

Supporting Information

Highly Efficient Alloyed NiCu/Nb₂O₅ Catalyst for Hydrodeoxygenation of Biofuel Precursor into Liquid Alkanes

Peiyang Wang,^{§a} Yaxuan Jing,^{§a} Yong Guo,^a Yan Cui,^b Sheng Dai,^b Xiaohui Liu^a and Yanqin Wang^{*a}

1. Supplementary experimental materials

All chemicals were purchased from Adamas Reagent Co. Ltd, except for metal precursors Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O and Cu(NO₃)₂·3H₂O, which were purchased from Sinopharm Chemical Reagent Co. Ltd.

The aldol adduct of furfural and acetone (FA) was prepared by aldol condensation of furfural with acetone in a 50 mL round-bottom flask. In a typical process, the reactions were carried out by adding 2 g of furfural, 20 g of 0.3M NaOH aqueous solution, 20 g methanol as solvent, and calculated amount of acetone (the molar ratio of furfural with acetone was 1:10) at room temperature. Under continuous stirring, the reactions were stopped not until the conversion of furfural > 99%. For the conversion of furfural (or HMF) analyses, an appropriate amount of the reaction mixture was sampled, followed by neutralizing with dilute hydrochloric acid and GC analysis for every 30 min. For aldol adducts separation, the aldol adducts were extracted from aqueous/methanol phase by 3 * 20 ml of dichloromethane. After the extraction, the selectivity to FA was analyzed by GC equipped with flame ionization detector (FID). FA was direct obtained by removing dichloromethane with rotary evaporation at 40 °C without further purification.

The BTHF used for kinetic reaction was the product of hydrogenation of 2-n-butyl-furan, for each reaction, 0.6 g 2-n-butyl-furan was hydrogenated by 2%Pd/Al₂O₃ under 160 °C, 3 MPa H₂ and 6.46 g cyclohexane as solvent for 12 h in sealed autoclave. After centrifugalization and evaporation, we obtained the BTHF determined by GC-MS system.

2. Supplementary results

Table S1. HDO of FA over various NiM/Nb₂O₅ catalysts after 2 hours.

Cat.	Yield of octane /%	Yield of heptane /%	Octane/hep tane ratio O/H	Yield of (1+2+3) /%	Yield of 4 /%	Yield of 5 /%	Yield of DOE /%	CB. /%
20%Ni/Nb ₂ O ₅	19.3	9.2	2.1	8.3	28.1	26.3	1.5	93.1
10%Ni10%Co/Nb ₂ O ₅	35.5	6.0	5.9	3.0	8.1	24.2	9.3	90.2
10%Ni10%Fe/Nb ₂ O ₅	37.4	8.0	4.7	3.5	5.6	33.5	2.4	90.3
10%Ni10%Cu/Nb ₂ O ₅	59.5	2.2	27.0	5.8	0.3	16.8	5.4	91.2

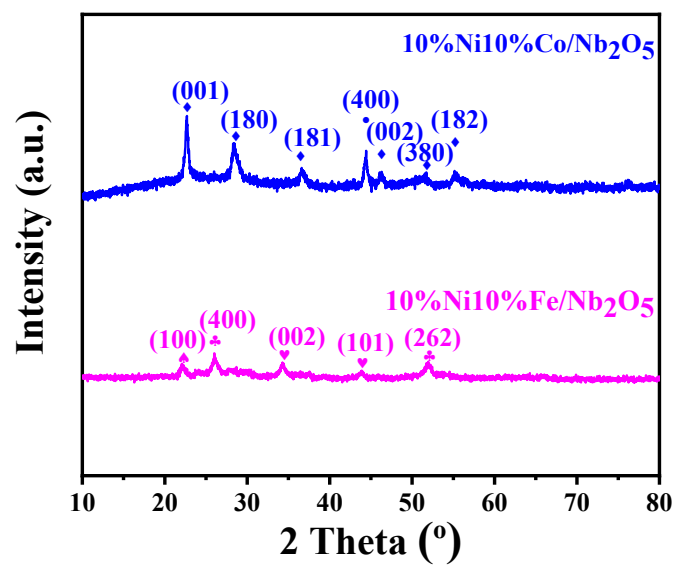


Figure S1. XRD patterns of various NiM/Nb₂O₅ catalysts

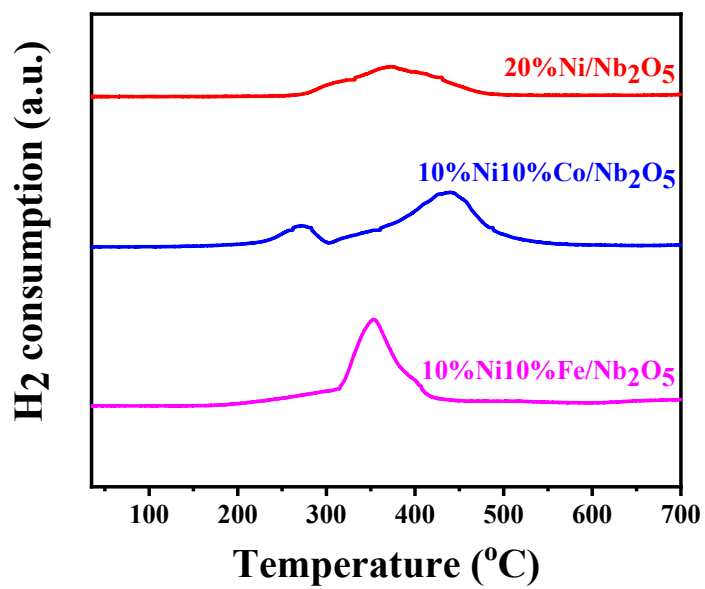


Figure S2. H₂-TPR patterns of various NiM/Nb₂O₅ catalysts.

Table S2. Summary of physicochemical properties of various NiM/Nb₂O₅ catalysts.

Cat.	Surface area	Pore size	Pore volume
	/m ² ·g ⁻¹	/nm	/cm ³ ·g ⁻¹
20%Ni/Nb ₂ O ₅	106.8	11.3	0.28
10%Ni10%Cu/Nb ₂ O ₅	71.1	13.1	0.22
10%Ni10%Co/Nb ₂ O ₅	68.0	13.1	0.20
10%Ni10%Fe/Nb ₂ O ₅	65.7	12.8	0.21
20%Cu/Nb ₂ O ₅	15.6	17.3	0.20
Nb ₂ O ₅ ^(a)	67.3	15.3	0.46

^(a)Reduced under 500 °C.

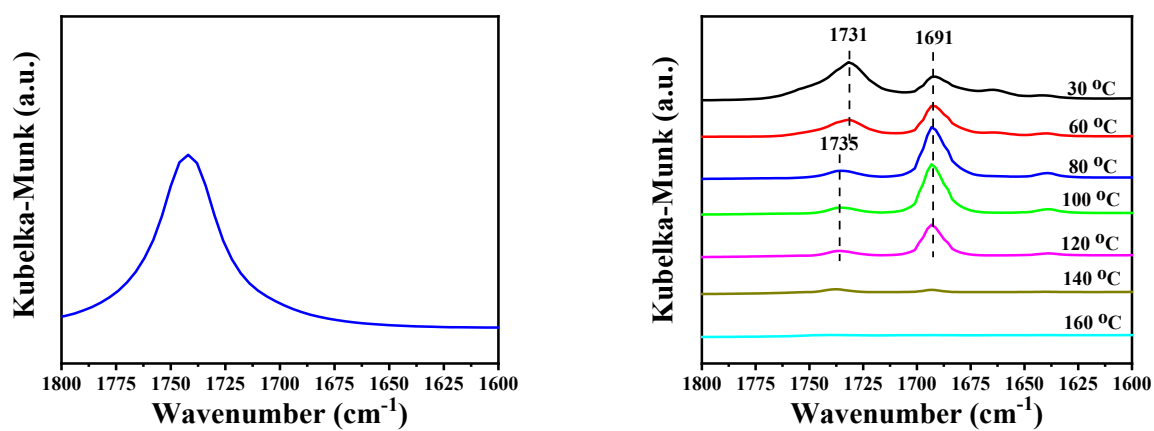


Figure S3. Standard FTIR spectra of octanal adspecies (<https://webbook.nist.gov/chemistry/>) and FTIR spectra of octanal adspecies at 30 °C and temperature programmed desorption of octanal over Nb₂O₅.

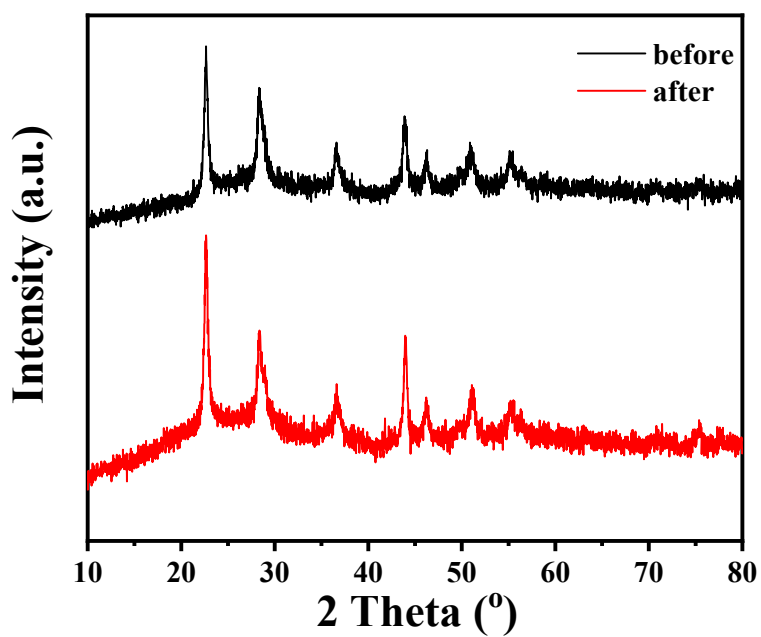


Figure S4. XRD patterns of fresh and used 10%Ni10%Cu/Nb₂O₅ after 4 runs.

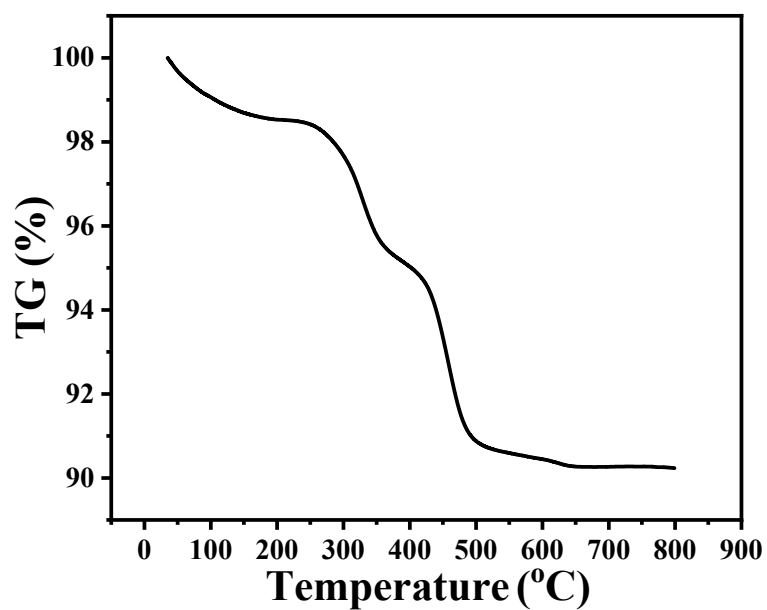


Figure S5. TG profile of spent 10%Ni10%Cu/Nb₂O₅ after 4 runs.

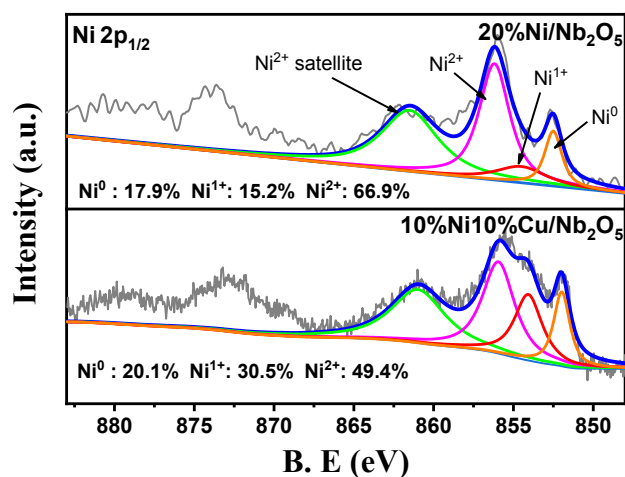


Figure S6. XPS spectra of (a) 20%Ni/Nb₂O₅ and (b) 10%Ni10%Cu/Nb₂O₅.

We conducted the XPS analysis and the results show that the Ni/Cu surface composition ratio is 0.87/0.88. The positively charged Ni species on Ni/Nb₂O₅ are dominated because of the electron-withdrawing effect of Nb₂O₅.¹ After introducing Cu, the NiCu/Nb₂O₅ has a higher fraction of Ni⁰ species, which favor the hydrogen dissociation. Meanwhile, the binding energy of all Ni species (Ni⁰, Ni¹⁺ and Ni²⁺) in NiCu/Nb₂O₅ shifted to lower binding energy, suggesting the electron transfer from Cu to Ni. The improved fraction of Ni⁰ species afford the high activity.

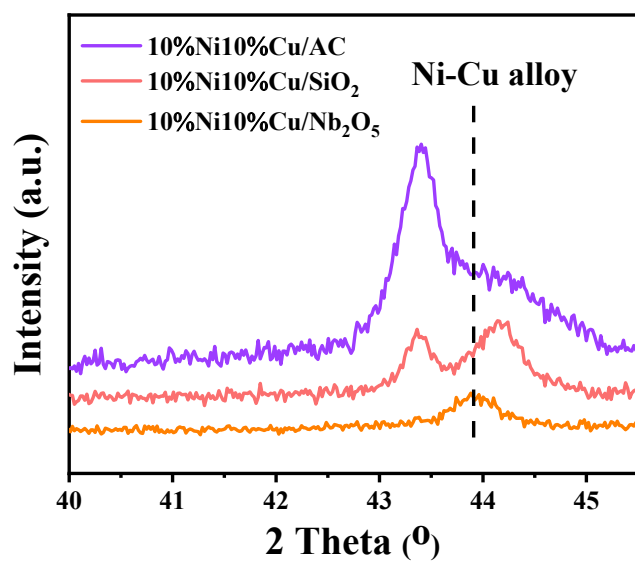


Figure S7. XRD patterns of 10%Ni10%Cu/AC, 10%Ni10%Cu/SiO₂, 10%Ni10%Cu/Nb₂O₅.

Table S3. HDO of FA over 10%Ni10%Cu/Nb₂O₅, 10%Ni10%Cu/AC and 10%Ni10%Cu/SiO₂ catalysts after 12 hours

Entry	Cat.	Yield of octane %	Yield of heptane %	Octane/heptane ratio / O/H	Yield of oxygenated compounds ^(a) /%	CB. %
1	10%Ni10%Cu/Nb ₂ O ₅	86.5	5.1	16.7	0.1	94.4
2	10%Ni10%Cu/AC	34.1	8.3	4.1	54.1	97.6
3	10%Ni10%Cu/SiO ₂	38.7	23.7	1.6	25.7	98.1

Reaction conditions: 0.1 g catalyst, 0.2 g FA, 6.5 g cyclohexane, 4 MPa H₂, 250 °C, 12 h

To further explore the uniqueness of Nb₂O₅ support and its effects for metal sites, we prepared the Ni-Cu/SiO₂ and Ni-Cu/AC as comparisons. The XRD pattern (Figure S7) that there are no obvious diffraction peaks ascribed to Ni-Cu alloy on these two catalysts, indicating that SiO₂ and AC, unlike Nb₂O₅, are not able to enable the formation of Ni-Cu alloy. The experimental results and octane/heptane ratio (Table S3) confirmed that the formation of Ni-Cu alloy could effectively restrained the undesirable decarbonylation.

References:

1 Y. Xin, L. Dong, Y. Guo, X. Liu, Y. Hu, and Y. Wang, *J. Catal.* 2019, 375, 202-212.