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Supporting Information

Hierarchically Structured Catalysts for Cascade and Selective Steam Reforming/Hydrodeoxygenation Reactions.

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Methods

Materials and synthesis

Cellulose extraction thimbles were obtained from Whatman; Tergitol 15-S-5 and orthosilicate (TEOS), ethyl alcohol, Tetraamineplatinum nitrate and iron nitrate were from Aldrich; Concentrated HCl was from Aldrich; All the chemicals were used as received.

Dual template method was used for the preparation of C/SiO_2 support with both microporous and macroporous structures.[1, 2] Cellulose extraction thimbles were used as template for generating macropores while surfactant was used as template for creating micropores. surfactantTergitol 15-S-5 hasbeen used as template to achieve the desired pore size (~10 Å). Specifically, template was first dissolved in de-ionized water and ethyl alcohol. Concentrated HCl was added to the solution, followed by tetraethyl orthosilicate (TEOS) (Aldrich). The molar ratios of Si: water: ethanol: HCl: Tergitol 15-S-5 was kept at 1: 5-10:5-10:0.04:0.05-0.1. The solutions were then shaken for 20-24 hours at room temperature. The cellulose thimbles was chopped to 1.0 cm x 1.0 cm pieces, and pre-treated at 350 °C for 1hr in air, during which a 78%wt weight lost was observed. The sol-gel solution was impregnated to the pre-treated cellulose and then dried at room temperature. After repeating the impregnation and drying processes four times, the dried samples were then treated at 325-350 °C for 1-4 h to *in situ* carbonize the surfactant onto the walls of the microporous SiO_2, forming C/SiO_2/cellulose.

Tetraamineplatinum nitrate and iron nitrate dissolved in deionized water were used for the preparation of the catalysts. 1%Pt/C/SiO_2, 10%Fe/C/SiO_2 and 1%Pt-10%Fe/C/SiO_2 (loadings in wt%) were prepared by incipient wetness impregnation. A calculated amount of tetraamineplatinum nitrate (or iron nitrate) was dissolved into a given amount of H_2O of equivalent pore volume of the support, the solution was then mixed with the support. Pt nanoparticles within the micropores of the C/SiO_2/cellulose (i.e., 1Pt-C/SiO_2/cellulose) were prepared via incipient wetness method, by which most of the Pt precursor solution is expected to stay in the micopores. The Pt precursor was decomposed by treatment under N_2 at 550 °C. The treatment under N_2 at 550 °C also resulted in the decomposition of cellulose and creation of macropores, 1Pt-C/SiO_2 (i.e. no cellulose). It should be noted that Pt is expected to be present outside of the micropores (which may degrade the performance of the monometallic catalyst), however, the sequential impregnation with Fe results in the formation of a PtFe alloy which is much more active for hydrodeoxygenation than reforming. For the 10Fe-C/SiO_2, and 1Pt10Fe-C/SiO_2 catalysts, Fe was deposited in the macropores (mostly) by incipient wetness impregnation on the C/SiO_2 and 1Pt-C/SiO_2, respectively, followed by treatment under N_2 at 350 °C. The notation of the catalysts is summarized in Table 1. For comparison experiments, 3%Pt/C (BP-700, nonporous carbon) and 10%Fe/C (TA70 activated carbon) were also prepared by incipient wetness impregnation method followed by a calcination at 350 °C for 2 h under N_2.

Characterization

The pore structures and pore sizes of C/SiO_2 support and catalyst were studied using N_2 adsorption/desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). BET surface area, porosity, and pore size analyses were determined using nitrogen adsorption/desorption collected with a Quantachrome Autosorb 6-B gas sorption system. The samples were degassed at 120 ° for 3 hours prior to the measurements. The surface area was determined from the isotherm using 5 points BET method. BJH and DFT method were used for the analysis of pore volume and pore size, respectively. XRD patterns were obtained on a Rigaku desktop X-ray diffractomer using Cu Kα (1.54059Å) radiation with the X-ray generator operating at 20kV and 30mA. The samples were prepared by packing ~5mg of solid in a 9.0mm cavity mount. Digital data were collected for a 2θ range 1.0-10.0^o at an angular resolution of 0.02 °/s. SEM was carried out on a LEO 982 field emission scanning electron microscopy. Scanning Transmission Electron Microscopy (STEM) was performed with FEI Titan 80-300 operated at 300 kV. The FEI Titan is equipped with CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging with ~0.1 nm resolution in scanning transmission electron microscopy (STEM) mode. The images were acquired on High Angle Annular Dark Field (HAADF) with an inner collection angle of 52 mrad. Compositional analysis was performed with EDAX Si (Li) energy dispersive spectroscopy (EDS) detector and FEI's TIA acquisition and analysis software. The TEM sample preparation involved mounting of powder samples on copper grids covered with lacey carbon support film and loading into the microscope. Before XRD and TEM characterization, samples were first reduced under the same pre-treatment conditions as those before reaction, and then cooled down to room temperature and passivated (0.1% O_2 in Ar, 3 hours).

Catalytic reactions

Catalytic reactions were conducted in a micro-tubular fixed-bed reactor with the details being provided elsewhere.[3] 100 mg sample was packed between quartz wool beds. The thermocouple was placed in the middle of the catalyst bed to monitor the reaction temperature. Before the reaction, catalysts were firstly pre-treated in H_2/N_2 (1:1 mol; 50

sccm) at 450 °C (ramping rate was 5 °C/min) for 2 hours, then purged with N_2 for 30 min. After that, a mixture of methanol and H_2O (H_2O to methanol molar ratio = 5), and guaiacol were introduced into the vaporizer (190 °C) using two syringe pumps and carried into the reactor by the flowing nitrogen gas. The methanol and guaiacol partial pressures could be adjusted by individually controlling the liquids and nitrogen flow rates. The line connecting the reactor to the cold trap was heated to ~190 °C to avoid the condensation of liquid products. A Shimadzu 2400 Gas Chromatograph (GC), equipped with an auto sampling valve, RTX (30 m, 0.53 mm, 40 µm) column, Flame Ionization Detector (FID), was connected to the line between the reactor outlet and cold trap to collect and analyze the products in effluent gas. After the cold trap, the dry gas was sent to an online micro GC (MicroGC 3000A equipped with molecular sieves 5A, plot U columns and Thermal Conductivity Detectors (TCD)) for the analysis of gas products (e.g., CH_4, CO_2, CO and H_2). Nitrogen was used as an internal standard. Response factors for guaiacol and the HDO reaction products were determined using pure compounds with known concentrations. The mass balance, unless otherwise noted, was at least 95%. Guaiacol conversion ($X_{guaiacol}$), products selectivity ($S_{products\text{-}i}$), and product yields ($Y_{products\text{-}i}$) were calculated as follows: $X_{guaiacol} = (Mol_{guaiacol\text{-}in} - Mol_{guaiacol\text{-}out})/Mol_{guaiacol\text{-}in;}S_{products\text{-}i} = (Mol_{product\text{-}i} \times \alpha_i)/(Mol_{reacted\ guaiacol} \times 7)$, α_i refers to the carbon number in product-i; $Y_{products\text{-}i} = X_{products\text{-}i} \times S_{products\text{-}i}$. The conversion, selectivity and yields are reported as the average over one hour at each temperature.

Pyrolysis of Loblolly pine

Pyrolysis was performed using a CDS pyroprope 5200. Pyrolysis conditions were controlled using CDS' software, 5000 DCI version 2.1.56. Analysis was performed using a LECO 7890A GC as part of the Pegasus GCxGC TOF MS instrument. Instrumental control, acquisition and data processing were performed using LECO's ChromaTOF software, version 4.32.

Loblolly pine (approximately 2 mg and size >200 µm) was quickly heated to 350°C and immediately pyrolyzed (ramp rate 20k °C/S) at 600°C for 20 seconds. The volatilized organic vapors were passed through a reactor bed containing the catalysts. The catalyst-to-biomass weight ratio was varied from 0 to 25. Before the pyrolysis measurements, the catalyst was reduced *in situ* at 450 °C (10 °C/min ramp) in flowing H_2 at 50 SCCM for 2 h. The reactor bed was held at 450 °C during pyrolysis experiments. After the catalysts bed, the organic vapors were then collected on a Tenax-TA sorbent at 40°C, which were then desorbed at 325 °C for 4 minutes and transferred directly into a Pegasus GCxGC TOF mass spectrometer. Front inlet conditions: temperature = 275 °C; He (99.999%) flow = 1 SCCM; split ratio: 1:200. The GC oven temperature program was as follows: 35°C for 5 min, then 3 °C/min to 200°C followed by 20°C/min to 300°C. An internal oven housing the second dimension column was set to the same temperature program, except all temperatures were 15°C higher. The first dimensional chromatographic separation was performed by a low-polarity column Rxi-5Sil-MS (structurally similar to 5% diphenyl/95% dimethyl polysiloxane); 30m; ID=0.25 mm, d.f. = 0.25 µm. The second dimensional chromatographic separation was performed by a mid-polarity column Rxi-17 (50% diphenyl/50% dimethyl polysiloxane); 1.5m; ID = 0.10 mm, d.f. = 0.10 µm. The fast pyrolysis of biomass results in a range of products that can be categorized as follows: char, gas (CO_x, H_2, light alkanes) and pyrolysis vapors which consist of light oxygenates, sugars, furans, aldehydes, ketones, esters and phenolics. . For convenient analysis, we segregated the multitude of post pyrolysis vapour products detected into 11 classifications: any acid containing compound (acids), aldehydes/ketones, alcohols, any furan containing compounds (furans), esters, bifunctional compounds (defined as species with 2 or more functionalities but excluding species with acid, furan or phenol/guaiacol functionality), phenolics, guaiacolics, paraffins (linear and branched), naphthenes (defined as either cyclic or olefinic hydrocarbons) and lastly aryl (e.g. benzene, toluene, naphthalene). GC area response normalized to the amount of biomass (weight) was employed to compare the performance of catalysts in terms of oxygen removal.

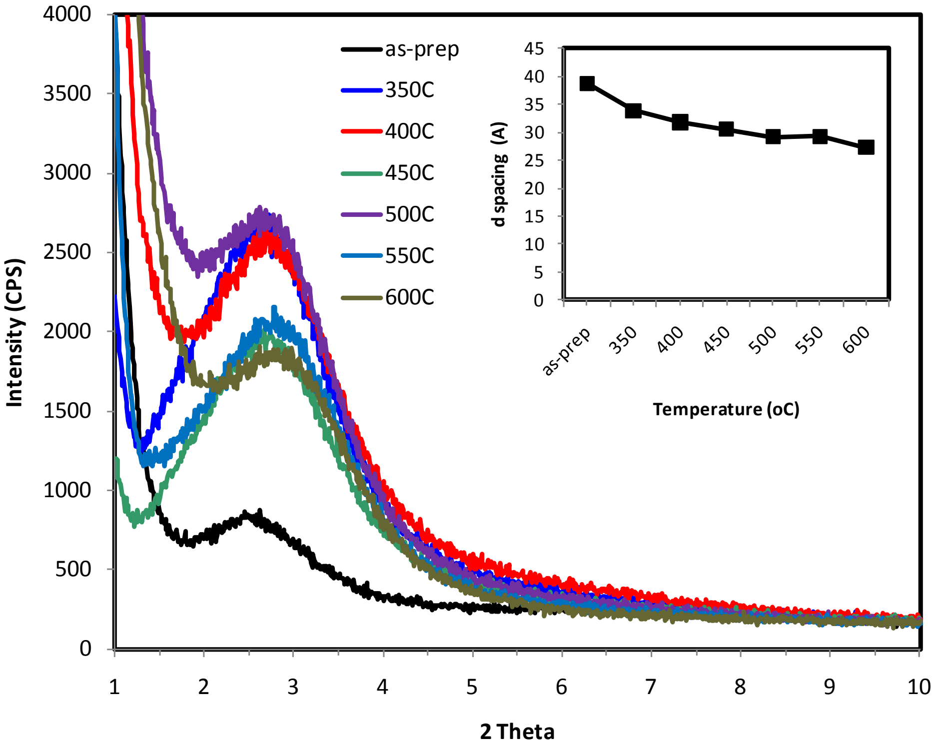

Fig. S1 XRD patterns of C/SiO2 sample prepared using Tergitol 15-S-5/TEOS (molar ratio = 0.1) followed by calcination at different temperatures under N2. Inset indicates d spacing of each sample.

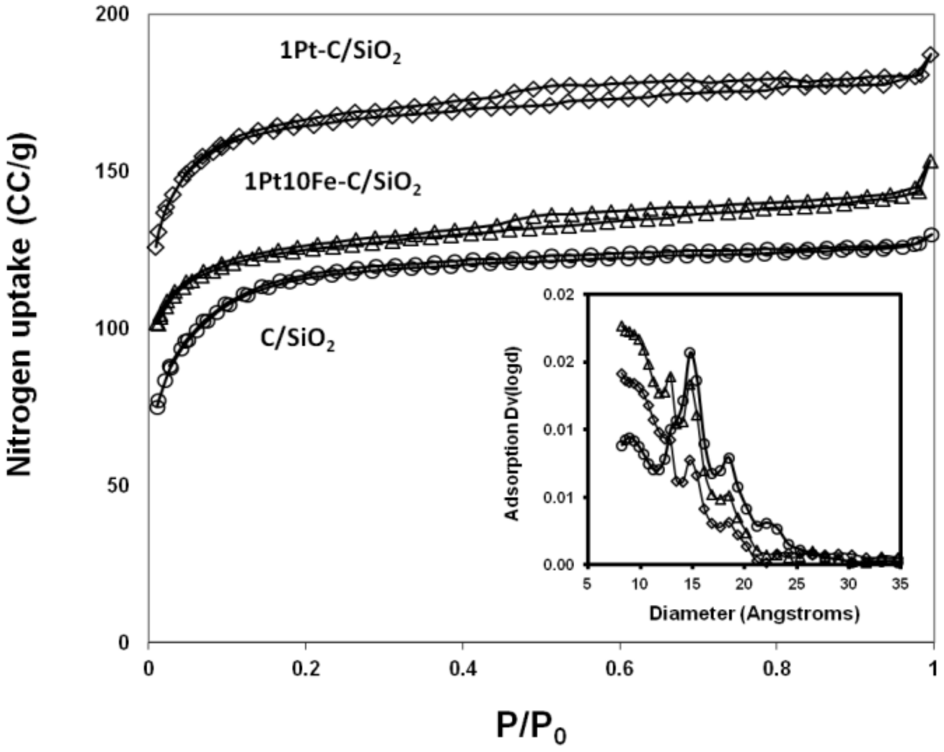

Fig. S2. N_2 adsorption-desorption isotherms and pore size distributions (inset) of the C/SiO_2, 1Pt-C/SiO_2, and 1Pt10Fe-C/SiO_2.

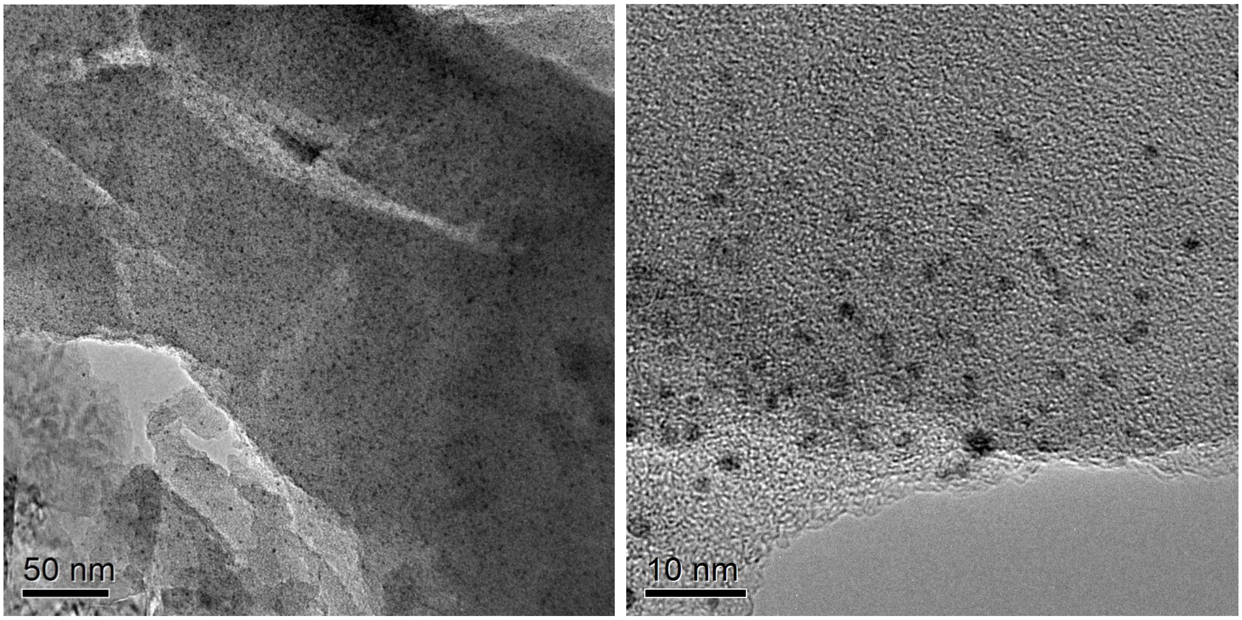

Fig. S3. TEM of spent 1Pt-C/SiO2 after steam reforming of methanol at 450 °C for 4 hours.

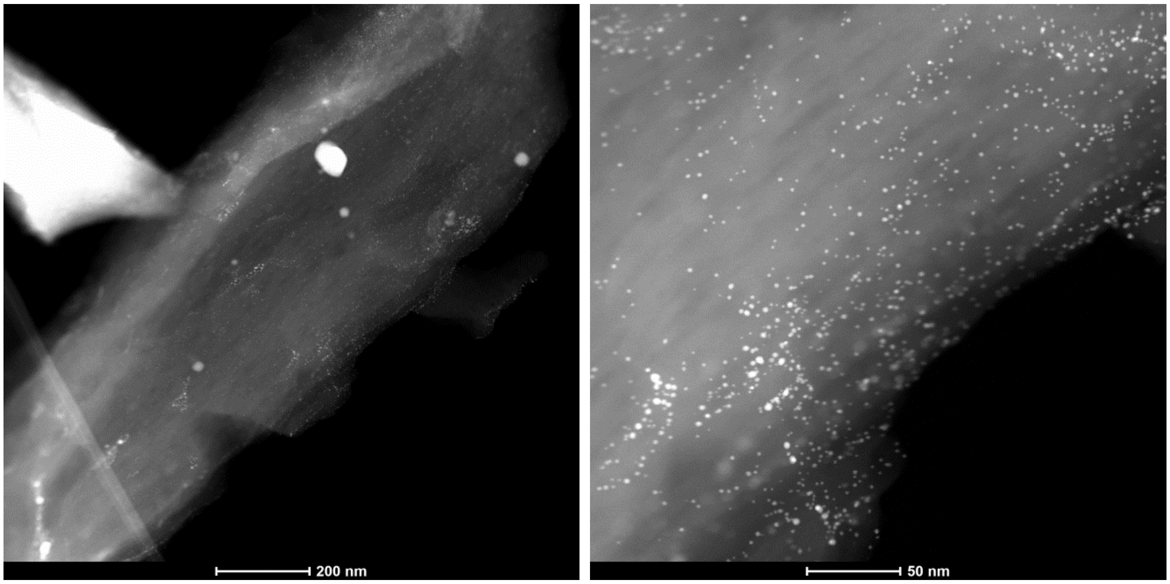

Fig. S4. STEM images of the 1%Pt-10%Fe/C/SiO_2

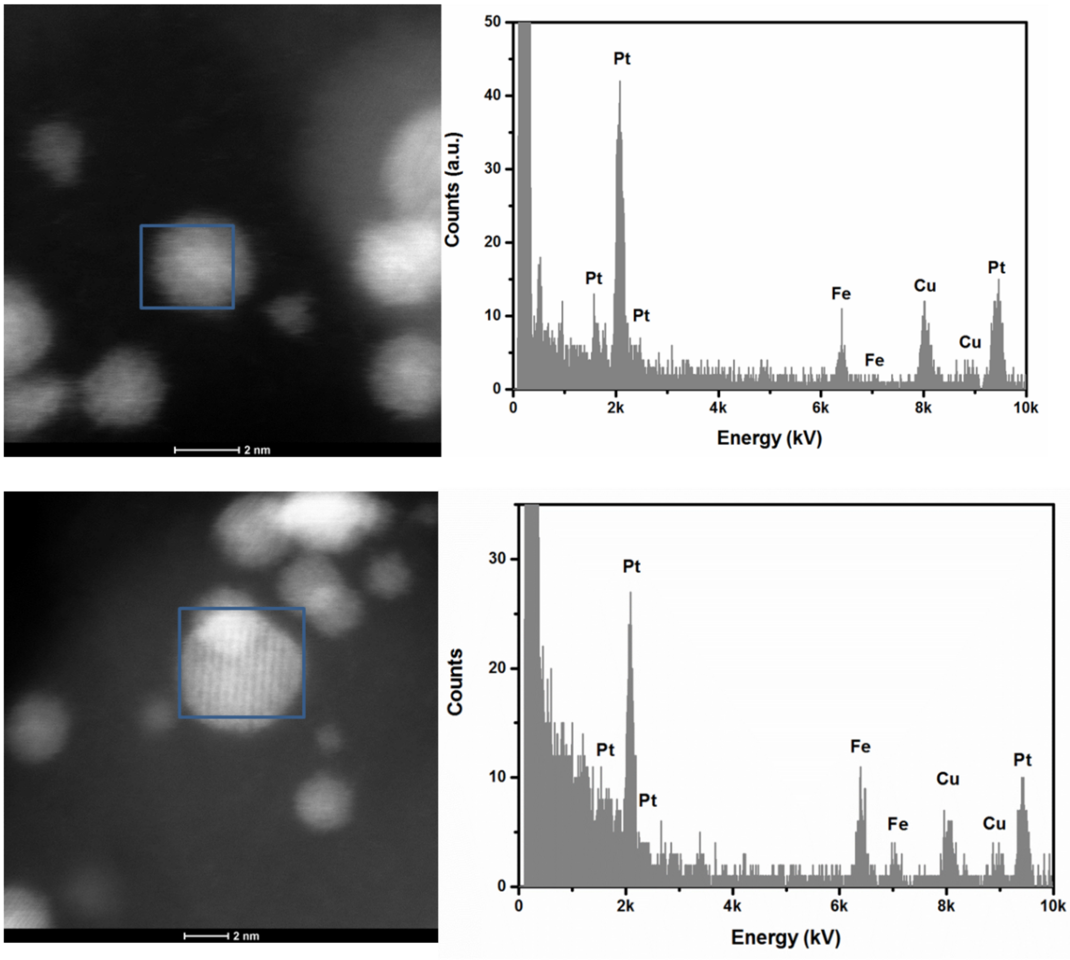

Fig. S5. STEM images (left) and corresponding EDS analysis (right) of small nanoparticles marked in the corresponding STEM image.

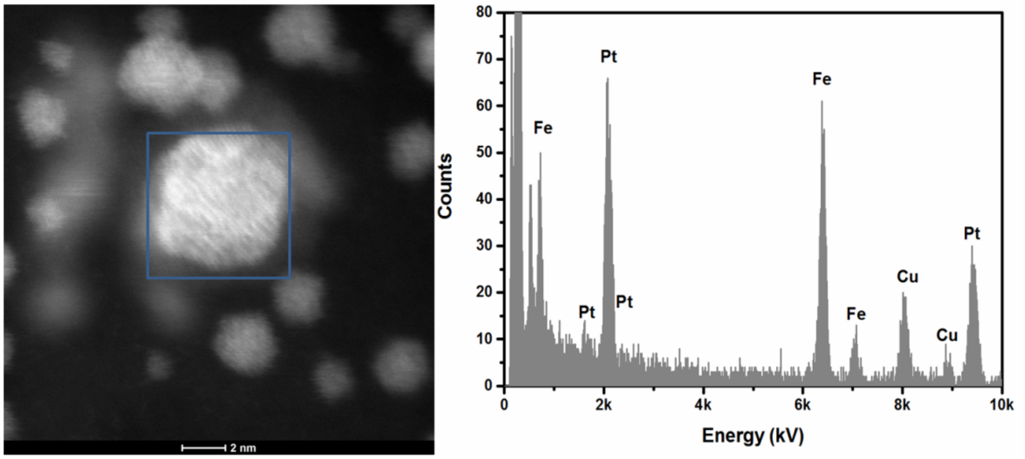

Fig. S6. STEM images (left) and corresponding EDS analysis (right) of larger iron particles decorated with Pt.

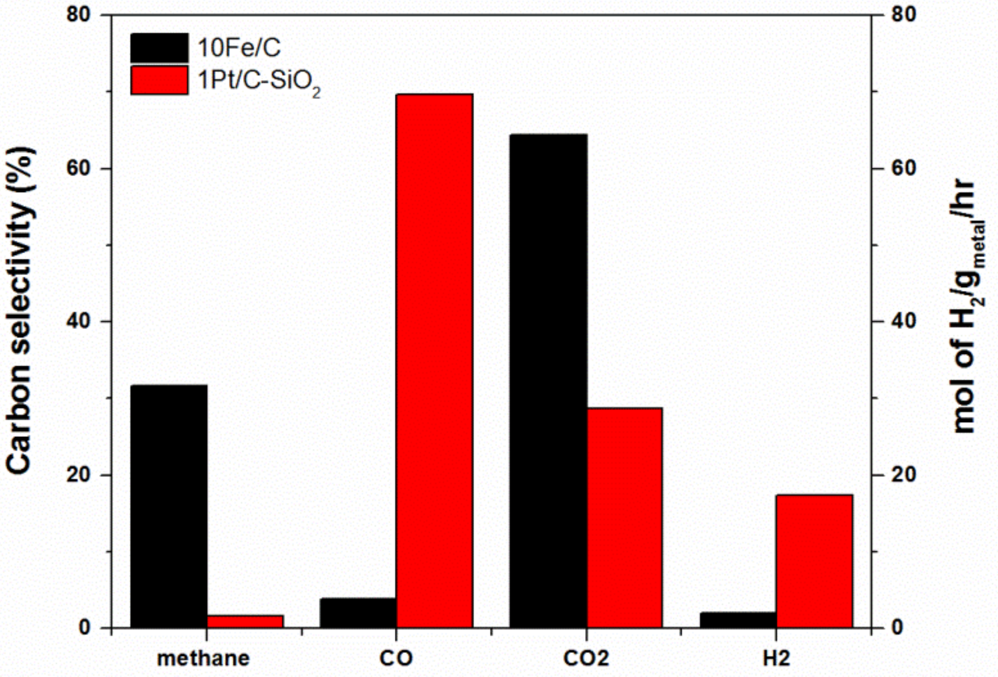

Fig. S7. Comparison of methanol steam reforming on 1Pt-C/SiO_2 and 10Fe/C. It is clear that both metal shows different performance in terms of carbon selectivity and hydrogen space time yield.

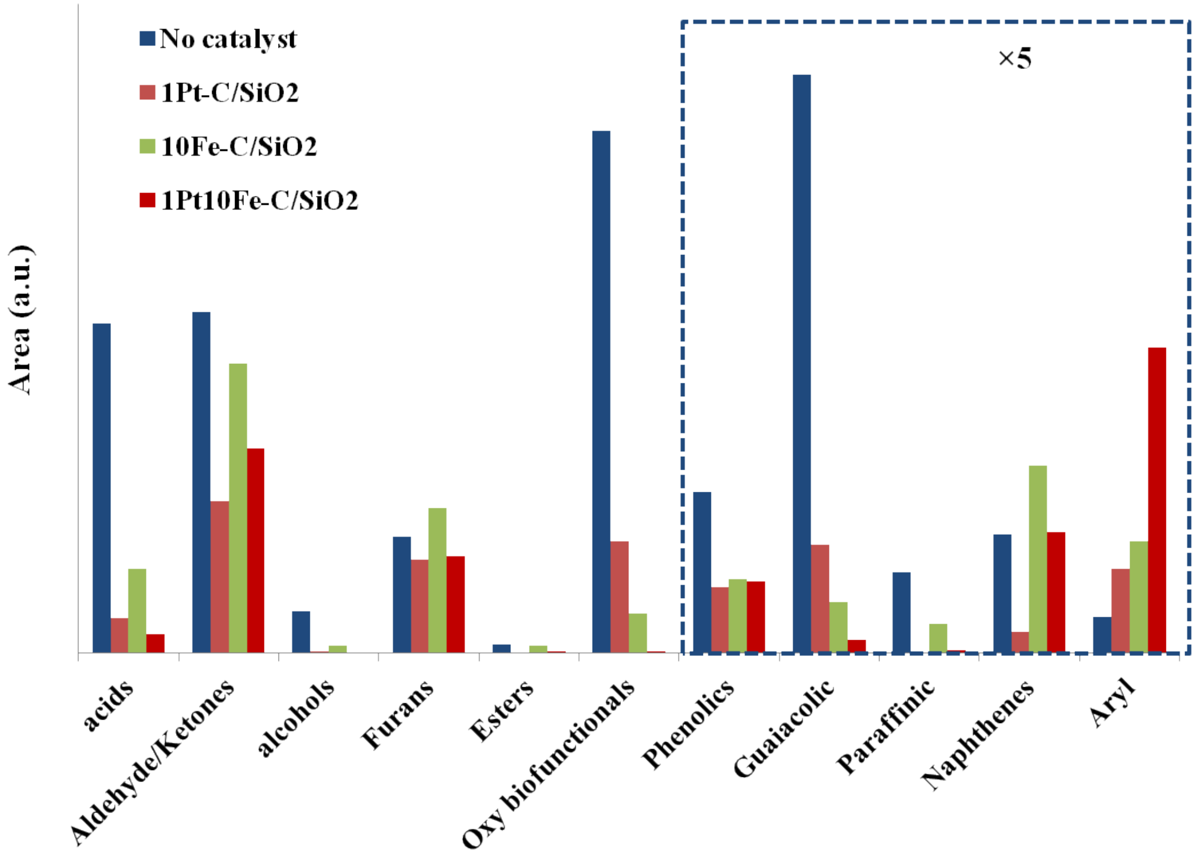

Fig. S8. Comparison of product distribution over different catalysts (12:1 catalyst-to-biomass ratio).

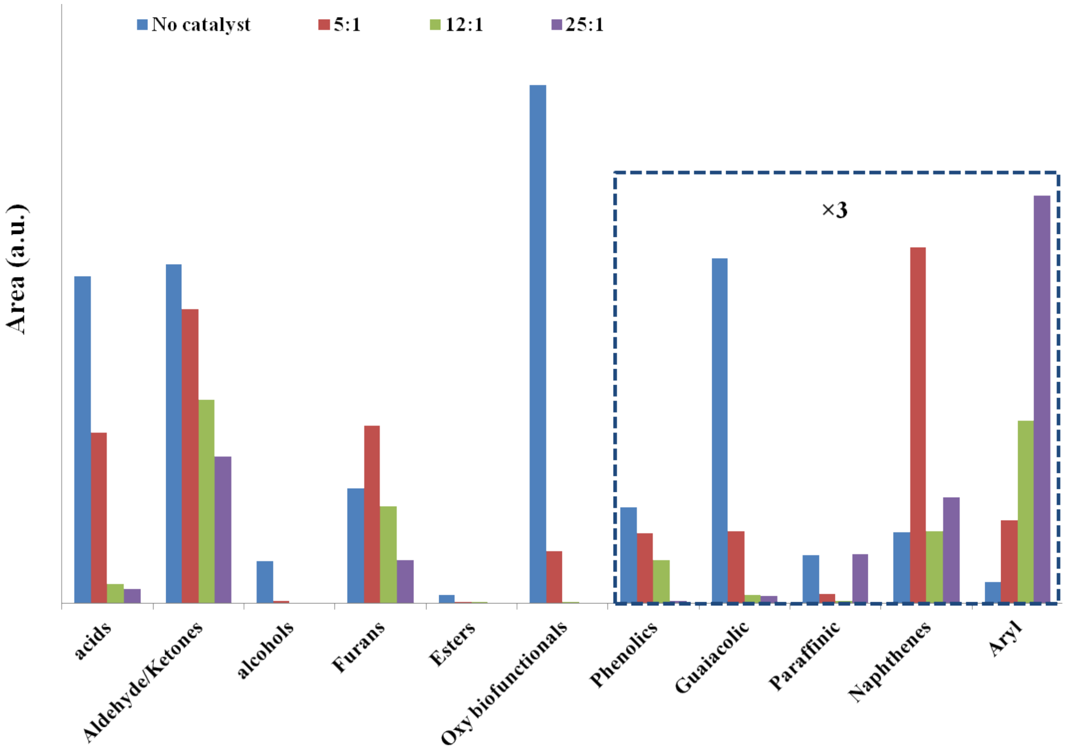

Fig. S9. Evolution of products distribution as a function of catalyst-to-biomass weight ratio. It is observed that with increasing catalyst-to-biomass ratio, there is a precipitous drop in phenolics and guaiacolics while the opposite is observed for ayrl generation. The selectivity to aryl products, in particular, stands out with a 25:1 catalyst-to-biomass ratio.

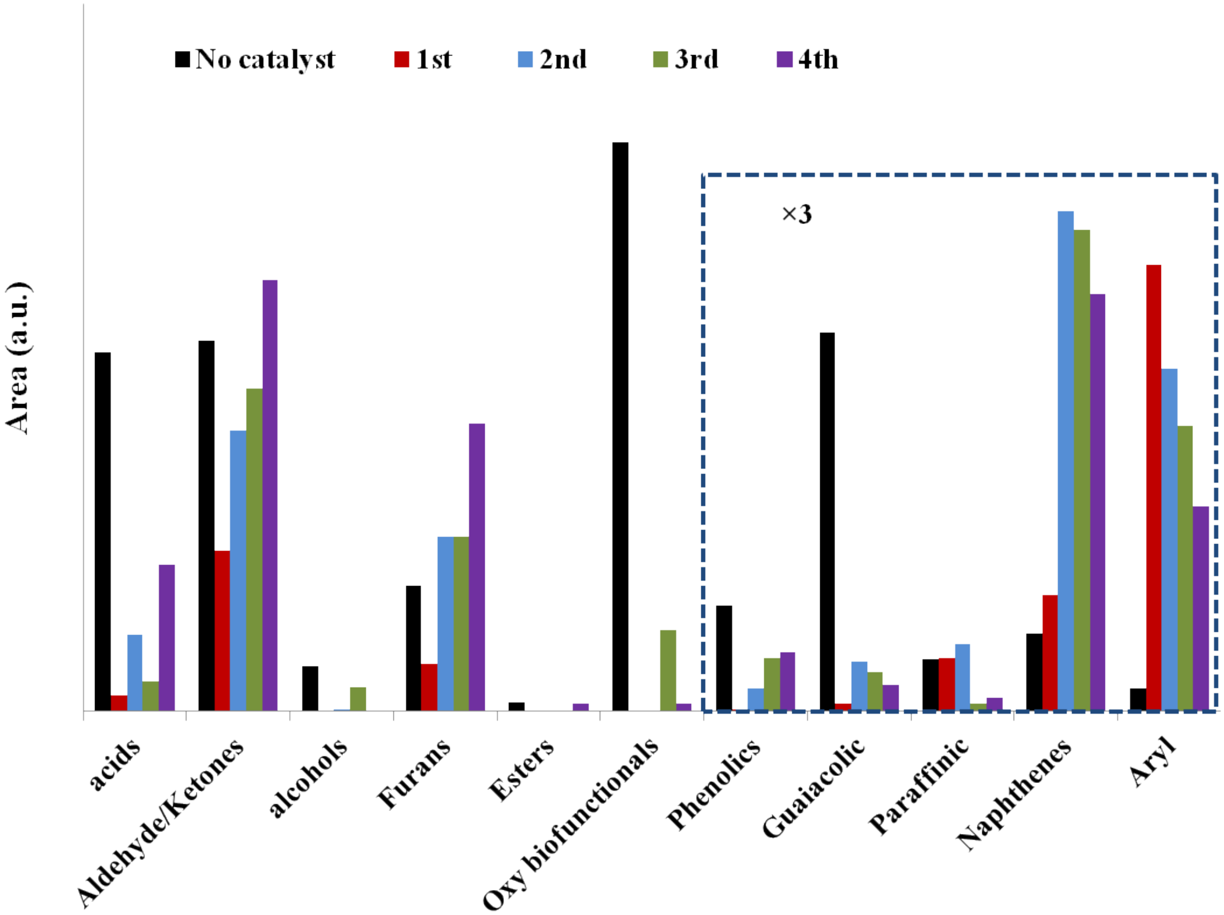

Fig. S10. Comparison of catalyst stability with multi-pass of pyrolysis vapor upgrading (25:1 catalyst: biomass ratio).

Table S 1. Notation and structural properties of the samples.

Sample information	Sample name	Surface area (m^2/g)	Pore Vol. (cc/g)	Pore Dia (Å)
With cellulose template	C/SiO_2	420	0.2	10-15
1 wt% Pt	$1Pt-C/SiO_2$	635	0.21	~10
1 wt% Pt, 10 wt% Fe	$1Pt10Fe- C/SiO_2$	484	0.15	<10

Table S2. Reaction of mixed guaiacol (GUA) and water with and without methanol (MeOH) as hydrogen source over $1Pt10Fe-C/SiO_2$

Condition	Conv.	Benz.	Tol.	Phen.	O-Cres.	Catech.
No MeOH	62.4	2.2	0.1	60.9	10.8	26.0
MeOH	83.1	13.2	2.2	69.6	14.6	0.0

Reaction conditions: T = 450 °C, % H_2O= 50%, %methanol = 10.6%, % GUA = 0.13%, W/F = 0.23 g.s/ml. Note: Conv.=Conversion, Benz.=Benzene, Tol.=Toluene, Phen.=Phenol, O-cres.=O-cresol, Catech.=Catechol

To further confirm our hypothesis of the hierarchical bimetallic catalysts in size selectivity and coupled steam reforming/hydrodeoxygenation, we tested the $1Pt10Fe-C/SiO_2$ catalyst using model compounds for pyrolysis vapors, methanol representing the light oxygenates and guaiacol representing the larger products. Table S2 shows a comparison between the catalyst activity after 2 hours TOS in guaiacol and steam with and without the addition of methanol. In the absence of methanol (H_2 source), the catalyst showed very fast deactivation and low activity to form the deoxygenated products (i.e., benzene). Almost no hydrogen was detected in the effluent gas, which confirmed that the steam reforming of guaiacol on the $1Pt10Fe-C/SiO_2$ catalyst is negligible. In the presence of methanol, the catalyst showed a high activity for hydrodeoxygenation of guaiacol, as evidenced by the high selectivities to benzene and toluene, respectively (Table 3). Apparently, methanol and steam can readily diffuse into the micropores where Pt is located, producing hydrogen for the subsequent hydrodeoxygenation of guaiacol over the Fe/PtFe nanoparticles[3, 4] located in the macropores of the C/SiO_2 support. In addition, our previous studies showed that carbon supported Pt exhibits substantial C-C cleavage activity in guaiacol hydrodeoxygenation at 450 °C, forming C1 species.[3] The fact that negligible C-C cleavage products were observed in coupled methanol steam reforming and guaiacol hydrodeoxygenation on $1Pt10Fe-C/SiO_2$ suggests that the interaction between guaiacol and Pt in the micropores is limited. It should be mentioned that Fe also shows activity in methanol steam reforming. However, in separate experiments (Fig. S7) methanol steam reforming activity on Fe was much lower than on Pt, and a much higher methane selectivity and lower hydrogen yield were observed on $10Fe-C/SiO_2$ compared to $1Pt-C/SiO_2$. Therefore, during the reaction of methanol, steam and guaiacol on $1Pt10Fe-C/SiO_2$, hydrogen is mainly generated by methanol steam reforming on Pt within the micropores.

Table S3. $C{\geq}5/C{\leq}4$ ratios for various pyrolysis experiments.

Catalyst	cat:bio	$C{\geq}5$ / $C{\leq}4$
no catalyst	-	0.47
$1Pt10Fe-C/SiO_2$	12:1	2.03

References

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