Supporting information

Synthesis of renewable alkylated naphthalenes with benzaldehyde and angelica lactone

Ran Wang,^{a,b} Guangyi Li,^a Jilei Xu,^c Aiqin Wang,^a Yu Cong,^a Xiaodong Wang,^a Tao Zhang^{a,d} and Ning Li^{*a,c}

- ^{*a*} CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
- ^b University of Chinese Academy of Sciences, Beijing 100049, China
- ^c Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics,
 Chinese Academy of Sciences, Dalian 116023, China
- ^d State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

*Corresponding author: Prof. Ning Li; Tel: +86-411-84379738; E-mail: lining@dicp.ac.cn

1. General information

1.1 Materials

Angelica lactone was prepared by the dehydration of levulinic acid over a commercial H-ZSM-5 zeolite (supplied by Nankai University, SiO_2/Al_2O_3 molar ratio = 25) catalyst. Typically, 25.0 g levulinic acid and 1.0 g catalyst were added into a distillation flask. The mixture was stirred at 433 K. The outlet of the flask was connected to a fractionation column, a water-cooled condenser and a vacuum pump. Due to the low solubility of angelica lactone in water, the dehydration products (*i.e.* angelica lactone and water) spontaneously became two phases in the second flask. After separated from water, the aldol condensation with benzaldehyde.

The acetic acid, methanol and methylene chloride used in this work were supplied by Damao Chemical Reagent Factory. The ammonium hydroxide was supplied by Xilong Scientific Co., Ltd. The rest of chemicals were purchased from Aladdin Biochemical Technology Co., Ltd and directly used as received.

All the zeolite catalysts (H-USY, H- β , H-ZSM-5) were purchased from Nankai University Catalyst Co., Ltd. Before being used for the activity tests, the zeolite catalysts were calcined at 823 K in air for 4 h. According to the information from supplier, the SiO₂/Al₂O₃ molar ratios of H- β , H-USY and H-ZSM-5 catalyst are 25, 11 and 25, respectively.

The Pd/C catalyst used in the hydro-liquefaction reaction was supplied by Aladdin Biochemical Technology Co., Ltd. According to the supplier, the Pd content in the catalyst is 5% by weight. Before being used for the hydrogenation of aldol condensation product (*i.e.* **1A**), the Pd/C catalyst was dried at 333 K in vacuum for 5 h.

1.2 Catalyst preparation

The ionic liquid [H₃N⁺-CH₂-CH₂-OH] [CH₃CH₂COO⁻] (denoted as EAPA) was prepared by ethanolamine and propionic acid according to the procedure described elsewhere.¹ Firstly, 0.2 mol ethanolamine was placed in a 100 mL round bottom flask. Under violent stirring, 0.2 mol propionic acid was added dropwise with a constant pressure funnel. A room-temperature water bath was used to remove the instant reaction heat generated during the process. After the

addition of propionic acid, the mixture was stirred for another 24 h. For comparison, ethanolamine formate (denoted as EAFA), ethanolamine acetate (denoted as EAOAc), ethanolamine butyrate (denoted as EABA) and ethanolamine valerate (denoted as EAVA) were prepared by the same method.

The SiO₂/Al₂O₃ solid catalyst was homemade by a sol-gel method reported elsewhere². Typically, 29.79 g tetraethoxysilane (TEOS) was dissolved in 200 mL ethanol. Its pH value was adjusted to 3.0 with glacial acetic acid. A transparent silica sol solution was obtained after being stirred at 323 K for 1 h. At this moment, 13.45 g aluminum nitrate nonahydrate was dissolved in 25 mL distilled water. Subsequently, the aforementioned solutions were stirred at 323 K for another 2 h. The ammonium hydroxide solution was used to keep a constant pH of 8.0. Another 150 mL ethanol was added to form a homogeneous hydrogel. After being aged at room temperature for 24 h, the liquid was removed by filtration. The obtained specimen was first washed with distilled water and then washed with ethanol for several times. The resulting gel was dried at 373 K for 24 h, grinded and calcined at 773 K for 4 h to obtain the SiO₂/Al₂O₃ catalyst.

1.3 Catalyst characterization

The X-ray powder diffraction (XRD) of the SiO₂/Al₂O₃ catalyst was acquired by a PW3040/60X' Pert PRO (PANalytical) diffractometer using Cu *Ka* radiation source ($\lambda = 0.15432$ nm). The images and elemental distribution of the homemade SiO₂/Al₂O₃ catalyst were analyzed by a scanning transmission electron microscopy (STEM) equipped with an energy dispersive X-ray spectroscopy (EDX) system. Nitrogen physisorption of the catalysts were carried out by a Micromeritics ASAP 2010 apparatus. Prior to the measurements, the samples were evacuated at 523 K for 5 h. NH₃-temperature programmed reduction (NH₃-TPD) of the solid acid catalysts were performed with a Micromeritics AutoChem II 2920 Characterization System. Prior to the NH₃-TPD tests, the catalysts were heated in He flow at 873 K for 1 h to get rid of the adsorbed impurities. After being cooled down in He flow to 373 K and the stabilization of baseline, the samples were heated from 373 K to 873 K at a rate of 10 K min⁻¹. The NH₃ desorbed from the catalysts was measured by a TCD detector. The Fourier Transform infrared spectra using pyridine as the probing molecule (py-FTIR) spectra were recorded on a

Bruker spectrometer equipped with liquid-nitrogen cooled MCT detector at a resolution of 4 cm⁻¹. Prior to pyridine adsorption, the solid acid catalysts were evacuated at 723 K for 30 min, then cooled to room temperature. At this stage, the spectrum was collected as the background reference. Subsequently, pyridine was introduced for the adsorption for 5 min at room temperature followed by evacuation for 30 min. Finally, we elevated the temperature to 423 K (or 598 K) and evacuated for 30 min. All the spectra were collected at room temperature and extracted with the background reference.

2. Aldol condensation of benzaldehyde and angelica lactone over ionic liquid catalysts

The aldol condensation reactions of benzaldehyde and angelica lactone were carried out in a 35 mL glass batch reactor under magnetic stirring. The temperature of batch reactor was controlled by an oil bath. In a typical run, 5 mmol benzaldehyde, 5 mmol angelica lactone and 0.25 mmol catalyst were used. Upon completion of the reaction, the product was diluted with tetrahydrofuran. The mixture was analyzed by an Agilent 7890A GC equipped with HP-5 column (30 m, 0.25 mm ID, 0.5 mm film) and a flame ionization detector (FID) using dodecane as the internal standard. For the 40-fold magnification experiment, 0.2 mol benzaldehyde, 0.2 mol angelica lactone and 0.02 mmol of EAPA were added to a 120 mL glass batch reactor. After the reaction was carried out at 313 K for 3 h under magnetic stirring, the product was dissolved in 150 mL dichloromethane and transferred to a separatory funnel. After washing out the ionic liquid catalyst in the product with 150 mL (50 mL \times 3 times) ultrapure water, anhydrous sodium sulfate was added to the dichloromethane phase to get rid of water. Finally, the golden yellow solid product **1A** was obtained after the removal of dichloromethane by distillation under reduced pressure.

3. Hydrogenation (or liquefaction) of 1A

The hydrogenation of **1A** was carried out in a 100 mL batch reactor (Parr company). In each test, 15 g **1A** was first dissolved in 45 mL methanol and then 0.1 g Pd/C was added to reaction system. Prior to the hydrogenation of **1A**, the batch reactor was purged with hydrogen. Subsequently, hydrogen was charged into the reactor and the system pressure was held constant

at 3 MPa during the whole process. After reacting at 313 K for 12 h, the Pd/C catalyst was filtered from the solution. Subsequently, the methanol was removed by vacuum distillation and the clear and transparent yellow liquid **2A** was obtained.

4. Cascade decarboxylation/alkylation reaction of 2A

The cascade decarboxylation/alkylation reaction of **2A** was conducted in a fix-bed tubular reactor that was made of 316L stainless steel. Before the activity test, the catalyst was tableted and granulated, and then the 40-80 mesh fraction was screened out for the activity test. To fix the catalyst bed in the constant temperature zone of oven, dense quartz granules (20-40 mesh) were used to pack the remaining part of the reactor and silica wool plugs were used to seal both ends. The reactions were performed in N₂ atmosphere. Before the activity test, the catalyst was stabilized at the reaction temperature for 0.5 h. The feedstock was co-fed with carrier gas (*i.e.* N₂) to the catalyst bed from the top of reactor using a HPLC pump. A gas-liquid separator (located in *n*-octane/dry ice-cold trap) was employed after the reactor tube. The reactions were performed at atmospheric pressure, and the gas phase products were directly analyzed on-line by an Agilent 7890B GC. The liquid products were periodically drained and immediately analyzed by an Agilent 7890A GC using octodecane as the internal standard.

5. Copies of GC chromatograms and NMR spectroscopy



Figure S1. GC chromatogram of the solvent-free aldol condensation product of benzaldehyde and angelica lactone over EAPA ionic liquid catalyst. Reaction conditions: 298 K, 1 h; 5 mmol benzaldehyde, 5 mmol angelica lactone and 0.25 mmol catalyst were used in each test.



Figure S2. Mass spectrogram of **1A** from the solvent-free aldol condensation of the benzaldehyde and angelica lactone over EAPA ionic liquid catalyst.



Figure S3. ¹H-NMR and ¹³C-NMR spectra of the **1A** from the solvent-free aldol condensation of benzaldehyde and angelica lactone over EA-based ionic liquid.



Figure S4. Conversions of benzaldehyde and the carbon yields of **1A** over EAPA and common organic or inorganic base catalysts. Reaction conditions: 298 K, 1 h; 5 mmol benzaldehyde, 5 mmol angelica lactone and 0.25 mmol catalyst were used in each test.



Figure S5. GC chromatogram of the condensation product of benzaldehyde and ethanolamine at room temperature.



Figure S6. Mass spectrogram of the condensation product of benzaldehyde and ethanolamine.



Figure S7. ¹³C-NMR and ¹H-NMR spectra of the condensation product of benzaldehyde and ethanolamine.



Figure S8. The photos a) before and b) after the addition of equimolar angelica lactone to the condensation product of benzaldehyde and ethanolamine at room temperature.



Figure S9. GC chromatogram of the products obtained after the addition of equimolar angelica lactone to the condensation product of benzaldehyde and ethanolamine at room temperature.



Figure S10. GC chromatogram of the hydrogenation (or liquefaction) product of **1A** over the Pd/C catalyst. Reaction conditions: 313 K, 12 h; 15 g **1A**, 45 mL methanol and 0.1 g Pd/C were used in the test.



Figure S11. Mass spectrogram of 2A from the hydrogenation of 1A over the Pd/C catalyst.



Figure S12. ¹H-NMR and ¹³C-NMR spectra of **2A** from the hydrogenation of **1A**.



Figure S13. GC chromatogram of the products from the cascade decarboxylation/alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst. Reaction conditions: 623 K, 0.1 MPa, WHSV = $0.5 \text{ g } \text{g}_{\text{cat}}^{-1} \text{ h}^{-1}$, carrier gas (*i.e.* N₂) flow = 50 mL min⁻¹.



Figure S14. Mass spectrogram of C_9 bicyclic aromatics from the cascade decarboxylation/ alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst.



Figure S15. Mass spectrogram of the C_{11} bicyclic aromatics from the cascade decarboxylation/alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst.



Figure S16. Mass spectrogram of the C_{12} bicyclic aromatics from the cascade decarboxylation/alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst.



Figure S17. Mass spectrogram of the C_{13} bicyclic aromatics from the cascade decarboxylation/alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst.



Figure S18. Mass spectrogram of the monocyclic aromatics from the cascade decarboxylation/alkylation reaction of 2A over the SiO₂/Al₂O₃ catalyst.



Figure S19. XRD pattern of the SiO₂/Al₂O₃ catalyst.

According to the XRD result illustrated in Figure S19, the homemade SiO_2/Al_2O_3 catalyst exhibits a broad peak at 23°, indicating this material has an amorphous structure.



Figure S20. STEM images of the SiO_2/Al_2O_3 catalyst under (a) low magnification and (b) high magnification.

As we can see from Figure S20, the SiO_2/Al_2O_3 particles are irregular in size and shape. No obvious lattice stripes were observed even under high magnification. This is consistent with what we observed from the XRD result (see Figure S19).



Figure S21. STEM image and the corresponding EDX elemental mapping of the SiO_2/Al_2O_3 catalyst. The blue, green, and red dots represent the elements of Al, Si, and O, respectively. The percentages of the elements Al and Si are illustrated as insets.

From the corresponding EDX elemental mapping of the SiO_2/Al_2O_3 catalyst (see Figure S21), it is noticed that the Al, Si and O elements (denoted by the blue, green, and red dots, respectively) were homogeneously distributed on the surface of SiO_2/Al_2O_3 catalyst. The Si/Al atomic ratio of the SiO_2/Al_2O_3 catalyst was measured as 3.8.

Catalyst	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	Pore volume	(µL g ⁻¹)	Average po	re size (nm)
SiO ₂ /Al ₂ O ₃	573.0	1.49		5.19	
H-USY	546.6	0.831		0.74×0.74 ª	r
Η-β	478.8	0.537		0.66×0.67	0.56×0.56 ^a
nano-SiO ₂	486.4	0.990		4.07	
H-ZSM-5	356.8	0.247		0.51×0.55	0.53×0.56 ^a
γ -Al ₂ O ₃	248.0	0.556		4.48	
a The	values	were	cited	from	literature. ³

Table S1. Specific BET surface area (S_{BET}), pore volume and average pore size of the investigated solid acid catalysts.

Table S2. Amounts of acid sites on the surfaces of solid acid catalysts

Catalyst	Total amount of acid sites (mmol g ⁻¹) ^{<i>a</i>}	Amount of total Lewis acid sites (mmol g^{-1}) ^b	Amount of total Brönsted acid sites (mmol g^{-1}) ^{c}	Amount of strong Lewis acid sites $(\text{mmol } g^{-1})^{d}$	Amount of strong Brönsted acid sites (mmol g ⁻¹) ^e
SiO ₂ /Al ₂ O ₃	0.515	0.346	0.169	0.209	0.024
H-USY	0.902	0.194	0.708	0.102	0.492
Η-β	2.586	1.194	1.392	0.954	0.756
nano-SiO ₂ ^f	0.041				
H-ZSM-5	1.633	0.197	1.436	0.143	1.361
γ-Al ₂ O ₃	0.275	0.275	0.000	0.066	0.000

^{*a*} Measured by NH₃-TPD.

 b Calculated based on NH₃-TPD and py-FTIR (after vacuation at 423 K) by total amount of acid sites \times the proportion of Lewis acid by the method described in literature.⁴

 c Calculated based on NH₃-TPD and py-FTIR (after vacuation at 423 K) by total amount of acid sites \times the proportion of Brönsted acid by the method described in literature.⁴

^dCalculated by total amount of Leiws acid sites × peak area of Lewis acid after vacuation at 598 K / peak area of Lewis acid after vacuation at 423 K.

^e Calculated by total amount of Brönsted acid sites × peak area of Brönsted acid after vacuation at 598 K / peak area of Brönsted acid after vacuation at 423 K.

f The total amount of acid sites of the nano-SiO₂ catalyst is too low to measure an effective ratio of Lewis or Brönsted acid sites.

References

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