1. Experiement

1.1 Preparation of catalysts

MgO and CaO powders were purchased from Aladdin Reagent Company and calcined in N_2 flow at 773 K for 4 h .

$CaO\text{-}CeO_2$ mixed oxide (Ca/Ce atomic ratio = 1：1) was obtained by co-precipitation. Typically, 2 mol L^{-1} ammonia solution was added into the aqueous solution contains 0.5 mol L^{-1} cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.5 mol L^{-1} $Ca(NO_3)_2.4H_2O$ to adjust pH within the range of 8~9. The solution was stirred vigorously for 1 h. After filtering and washing, the precipitate was dried overnight, and then calcined in a muffle oven at 923 K for 8 h.

KF/Al_2O_3 was obtained by the wetness impregnation of $\gamma\text{-}Al_2O_3$ with an aqueous solution of KF followed by drying at 393 K overnight. The KF loading on catalyst is 40% by weight (denoted as 40 wt%).

Mg-Al hydrotalcite ($[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125} \cdot mH_2O$) was prepared according to literature[1, 2]. A solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in 200 mL deioned water was pumped into a mixture of NaOH and Na_2CO_3. The addition process was conducted at 343 K water bath under vigorous mechanical agitation. Then the gel was aged at this temperature for 16 h. The solid as obtained was filtered, washed until filtrate pH became 7 and dried overnight at 353 K. The dried precursor was calcined in nitrogen flow at 723 K for 8 h. In the previous work of Corma et al.[3], it was found that the rehydration of the calcined Mg-Al hydrotalcite (MgAl-HT) could significantly improve its activity in the Claisen-Schmidt condensation between benzaldehyde and acetophenone. The best activity was observed when a MgAl-HT with water content of 35wt.% was used as catalyst. To check if there is similar effect in the self aldol condensation of cyclopentanone, we compared the catalytic performances of calcined and rehydrated MgAl-HT. The rehydration step was carried out by directly adding the optimal amount of water (35wt.% water) on the calcined MgAl-HT just before reaction. From the results shown in Figure S5, no evident difference was observed, which can be explained by the rehydration of calcined MgAl-HT by the water generated from the self aldol condensation of cyclopentanone.

Li-Al hydrotalcite ($[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$) was prepared by the method described in literature[4]. 125 mL $Al(NO_3)_3 \cdot 9H_2O$ (0.4 mol L^{-1}) aqueous solution was added dropwise to 300 mL mixed solution of $LiOH \cdot H_2O$ (1.5 mol L^{-1}) and Na_2CO_3 (0.08 mol L^{-1}) under vigorous stirring at room temperature. The suspension was aged at 348 K for 24 h, filtered and washed until neutral. The dried precursor was activated by nitogen flow at 723 K for 8 h.

All the solid base catalysts were activated in N_2 for 2 h at their calcination temperature respectively before being used for the catalytic evaluation.

The active carbon (AC) support used in the hydrodeoxygenation (HDO) process was supplied by NORIT Company. Before the usage, the AC support was treated by HNO_3 to increase its hydrophilicity. SiO_2 and SiO_2-Al_2O_3 (SiO_2/Al_2O_3 molar ratio: 37) were purchased from Qingdao Ocean Chemical Ltd.. H-BETA zeolite with SiO_2/Al_2O_3 molar ratio of 394 was provided by Nankai University. Zirconium phosphate (ZrP) was obtained according to Okuhara et al.[5] by the precipitation of 1.0 mol L^{-1} $ZrCl_2O \cdot 8H_2O$ and 1.0 mol L^{-1} $NH_4H_2PO_4$ aqueous solution at a molar ratio of P/Zr = 2.0. The precipitate was filtrated, washed with water, dried at 373 K overnight and calcined at 673 K for 4 h.

The Pd catalysts used in HDO reaction were prepared by the incipient wetness impregnation of different supports with the aqueous solution of $PdCl_2$. To facilitate the comparsion, the Pd content in all catalysts are fixed as 5 wt%. The catalysts were reduced by H_2 flow (60 mL min^{-1} $gcat^{-1}$) at 623 K for 2 h, cooled down in hydrogen flow to room temperature and passivated with 1% O_2 in N_2.

Ni-SiO_2 was obtained by the deposition-precipitation method according to previous work of Lercher and Zhao et al.[6]. Typically, 250 mL $Ni(NO_3)_3 \cdot 6H_2O$ (0.14 mol L^{-1}) aqueous solution was divided into two parts. 6.3 g urea was added to one part (50 mL), then the urea solution was added dropwise to the rest $Ni(NO_3)_3 \cdot 6H_2O$ solution (200 mL) together with 1.9 g SiO_2 and 0.3 mL HNO_3 (65 wt.%) at 353 K waterbath under vigorous stirring. After the precipitation process, the resulting suspension was rapidly heated to 363 K and maintained stirring for

10 h. Then the solid was filterd, washed to neutral, dried overnight, and calcined in air at 923 K for 4 h. The comparative catalyst Cu/SiO_2 was prepared by same method with the aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. The theoretical metal content in both Ni-SiO_2 and Cu-SiO_2 catalysts were controlled as 40 wt.%. The Ni-SiO_2 and Cu-SiO_2 catalysts as prepared were reduced by H_2 flow (60 mL min^{-1} gcat^{-1}) at 733 K for 2 h, cooled down in hydrogen flow to room temperature and passivated with 1% O_2 in N_2.

2. Activity test

2.1. Aldol condenstion

The self adol condensation of cyclopentanone was carried out by a Parr batch reactor. Typically, 4.0 g cyclopentanone and 0.4 g catalyst were put into the Parr batch reactor. Before the reaction, the reactor was purged with argon for three times. The mixture was stirred at 423 K for 8 h. After cooling down, the catalyst was removed by centrifugation. The liquid product was diluted by ethyl acetate and analyzed by an Agilent 6890N GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm I.D., 0.5 μm film) and a flame ionized detector (FID). The cyclopentanone conversion was calculated by its consumption. The carbon yield of 2-cyclopentylidene-cyclopentanone (i.e. **1a** in Scheme 1) was defined as: 2×(The mole of **1a** generated during the reaction)/(The mole of cyclopentanone in the feedstock) ×100%.

2.2. Hydrodeoxygenation (HDO)

The HDO of 2-cyclopentylidene-cyclopentanone (i.e. **1a** in Scheme 1) from the self aldol condensation of cyclopentanone was carried out at 643 K in a 316L stainless steel tubular flow reactor described in our previous work[7-10]. For each reaction, 1.8 g catalyst was used. The purified precursor (i.e. **1a** in Scheme 1) was pumped into the reactor at 0.04 mL min^{-1} from the bottom along with hydrogen at a flow rate of 120 mL min^{-1}. After passing a gas-liquid separator, the products became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in reaction system at 6 MPa and analyzed online by an Agilent 6890N GC. The CO_2 in the gaseous product was analyzed by a thermal conductivity detector

(TCD) equipped with an Alltech HAYESEP DB 100/120 packed column (30 feet, 1/8 inch O.D., 2.0 mm I.D.). The alkanes in the gaseous product were analyzed by FID equipped with an Rt®-Q-BOND capillary column (30 m, 0.32 mm I.D., 10 μm film). The liquid products were drained periodically from the gas-liquid separator and analyzed by an Agilent 6890N GC.

Method for the calculation of carbon yield in HDO step:

Carbon yield of C_1-C_5 light alkanes (%) = Sum of carbon in the C_1-C_5 alkanes detected from the gas phase products in unit time/Carbon fed into the reactor in unit time × 100% + Sum of carbon in the C_5 alkane detected from liquid phase products/Carbon fed into the reactor × 100%

Carbon yield of bi(cyclopentane) (%) = Sum of carbon in the bi(cyclopentane) detected from the liquid phase product/Carbon fed into the reactor × 100%

Carbon yield of C_{10} oxygenates (%) = Sum of carbon in the 2-cyclopentylcyclopentanone and 2-cyclopentylcyclopentanol detected from the liquid phase product/Carbon fed into the reactor × 100%

3. Characterization

3.1. XRD

XRD patterns of different Pd catalysts were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer, using Cu Kα monochromatized radiation ($\lambda = 0.1541$ nm) at a scan speed of 5° min^{-1}. From the results shown in Figure S6, we can only observe the peaks of supports and metallic Pd. The average sizes of Pd particles on different catalysts were estimated by Debye-Scherrer equation (see Table S1).

3.2. N_2-adsorption

The BET surface area of the catalysts were determined by nitrogen adsorption at 77 K using an ASAP 2010 apparatus. Before each measurement, the samples were evacuated at 573 K for 3 h.

3.3. CO_2-TPD

The basity of the different solid base catalysts used in this work were characterized by the CO_2-TPD which was carried out with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at its preparation temperature for 1 h and cooled down in He flow to 353 K. After the saturated adsorption CO_2 by impulse injection, the sample was heated at 353 K in He for 45 min to remove the physically adsorbed CO_2. Desorption of CO_2 was conducted in He flow from 353 K to 1073 K at a heating rate of 10 K min^{-1}. The desorbed CO_2 molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit.

3.4. NH_3-TPD

The acidities of the different solid base catalysts used in this work were characterized by the NH_3-TPD which was carried out with the same system as we used for CO_2-TPD. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at its preparation temperature for 1 h and cooled down in He flow to 373 K. After the saturated adsorption NH_3, the sample was heated at 373 K in He for 45 min to remove the physically adsorbed NH_3. Desorption of NH_3 was conducted in He flow from 373 K to 1073 K at a heating rate of 10 K min^{-1}. The desorbed NH_3 molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit.

3.5. Hydrogen-oxygen (H_2-O_2) titration

The dispersion of Pd and metallic surface were determined by the method of hydrogen-oxygen titration using a Micromeritics Autochem II 2920 automated chemisorption analyzer. Prior to measurement, the sample was pretreated at 623 K for 1 h in a flow of 10% H_2/Ar, purged in Ar at 633 K for 30 min and cooled down to 323 K in Ar. Subsquently, the pre-oxidation of sample was performed by switching to a flow of 2% O_2/He for 30 min to form Pd-O surface species, and then purged with pure argon for 30 min. Finally, 10% H_2/Ar was dosed until all surface Pd-O species reacted with hydrogen to form water and Pd–H surface species. The metal dispersions and metallic surface areas of different Pd catalysts (see Table S1) were calculated by the hydrogen consumption which was quantitatively measured with a high sensitivity thermal conductivity detector (TCD) (assuming 1.5 H_2 molecules are consumed for each surface Pd atom).

3.6. Inductively coupled plasma (ICP) analysis

The concentrations of Ni (or Cu) in the HDO product of **1a**, fresh and used Ni-SiO_2 (or Cu-SiO_2) catalysts were measured by Thermo IRIS Intrepid II inductively coupled plasma (ICP). From the results listed in Table S2, no Ni or Cu was identified in the HDO product of **1a**, which means that the concentrantion of Ni or Cu in the HDO product of **1a** is below 0.1 ppm i.e. the lower limitation of the equipment. From the comparsion of Ni (or Cu) contents in the fresh and used Ni-SiO_2 (or Cu-SiO_2) catalysts, no evident change was observed (see Table S2). According to these results, we believe the Ni-SiO_2 and Cu-SiO_2 catalysts are very stable under the investigated conditions, which is a reason for their stable catalytic performances in the HDO of **1a**.

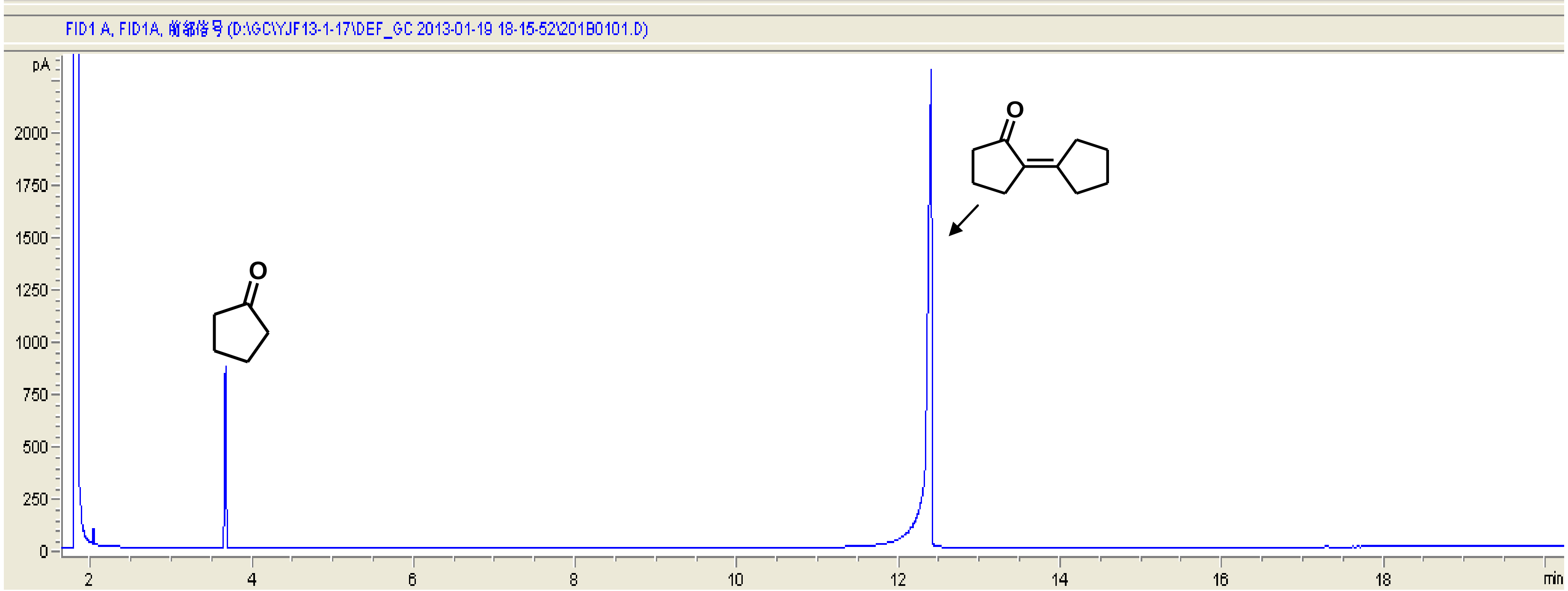

Figure S1. Gas chromatogram of the liquid product from the self aldol condensation of cyclopentanone.

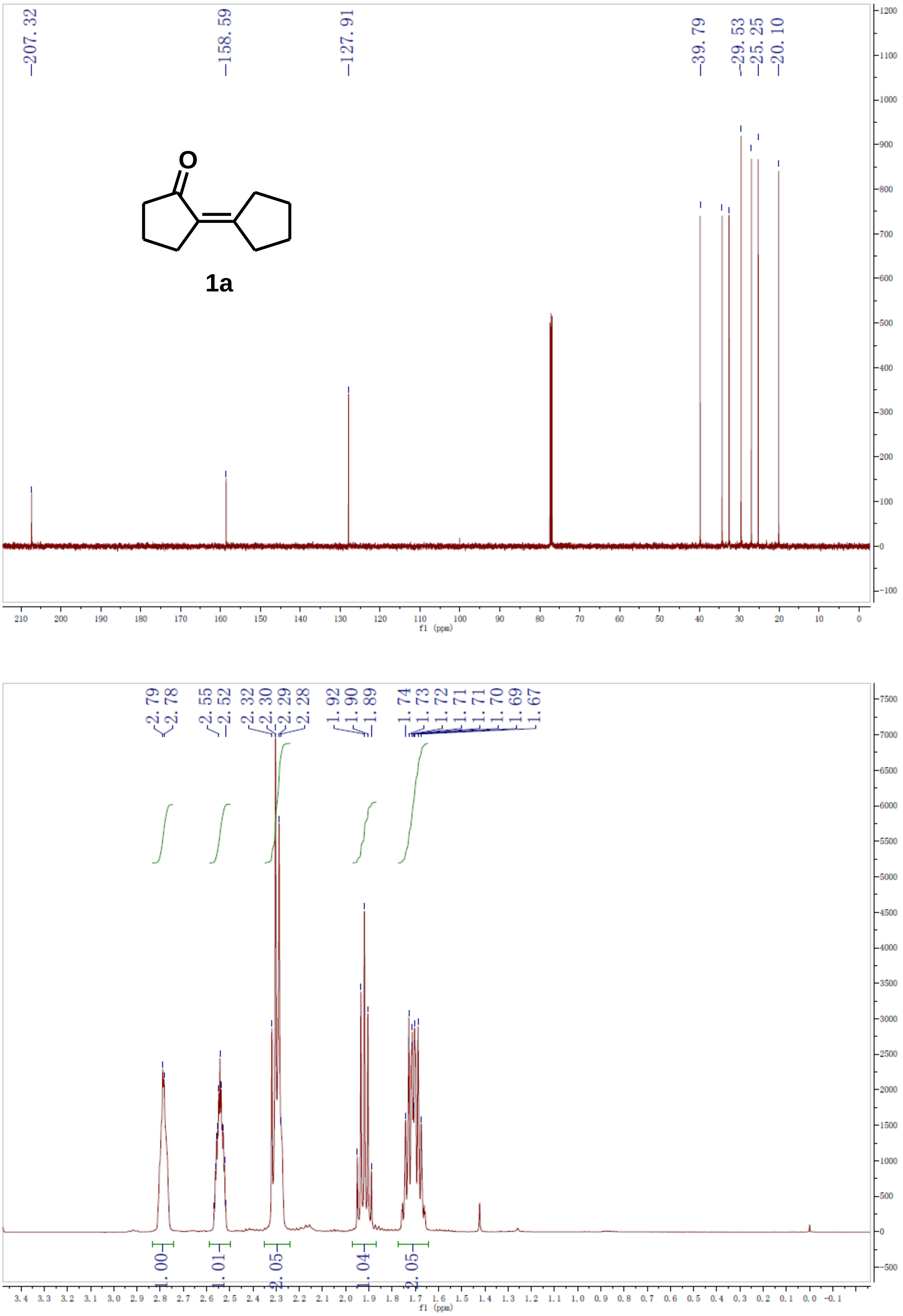

Figure S2. ^{13}C and ^{1}H NMR spectra of **1a** from the self aldol condensation of cyclopentanone.

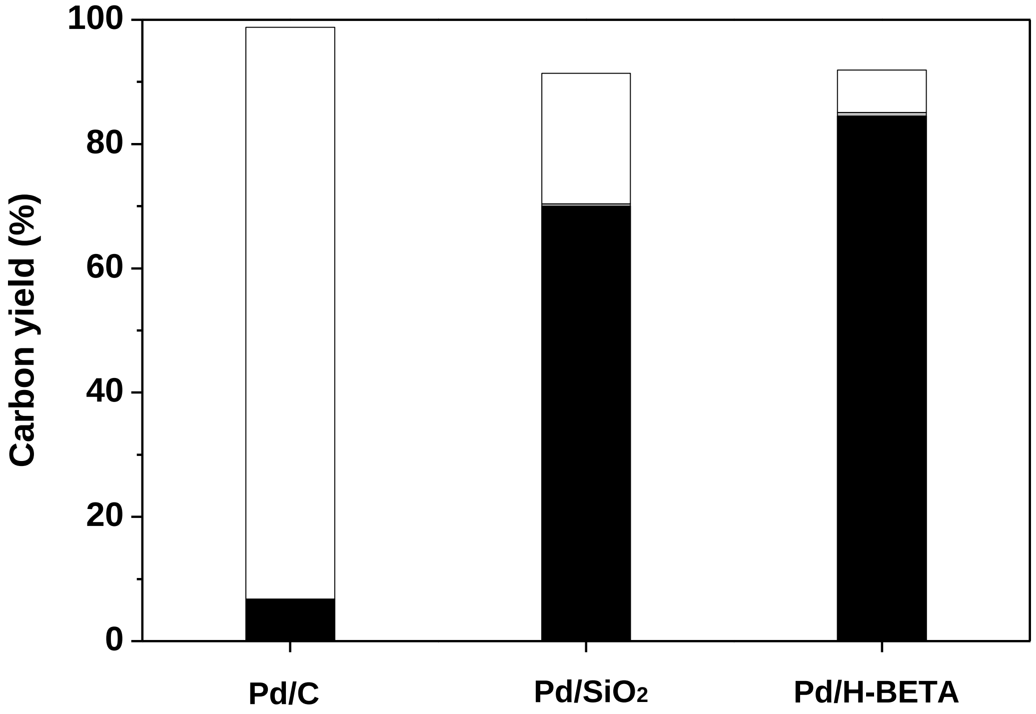

Figure S3. Carbon yields of bi(cyclopentane) (black bar), C_1-C_5 light alkanes (grey bar) and C_{10} oxygenates (white bar) over different catalysts. Reaction conditions: 453 K, 6 MPa; 1.8 g catalyst; liquid feedstock 2-cyclopentylidene-cyclopentanone (i.e. **1a** in Scheme 1) flow rate 0.04 mL min^{-1}; hydrogen flow rate: 120 mL min^{-1}.

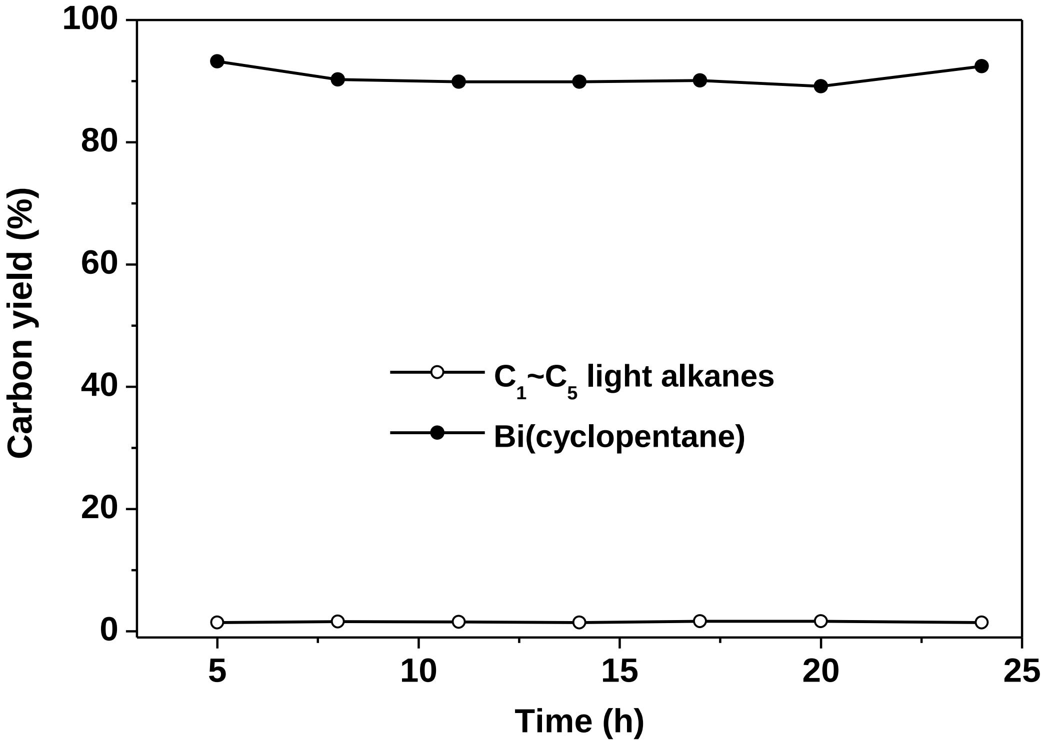

Figure S4. The carbon yields of different alkanes over Ni-SiO_2 as the function of reaction time. Reaction conditions: 503 K, 6 MPa; 1.8 g catalyst; liquid feedstock 2-cyclopentylidene-cyclopentanone (i.e. **1a** in Scheme 1) flow rate 0.04 mL min^{-1}; hydrogen flow rate: 120 mL min^{-1}.

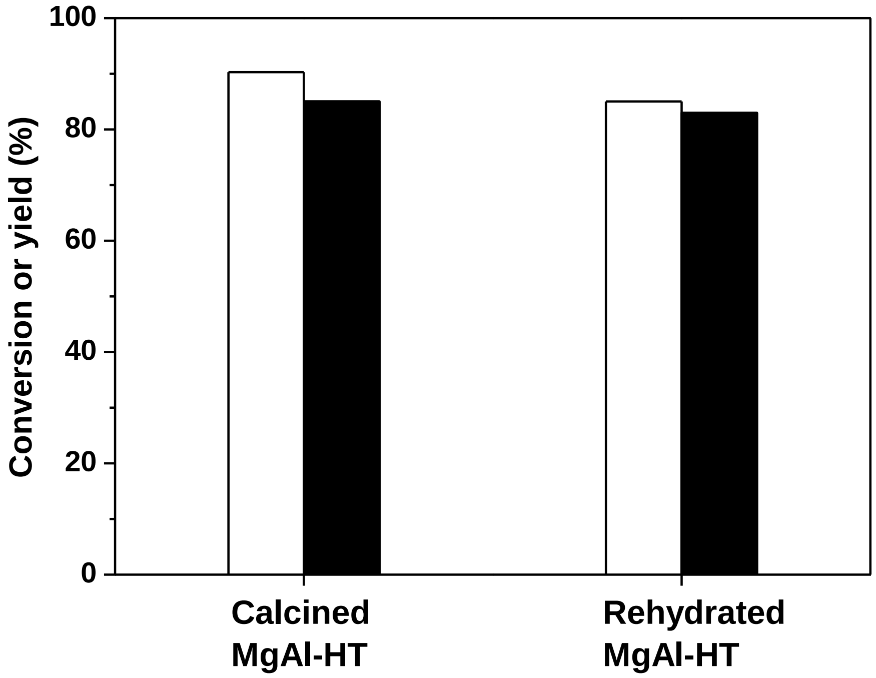

Figure S5. Conversion of cyclopentanone (white bar) and carbon yield of **1a** (black bar) over calcined and rehydrated MgAl-HT catalysts. The reaction was performed with 4.0 g cyclopentanone and 0.4 g catalyst at 423 K for 8 h in a batch reactor.

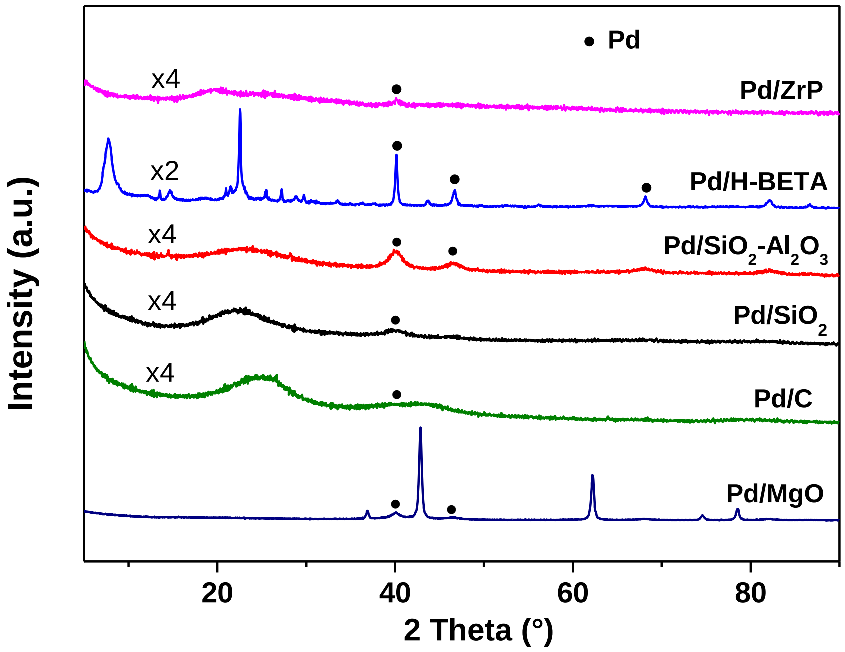

Figure S6. XRD patterns of different Pd catalysts.

Table S1. Average sizes of Pd particles, metal dispersions and metallic surface areas on different Pd catalysts.

Catalyst	Dp (nm)[a]	Metal dispersion (%)[b]	Metallic surface area (m^2 g^{-1})[b]
Pd/MgO	10.0	6.2	1.39
Pd/C	6.5	12.2	2.72
Pd/SiO_2	4.3	27.4	5.80
Pd/SiO-Al_2O_3	5.6	14.3	3.19
Pd/H-BETA	43.0	0.7	0.16
Pd/ZrP	35.0	3.5	0.78

a: Estimated from XRD results by Debye-Scherrer equation.

b: Calculated from the results of hydrogen-oxygen titration.

Table S2. Concentrations of Ni (or Cu) in hydrodeoxygenation (HDO) products of **1a**, fresh and used Ni-SiO_2 (or Cu-SiO_2) catalysts.

Catalyst	Liquid product from the HDO of **1a**	Solid sample	
		Fresh catalyst	Used catalyst[a]
Ni-SiO_2	< 0.1 ppm	34.0%	33.8%
Cu-SiO_2	< 0.1 ppm	37.6%	37.2%

a: After being used in the HDO of **1a** at 503 K and 6 MPa for 12 h.

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