Electronic Supplementary Material (ESI) for Green Chemistry.

Conversion of Biomass Derived Valerolactone into High Octane Number Gasoline with Ionic Liquid

Jiayu Xin, Dongxia Yan, Olubunmi Ayodele, Zhan Zhang , Xingmei Lu, Suojiang Zhang*

[a] Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex System
Institute of Process Engineering, Chinese Academy of Sciences
Zhongguancun, Beiertiao, Haidian, Beijing 100190 (China)
Fax: (+86) 10-8262-7080
E-mail: sjzhang@ipe.ac.cn

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Materials and methods

Preparation of Pd/C

Palladium catalyst was prepared by impregnation on the carbon support with a 0.047 M solution of H_2PdCl_4. Activated carbon was coped with 30 % HNO_3 before use. According to theoretical calculations, a certain amount of chloride precursor (H_2PdCl_4) was added into 3.0 g activated carbon dropwise which mixed with 60 ml distilled water at 60 ^oC, For deposition, aqueous Na_2CO_3 solution (2 mol/L) was added to the impregnating solution in order to maintain constant pH. After stirred for 8 h, the reduction was performed in liquid phase using formaldehyde at 80 ^oC for 2 h. Then, the catalyst was washed with 80 ^oC distilled water and dried at vacuum oven for 18 h.

Preparation of Pd/ZSM-8

ZSM-8 was purchased from J&K Scientific Ltd. and calcined at 600 ^oC for 4 h. Then the ZSM-8 was subjected to ion-exchange treatment at 60 ^oC using 1 mol/L ammonium nitrate with volume ratio of ammonium salt solution and zeolite of 6:1. Then ZSM-8 is washed with deionized water for 3 times and dried at 120 ^oC over night, and calcined at 500 ^oC for 5 h to obtain hydrogenous zeolite. After hole-processed at 60 ^oC for 3 hours using 1 mol/L hydrochloric acid, washed with deionized water, dried at 120 ^oC for 12 h, and calcined at 500 ^oC for 3 h, the ZSM-8 was then contacted with H_2PdCl_4 with aqueous Na_2CO_3 solution (2 mol/L) as a precipitating agent. The solid is washed with deionized water until no chloride ions are present, dried at 120 ^oC over night and calcined at 600 ^oC for 4 in a muffle furnace.

Hydrogenation of 1-butene and 2-butene with Pd/C

Hydrogenation was performed in a 100 ml stirred stainless steel reactor. Reaction temperature was maintained by placing the reactor in a heating coat. Butene was firstly pumped into the reactor by a syringe pump, after reached the designed temperature, H_2 was pumped and maintained with designed reaction time.

Isomerization of *n*-butane to isobutane

Conversion of *n*-butane to isobutane is carried out in a fixed bed reactor using extrusion-molded catalyst at 350 and 380 degrees C, 0.3-3 MPa, and 0.5-20 hour-1, moving bed reactor using catalyst pellets at 150-600 ^oC, 0.3 MPa, and WHSV of 1 h^{-1}.

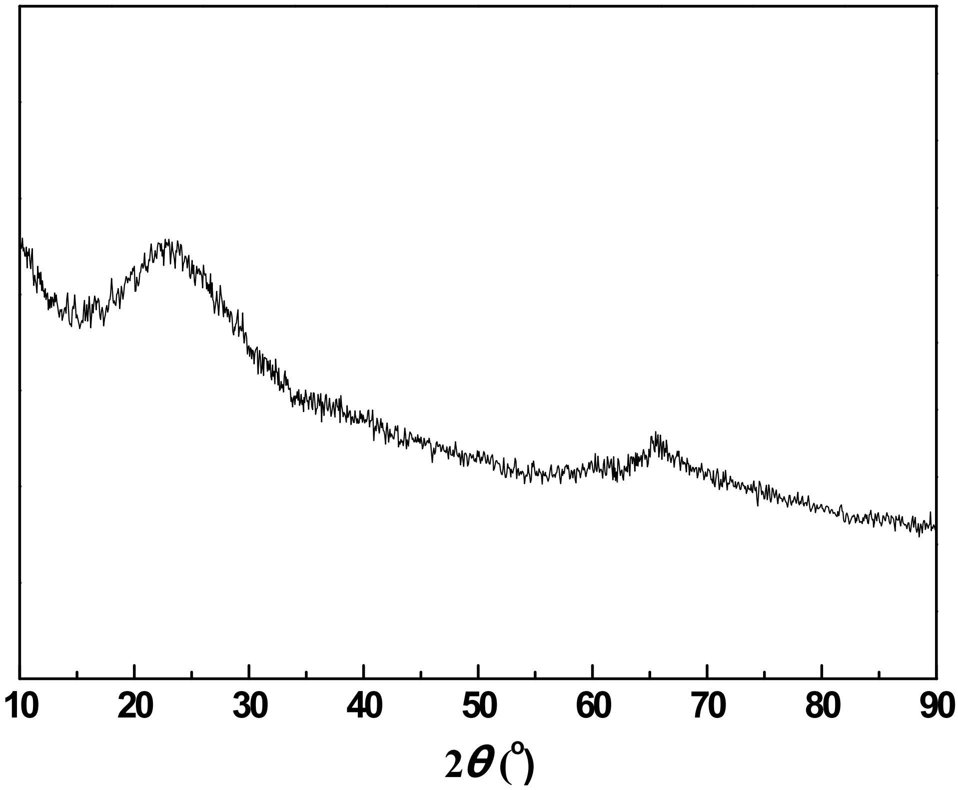

Figure S1. XRD pattern of SiO_2/Al_2O_3 catalyst

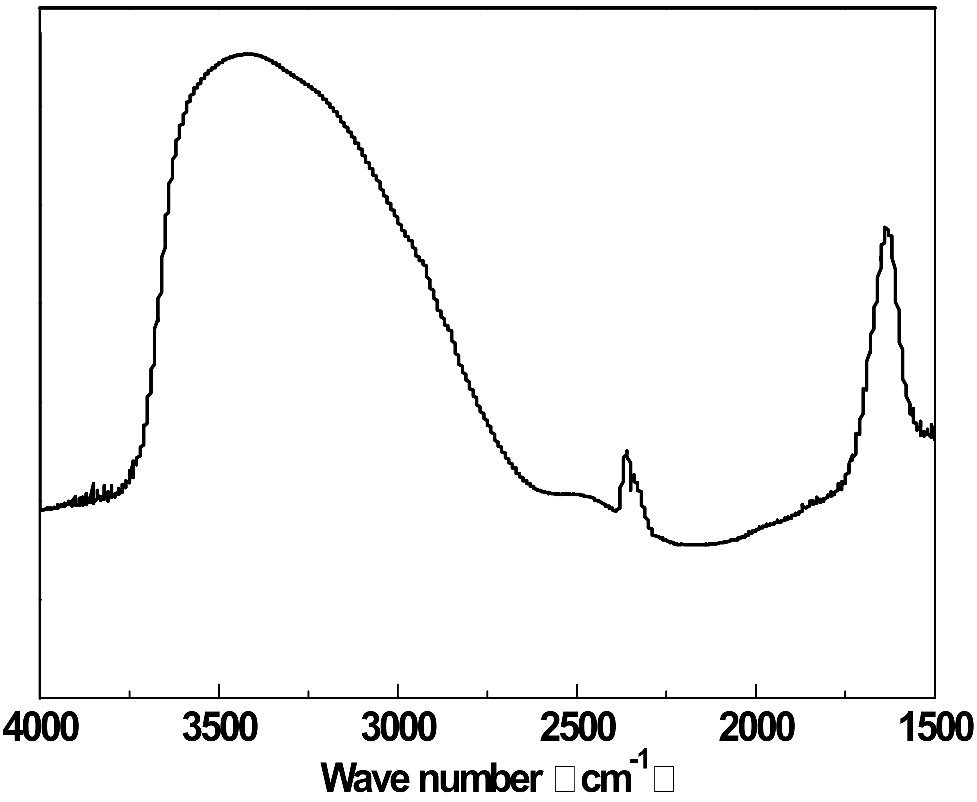

Figure S2. FT-IR spectrum of SiO_2/Al_2O_3 catalyst

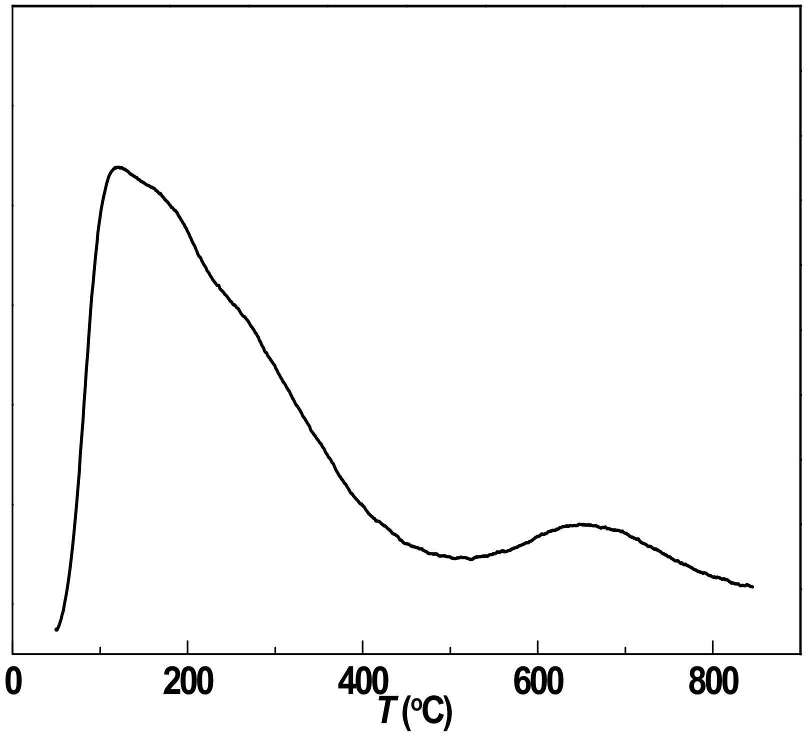

Figure S3. NH_3 -TPD profiles of SiO_2/Al_2O_3 catalyst

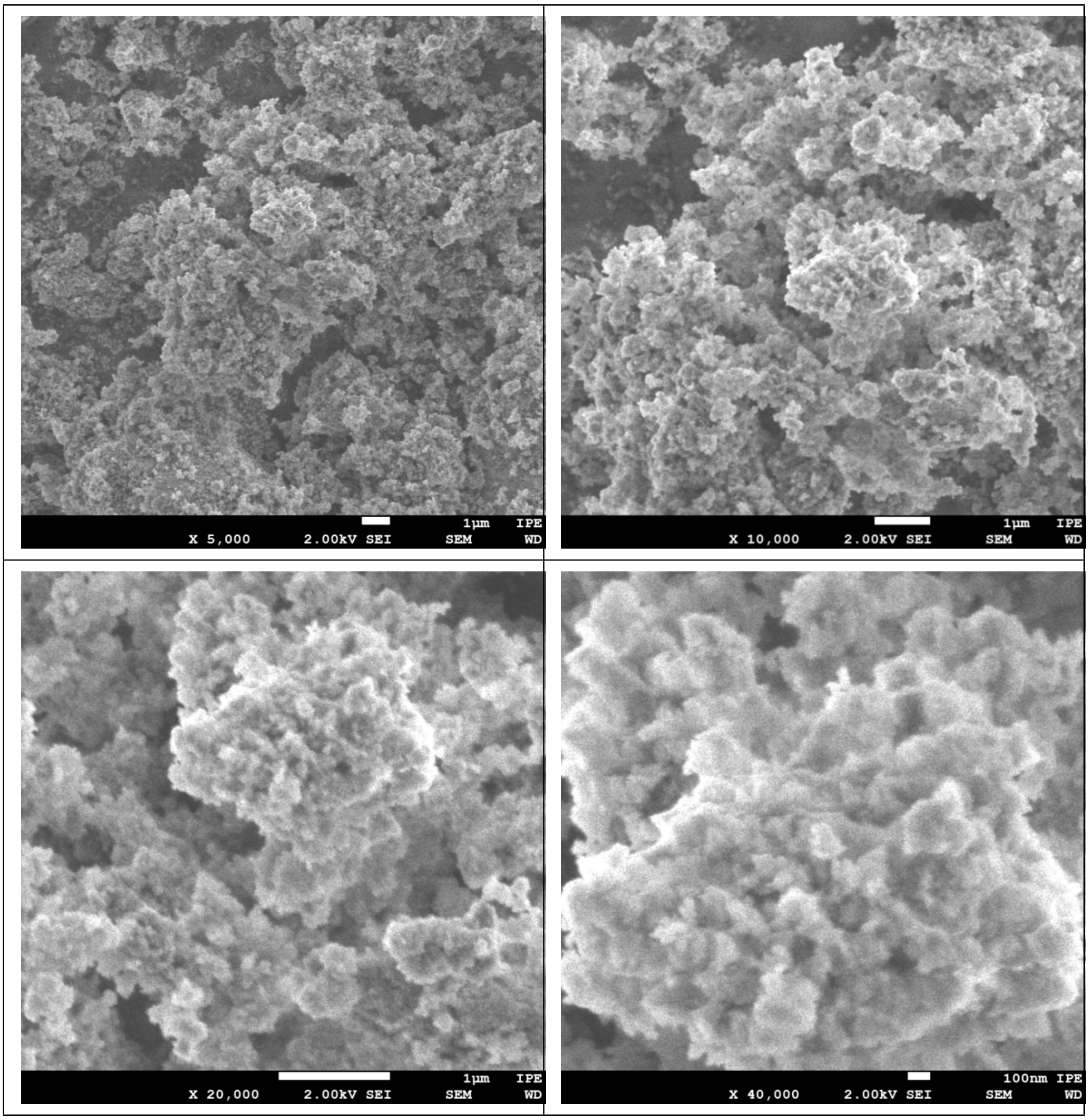

Figure S4. SEM image of SiO_2/Al_2O_3 catalyst

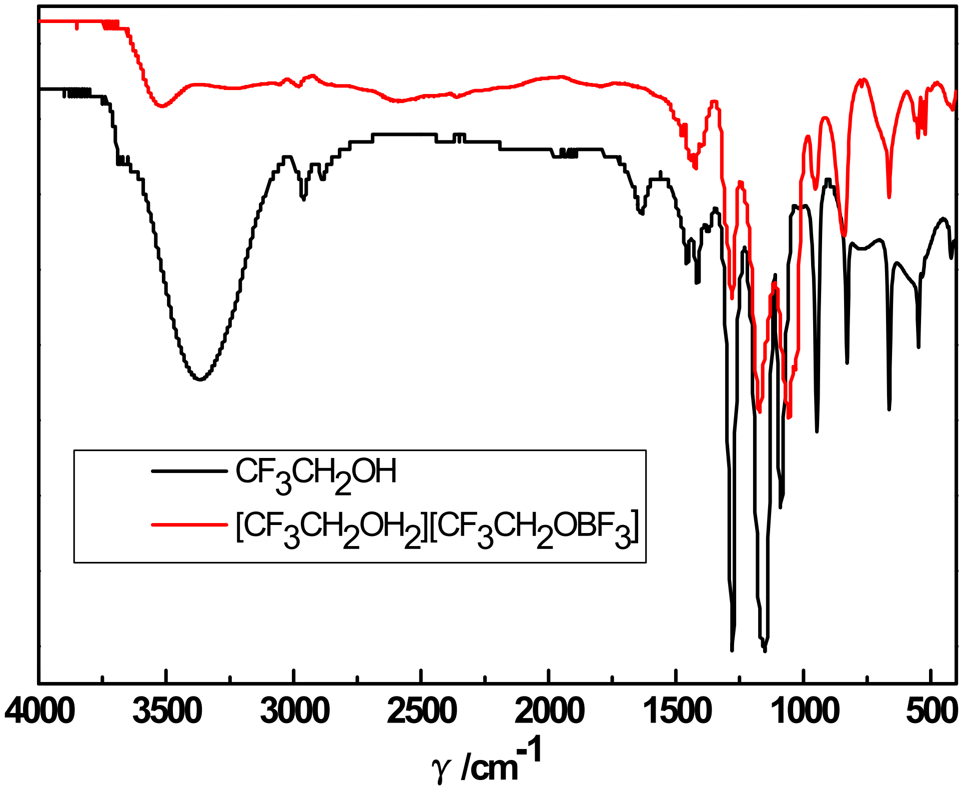

Figure S5. FT-IR spectrum of CF_3CH_2OH and $[CF_3CH_2OH_2][CF_3CH_2OBF_3]$

Table S1. Low temperature physical adsorption–desorption of nitrogen by SiO_2/Al_2O_3 catalyst

BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	Nanoparticle Size (nm)
476.9	0.57	4.8	12.6

Table S2. Hydrogenation of 1-butene and 2-butene over Pd/C

Entry	Reactant	H_2 pressure (MPa)	Time (h)	Temp.(^oC)	Yield of n-butane (%)
1	1-butene	5	2	180	>99
2	2-butene	5	2	180	>99
3	1-butene	2	2	120	97
4	2-butene	2	2	120	98

Conditions: 100 ml batch type reactor, 5 ml compressed (liquefied at room temperature) butene reactant, 0.1 g catalyst, with continuous stirring at 600 rpm; the products were analyzed by GC-FID.

Table S3. Isomerization of n-butane over Pd/ZSM-8

Entry	Reactant	H_2 pressure (MPa)	Temp.(^{o}C)	Isobutane (%)
1	*n*-butane	0.3	350	55
2	*n*-butane	0.3	380	62

Conditions: fixed-bed reactor, 1 g catalyst, WHSV, 1 h^{-1}; the products were analyzed by GC-FID.

Table S4. Reusability of $[CF_3CH_2OH_2][CF_3CH_2O\text{-}BF_3]$

Exp. cycles	1	2	3	4	5	6	7	8	9	10	11	12
Time (min)	10	10	10	10	10	10	10	10	10	10	10	10
Temp.(℃)	10	10	10	10	10	10	10	10	10	10	10	10
C5 (%)	1	2	1	2	2	1	2	2	1	1	1	1
C6 (%)	2	2	2	3	3	3	3	3	3	2	2	2
C7 (%)	2	3	3	4	4	4	4	4	3	3	3	2
C8 (%)	82	78	73	69	63	58	50	49	46	44	41	38
TMP (%)	73	69	64	59	54	48	41	40	39	37	35	32
DMH (%)	9	9	9	10	9	10	9	9	7	6	5	5
TMP/DMH	8	8	7	6	6	5	5	5	6	6	7	6
C9+ (%)	13	14	20	23	28	34	42	42	47	50	54	58
RON	95.4	94.9	93.5	92.6	91.6	90.1	88.9	88.9	88.8	88.5	88.0	87.3

Table S5. Detected compounds produced by alkylation of butenes (1-butene and 2-butene) and isobutane by GC-Fid

No.	Retention time	Carbon number	Compound
1	10.536	C4	isobutane
2	11.979	C5	2-methylbutane
3	14.496	C6	2,3-dimethylbutane
4	14.591	C6	2-methylpentane
5	15.155	C6	3-methylpentane
6	17.289	C7	2,4-dimethylpentane
7	17.684	C7	2,2,3-trimethylbutane
8	19.114	C7	2-methylhexane
9	19.526	C7	2,3-dimethylpentane
10	19.86	C7	3-methylhexane
11	21.035	C8	2,2,4-trimethylpentane
12	23.666	C8	2,5-dimethylhexane
13	23.872	C8	2,4-dimethylhexane
14	23.999	C8	2,2,3-trimethylpentane
15	25.29	C8	2,3,4-trimethylpentane
16	25.787	C8	2,3,3-trimethylpentane
17	25.903	C8	2,3-dimethylhexane
18	26.015	C8	3-ethyl-2-methylpentane
19	26.122	C8	2-methylheptane
20	26.25	C8	4-methylheptane
21	26.527	C8	3,4-dimethylhexane
22	26.699	C8	3-methylheptane
23	27.778	C9	2,2,5-trimethylhexane
24	27.778+	C9+	