A Tunable Process: Catalytic Transformation of Renewable Furfural with Aliphatic Alcohols in the Presence of Molecular Oxygen

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Supporting Information

Experimental

General methods

All reagents used are analytical grade and obtained from commercial. Oxygen supplied in a high-pressure cylinder was used through a reducing valve without further treatment.

The preparation and characterization of different catalysts

Synthesis of the support Fe_xO_y-Hydroxyapatite (FH)

At room temperature, an aqueous solution of Fe^{3+} and Fe^{2+} (mole ratio was 2:1) obtained by dissolving $FeCl_3·6H_2O$ (3.7 mmol) and $FeCl_2·4H_2O$ (1.85 mmol) in deoxygenated water (30 mL) under Ar atmosphere was added dropwise to a 25% ammonia water (15 mL) under vigorous stirring, as mentioned in section 1.1. After being stirred for 15 min, two 80 ml aqueous solutions of $Ca(NO_3)_2·4H_2O$ (33.7 mmol) and $(NH_4)_2HPO_4$ (20 mmol), with pH being adjusted to 10.3 as mentioned in section 1.2, were added dropwise simultaneously. The resultant grey suspension was heated to 90 ºC immediately and stirred for 2 h, and then cooled to room temperature and aged overnight. The obtained red brown precipitates were filtered, washed repeatedly with deionized water till neutrality, freeze-dried and calcined at 400 ºC for 5 h. The final brown powder was FeOx modified Hydroxyapatite which was denoted as FH.

The preparation of nano Au supported catalyst

Gold was deposited onto the three supports via a deposition-precipitation method. Typically, 40 mL $HAuCl_4$ aqueous solution (1.25 mg Au/mL) was taken into a beaker, and its pH value was adjusted to 9 by dropwise addition of aqueous solution of 0.1 M NaOH under vigorous stirring and monitored with a pH meter. 1.0 g supports (H, CeO_2, Fe_3O_4, and FH) were separately added to the solution under stirring, and the pH values of the resulted suspension were readjusted to 9 by 0.1 M NaOH aqueous solution. Then the suspension was heated to 65 ºC and stirred for 1 h. The precipitates were filtered, washed with deionized water for several times and then dried at 60 ºC overnight. The samples only were dried at 60 ºC and further calcined at 400 ºC for 3 h (denoted as Au/H, Au/Fe_3O_4, Au/CeO_2 and Au/FH catalyst).

The characterization of different Au supported catalysts

The measurement of X-ray diffraction (XRD) was performed by diffractmeter with Cu Ka radiation source at 35 kV, 40 mA (0.02 º resolution) and was collected from 10 to 80 º [2θ]. The morphology of catalytic materials was obtained by scanning electron microscope (SEM: JSM-6301F, JEOL) and transmission electron microscope (TEM: JEM-2100, JEOL). BET surface areas, pore volumes, and average pore diameters of the prepared samples were obtained from N_2 (77 K) adsorption measurement using a Micromeritics ASAP2020M system. Therein, the samples were pretreated under vacuum at 250 ºC for 4 h before the measurement. The average pore diameter data were calculated according to the Barrett-Joyner-Halenda (BJH) model in absorption and desorption period. Ammonia temperature programmed desorption (TPD) were carried out using a Micromeritics 2920 Autochem II Chemisorption Analyzer. Samples were first pretreated at 450 ºC for 1 h under He at a flow rate of 30 mL/min and cooled to room temperature, and were absorbed under NH_3 at a flow rate of 30 mL/min. During the TPD experiments, the temperature was set at 650 °C by means a temperature ramp of 10

°C/min using helium gas as carrier flowing at 60 mL/min. Effluent gas was dried by powder KOH and the concentrations of ammonia were recorded by thermal conductivity detector.

General procedure for the reaction of furfural and different alcohols in the presence of dioxygen

All catalytic experiments are performed in a 120 mL autoclave equipped with the magnetic stirring and automatic temperature control. A typical procedure for the reaction of furfural and alcohol is as follows: a 15 mL of alcohol solution of furfural (0.2 g), Au/FH (0.05 g) and K_2CO_3 (0.05g) is charged into the reactor, and the atmosphere inside is replaced with the pure oxygen after the reactor is sealed. Under stirring, oxygen is charged to 0.3 MPa at room temperature and the autoclave is preheated to 140 ºC, and then kept for 4 h. After reaction, the autoclave was cooled and the obtained mixture is analyzed by GC and GC-MS after the excess gas is purged.

BET measurement of different Au supported catalysts

In Table 1s, the results of BET measurement are presented. It can been seen that the surface area and pore volume of Au/FH are larger than those of Au/H, Au/Fe_3O_4 and Au/CeO_2 catalysts. Moreover, the average pore diameter of Au/FH is also larger than that of other catalysts. These data indicated that the dispersion of Au particle in Au/FH is better and the contact with the reactant is more frequent which impels the rapid proceeding of the reaction. It is also proved by the data of catalytic test.

Table 1s The textural properties of different Au supported catalysts

Catalysts	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)		Average pore diameter (nm)	
		BJH adsorption	BJH desorption	BJH adsorption	BJH desorption
Au/FH	87.16	0.1393	0.2193	64.30	92.96
Au/H	61.84	0.08686	0.1216	55.42	77.81
Au/Fe_3O_4	37.45	0.05111	0.08308	53.07	82.27
Au/CeO_2	2.185	0.002281	0.002019	44.52	51.99

volume of pores cumulated between 17.000 Å and 3,000.000 Å diameter

XRD Patterns of different Au supported catalysts

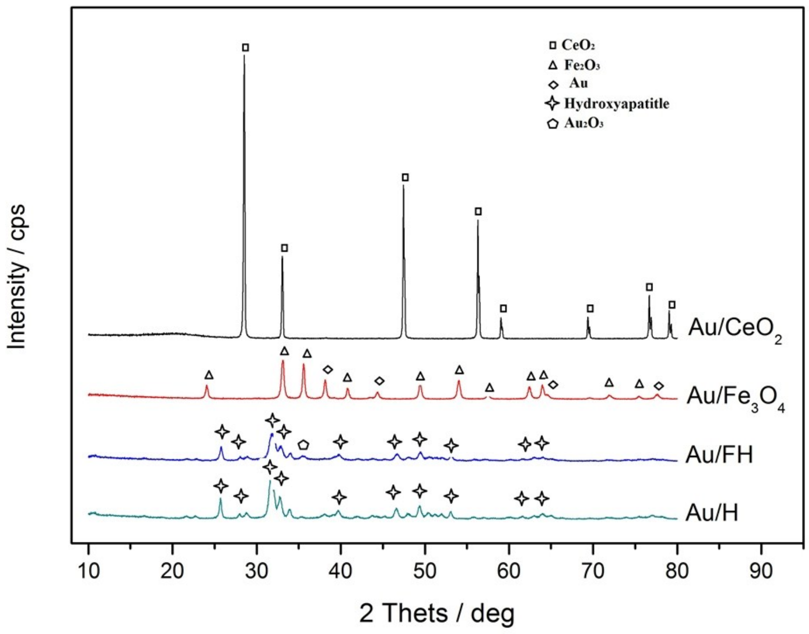

Figure 1s. The XRD patterns for different Au supported catalysts

The results of XRD characterizations on the different Au supported catalysts are shown in Figure 1s. For the Au/CeO_2 catalytic material, the main peaks are contributed to the diffractions of cubic CeO_2 crystal, and the characteristic diffraction peaks of Au is weak, which indicated the crystallites of Au in Au/CeO_2 are not very regular. For the Au/Fe_3O_4 catalytic material, it is found that the distinct peaks of nano Au appeared on Fe_3O_4, in which the peaks at 2θ =38.2°, 44.3°, 64.6°and 77.5° are assigned to the diffraction of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal of Au competent, and the peaks at 2θ = 24.1°, 33.1°, 35.6°, 40.8°, 49.3°, 54.0°, 62.3°, 63.9°, 71.8° and 72.2° are attributed to the representative diffractions of Fe_2O_3 competent. For the Au/FH and Au/H catalytic materials, the main peaks should be attributed to the diffractions of hydroxyapatite, while the typical diffraction peak of Au_2O_3 appears at 2θ being 35.6° that can be reactive species for oxidation processes in the FMO system and FPO system.

TEM images of different Au supported catalysts

In the following, the Au supported catalytic materials are further characterized by TEM technique. As shown in Figure 2s, the size of most particles in Au/FH and Au/H samples before calcination is similar with that in Au/FH and Au/H catalysts after calcination (about 3-5nm).However, the size of particles in Au/CeO_2 catalyst (about 17 -19nm) is larger than that in Au/FH catalyst, therefore the catalytic activity of the Au/CeO_2 catalyst is much lower than that of the Au/FH catalyst in the reaction.

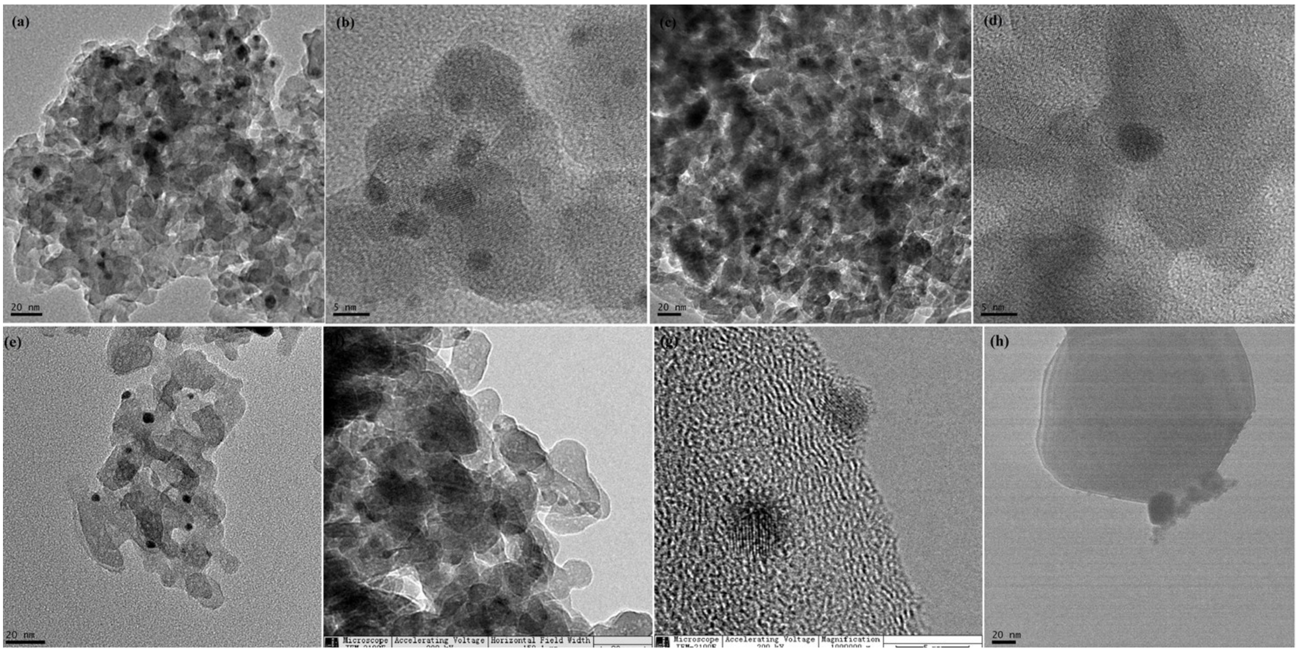

Figure 2s. The TEM results for the Au supported catalysts (Au/FH: a, b -before calcination; c, d- after calcination; Au/H: e-before calcination; f, g-after calcination; Au/CeO_2: h-after calcination)

TPD measurement

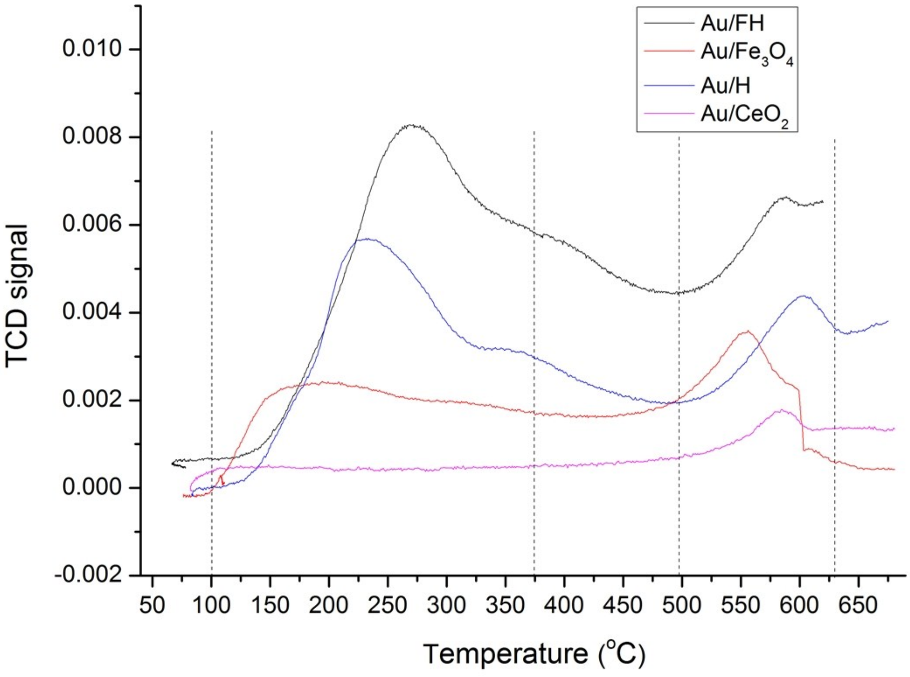

Figure 3s. The TPD results for different Au supported catalysts

The NH_3-TPD detection was performed and the results are given in Figure 3s. It is found that the highest peak of Au/FH was about 278 ºC, that of Au/Fe_3O_4 was 560 ºC, that of Au/H was about 220 ºC, and that of Au/CeO_2 was 580 ºC. Thus, Au/FH and Au/H mainly have weak acid sites, Au/Fe_3O_4 and Au/CeO_2 has middle acid sites. It can be concluded that the numerous weak acid sites were helpful to catalytic reaction in FAO system.

Detailed GC Measurement conditions and the spectrum for the product analysis

Gas chromatography measurements were conducted using an Agilent model 4890D gas chromatograph with a flame ionization detector. A HP-5 capillary column (30m×0.25mm× 1.0um) and HP-5MS (30m×0.25mm×025um) capillary column were used to separate different reaction products for the catalytic oxidation of numerous aromatic alcohols, respectively.

General GC conditions---detector temperature: 250 ºC; injection temperature: 220 °C; Carrier gas: nitrogen; the rate of carrier gas: 1.0 ml / min. The internal standard method is employed for the calculation of conversion and selectivity, and the internal standard is 1, 3-dichlorobenzene during analysis.

The GC/MS spectra of products

The qualitative analysis of products are conducted with an Aglient 6890/5973 GC-MS equipped with a HP-5MS capillary column (30m×0.25mm×0.25μm), and the corresponding GC/MS spectra for the products of oxidation of different alcohols are shown in Figure 3s-4s.

Based on the GC-MS spectra, it is indicated that the main product is methyl 2-furoate in the FMO system; while, the main product is 3-(furan-2-yl-)-2-methylacryaldehyde in the FPO system under similar conditions.

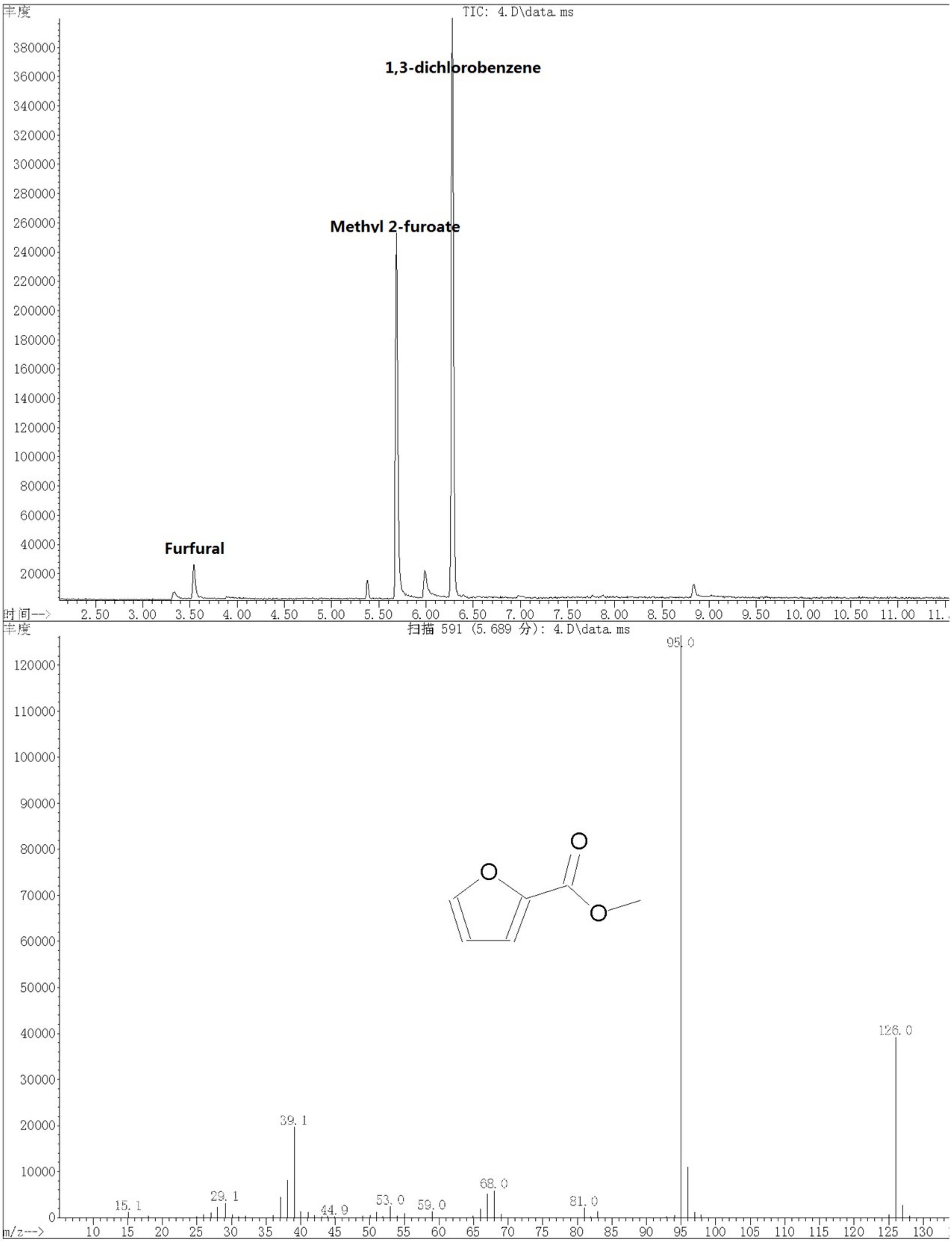

Fig 3s. the GC-MS spectrum of the reaction of furfural, methanol and molecular oxygen.

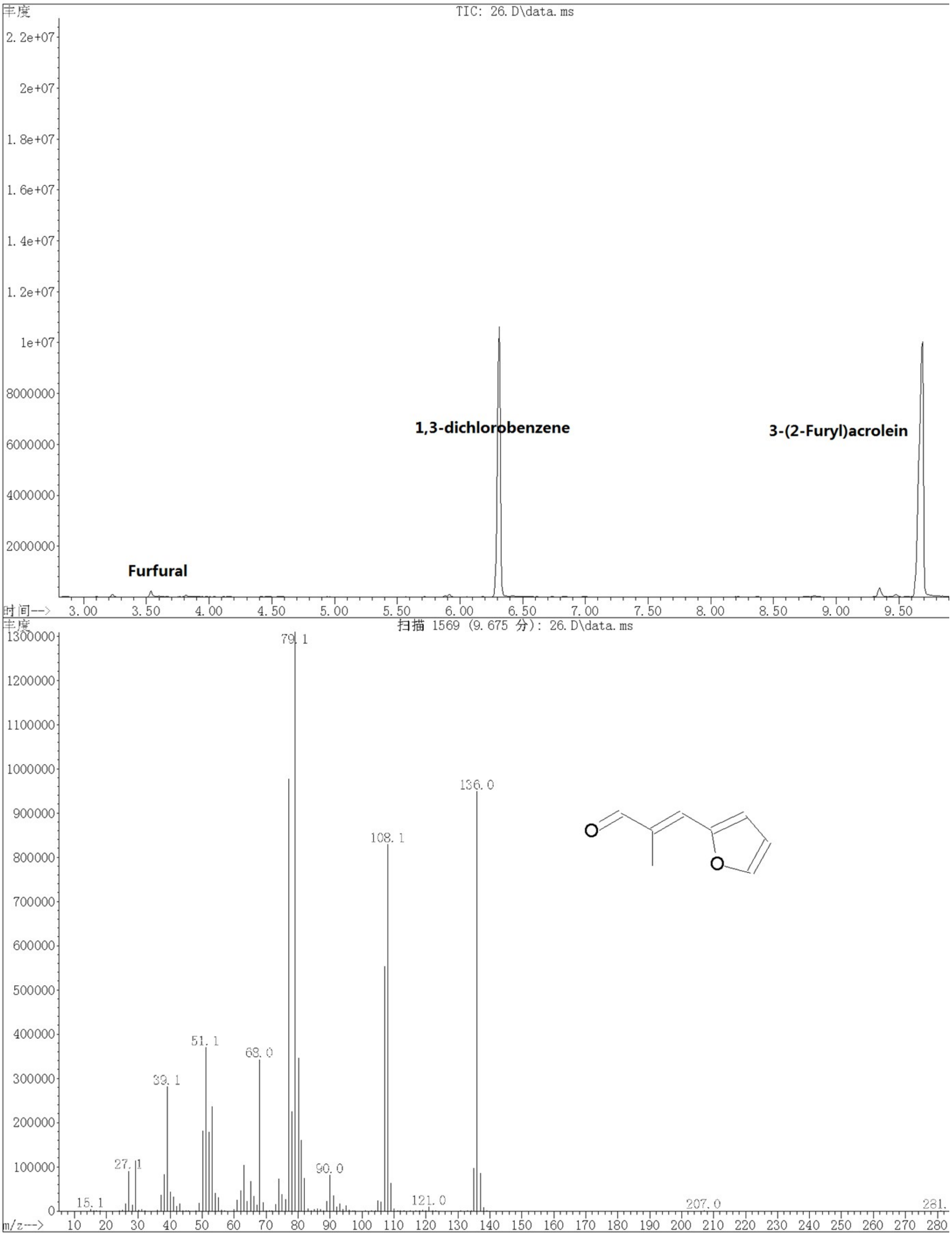

Fig 4s. the GC-MS spectrum of the reaction of furfural, molecular oxygen and n-propanol.