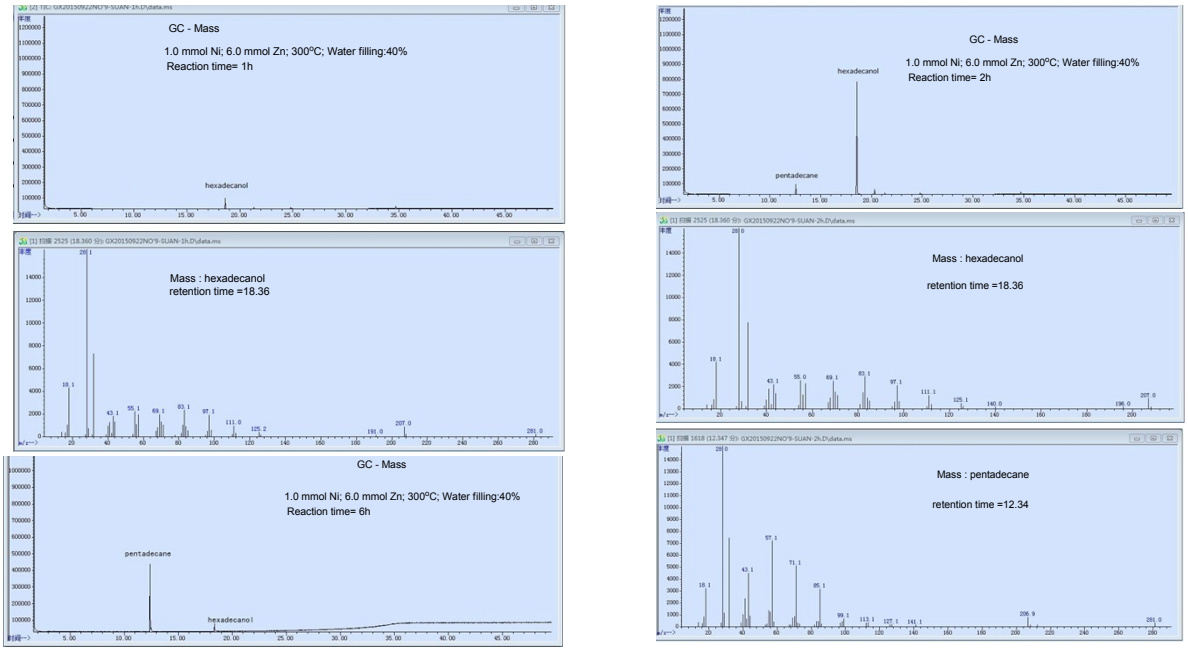


Fig SI-7.　GC-Mass of reaction products at 1h、2h、6h. (palmitic acid: 0.2 mmol, Zn: 6 mmol, Ni: 1mmol, water filling: 40%, temperature: 300 °C)

In order to double checked components of reaction products in 0.5h、1h、2h under the optimum conditions, we used GC-FID follows the track of reaction . The result was compared with that of experiment, showing good agreement with GC-Mass.

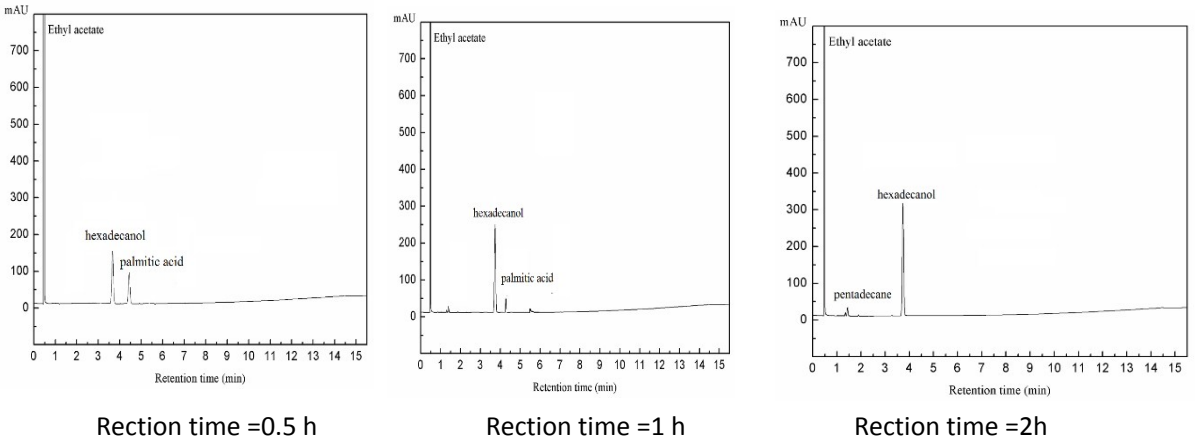


Fig. SI-8. GC-FID of reaction products at 0.5h、1h、2h (palmitic acid: 0.2 mmol, Zn: 6 mmol, Ni: 1mmol, water filling: 40%, temperature: 300 ^{o}C)

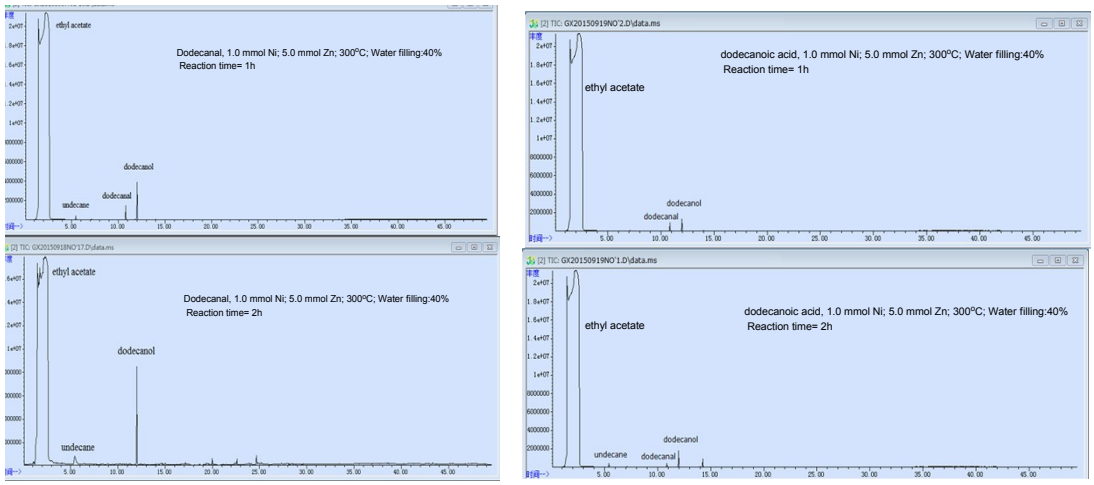


Fig. SI-9. GC-Mass of reaction products（dodecanoic acid and dodecanal）at 1h、2h.