Supporting information

Influence of Brønsted acid sites on the product distribution in hydrodeoxygenation of methyl laurate over supported Ru catalysts

Leilei Zhou,[a,b,c] Weiwei Lin,[a,c] Xinchao Wang,[a,b,c] Zhuangqing Wang,[a,b,c] Yinze Yang,[a,b,c] Liyan Zhang,[a,b,c] Haiyang Cheng,*[a,c] Masahiko Arai [a,c] and Fengyu Zhao [a,b,c]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, No. 5625 Renmin Rd., Changchun, 130022, China

[b] School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei 230026, China

[c] Jilin Province Key Laboratory of Green Chemistry and Process, Changchun Institute of Applied chemistry, Chinese Academy of Sciences, No. 5625 Renmin Rd., Changchun, 130022, China

Corresponding Author E-mail: hycyl@ciac.ac.cn

Table S1 Catalytic performances of Ru nanoparticles loaded on various supports for the hydrodeoxygenation of methyl laurate at initial period

Catalyst	Time (min)	Conv. (%)	Selectivity (%)				Rate (mmol min^{-1} g_{Ru}^{-1})[b]
			n-$C_{11}H_{24}$	*n*-$C_{12}H_{26}$	*n*-$C_{11}H_{23}COOH$	Others[a]	
Ru/H-Z5(18)	15	22.4	32.6	15.2	38.4	13.8	4.15
Ru/H-Z5(25)	15	22.2	26.9	10.7	46.4	16.0	4.11
Ru/H-Z5(27)	15	23.0	26.7	8.8	50.8	13.7	4.26
Ru/Na-Z5(27)	15	19.6	46.0	10.9	33.3	9.8	3.63
Ru/H-Z5(50)	15	14.5	76.4	8.0	2.5	13.1	2.69
Ru/Al_2O_3	30	23.3	87.7	5.2	1.1	6.0	2.16
Ru/SiO_2	30	18.5	77.3	7.8	3.6	11.3	1.71

Reaction conditions: 0.5 mmol methyl laurate, 60 mg catalyst, 10 mL *n*-hexane, 3 MPa H_2, 200 ºC, 700 r•min^{-1}.

[a] Others are 1-$C_{12}H_{25}OH$, *n*-$C_{11}H_{23}COOC_{12}H_{25}$ and small amounts of *n*-C_9H_{20} and *n*-$C_{10}H_{22}$.

[b] Reaction rate: Amount of methyl laurate consumed per min per gram of Ru.

Table S2 Catalytic performance, BET surface area, and metal particle size for Ru based catalysts

Catalyst	S_{BET} (m^2 g^{-1})[a]	Particle size (nm)[a]	Rate (mmol min^{-1} g_{Ru}^{-1})[b]	Selectivity to *n*-$C_{12}H_{26}$ / Conversion / Time (% / % / h)[c]
Ru/H-Z5(18)	374	5.6	4.15	41/87/4
Ru/H-Z5(25)	389	8.1	4.11	43/90/4
Ru/H-Z5(27)	445	6.4	4.26	33/90/4
Ru/Na-Z5(27)	528	9.3	3.63	24/86/4
Ru/H-Z5(50)	506	7.7	2.69	9/83/4
Ru/Al_2O_3	114	7.2	2.16	3/84/6
Ru/SiO_2	282	11.3	1.71	5/92/15

[a] The data come from **Table 1**.

[b] The data come from **Table S1**.

[c] The data come from **Table 2**.

Table S3 Results of hydrodeoxygenation of methyl laurate over different catalysts

Catalyst	Brønsted acid (mmol/g)	Lewis acid (mmol/g)	Conv. (%)	Selectivity (%)			Ratio of *n*-$C_{12}H_{26}$/*n*-$C_{11}H_{24}$
				n-$C_{11}H_{24}$	*n*-$C_{12}H_{26}$	Others [a]	
Ru/H-Z5(27)	0.42	0.16	90	54	33	13	0.61
Ru/Na-Z5(27)	0.28	0.15	86	64	24	12	0.38
Ru/Na-Z5(27)-IM[b]	0.014	0.15	100	85	7	8	0.08

Reaction conditions: 0.5 mmol methyl laurate, 60 mg catalyst, 10 mL *n*-hexane, 3 MPa H_2, 200 ºC, 4 h, 700 r•min^{-1}. The catalysts were prepared by urea precipitation method. [a] Others are 1-$C_{12}H_{25}OH$, *n*-$C_{11}H_{23}COOH$, *n*-$C_{11}H_{23}COOC_{12}H_{25}$ as well as a small amount of *n*-C_9H_{20} and *n*-$C_{10}H_{22}$ was detected. [b] Prepared by impregnation method.

For the Ru/Na-Z5(27), it was prepared by urea precipitation method with $RuCl_3$ and the commercial

Na-Z5(27), during the preparation Na^+ in Na-Z5(27) was exchanged by NH_4^+ from the decomposing of urea and water, and some new Brønsted acid sites may be regenerated during the calcination and reduction. Therefore, the amount of Brønsted acid sites in Ru/Na-Z5(27) was not significantly lower than that in Ru/H-Z5(27). Then, a Ru/Na-Z5(27)-IM was prepared by impregnation method in the absence of urea (without cation exchange), the amount of Brønsted acid sites decreased significantly on the Ru/Na-Z5(27)-IM (**Fig. S9 and Table S3**). It presented a remarkable decrease in the ratio of *n*-$C_{12}H_{26}$/*n*-$C_{11}H_{24}$ and the selectivity to *n*-$C_{12}H_{26}$ compared to Ru/H-Z5(27) and Ru/Na-Z5(27).

Table S4 The influence of SiO_2/Al_2O_3 ratio on the catalytic performances over Pt/H-Z5, Ir/H-Z5 catalysts

Catalyst	Time (h)	Conversion (%)	Selectivity (%)			Ratio of *n*-$C_{12}H_{26}$/*n*-$C_{11}H_{24}$
			n-$C_{11}H_{24}$	*n*-$C_{12}H_{26}$	Others[a]	
Pt/H-Z5(25)	4	60.0	19.4	48.8	31.8	2.52
Pt/H-Z5(50)	10	63.8	61.8	25.5	12.7	0.41
Ir/H-Z5(25)	6	60.3	33.7	37.0	29.3	1.10
Ir/H-Z5(50)	15	63.6	58.7	27.1	14.2	0.46

Reaction conditions: 0.5 mmol methyl laurate, 60 mg catalyst, 10 mL *n*-hexane, 3 MPa H_2, 200 ºC, 700 r•min^{-1}.

[a] Others are 1-$C_{12}H_{25}OH$, *n*-$C_{11}H_{23}COOH$, *n*-$C_{11}H_{23}COOC_{12}H_{25}$ as well as a small amount of *n*-C_9H_{20} and *n*-$C_{10}H_{22}$ was detected.

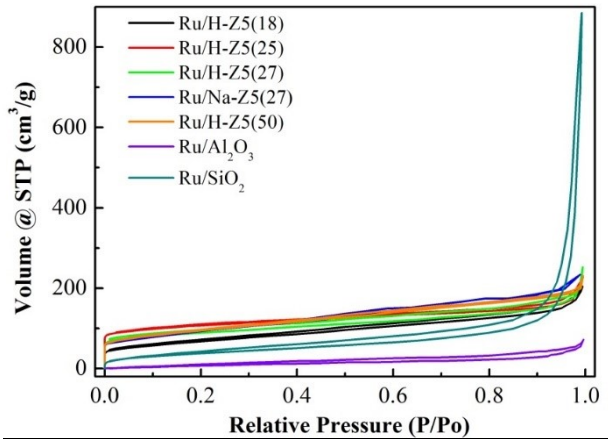

Fig. S1 N_2 adsorption/desorption isotherms of Ru based catalysts at -196 ºC.

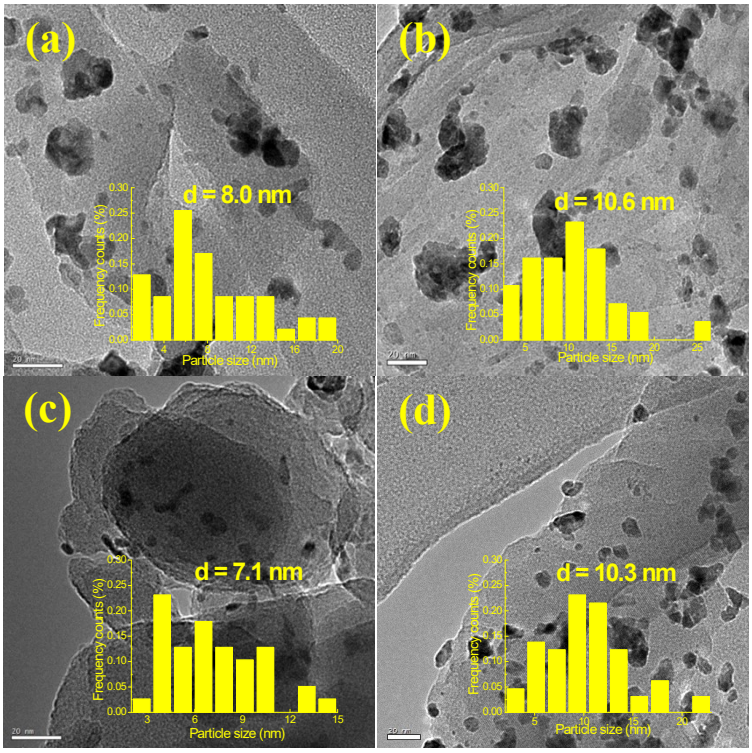

Fig. S2 TEM images of (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), and (d) Ru/H-Z5(50) with the corresponding histograms of metal particle size distribution. The white scale bar given is 20 nm.

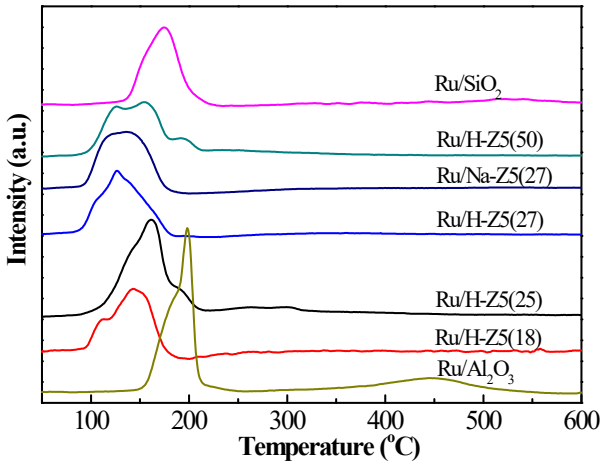

Fig. S3 H_2-TPR curves of Ru based catalysts.

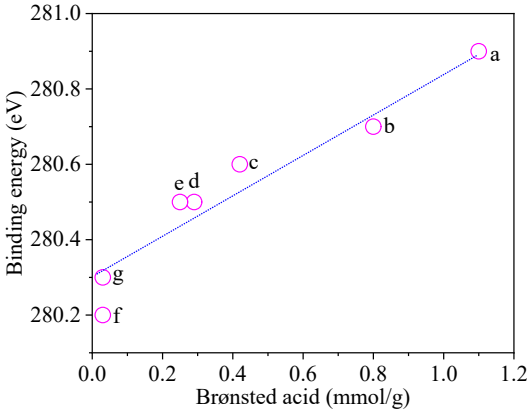

Fig. S4 Relationship between the amount of Brønsted acid sites and the binding energy of Ru^0 species. (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), (d) Ru/Na-Z5(27), (e) Ru/H-Z5(50), (f) Ru/Al_2O_3, (g) Ru/SiO_2.

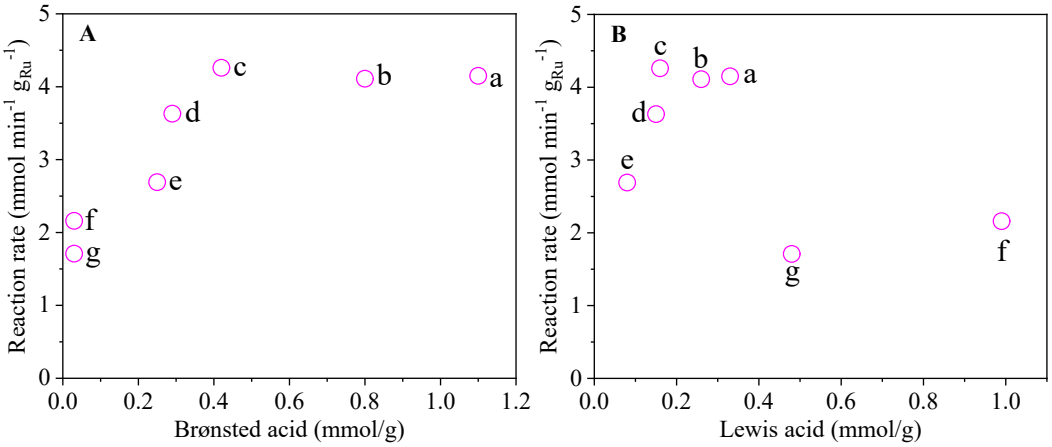

Fig. S5 Relationship of reaction rate at lower conversion (<23%) with the amount of Brønsted acid sites (A) or Lewis acid sites (B) over different catalysts (Data come from **Tables 3**, **S1)**. (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), (d) Ru/Na-Z5(27), (e) Ru/H-Z5(50), (f) Ru/Al_2O_3, (g) Ru/SiO_2.

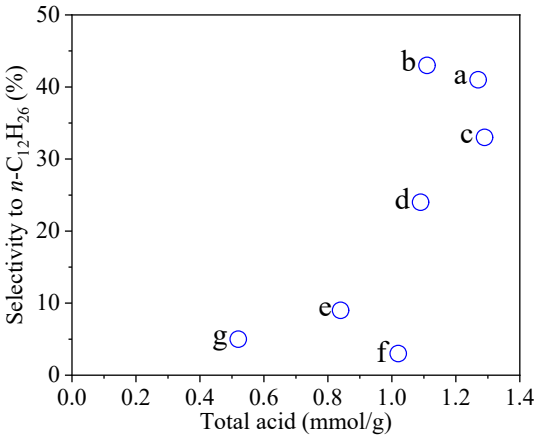

Fig. S6 Relationship between the selectivity to n-$C_{12}H_{26}$ at the conversion levels of 83%-92% and the amount of total acid sites over the Ru based catalysts. The data come from **Tables 2, 3**. (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), (d) Ru/Na-Z5(27), (e) Ru/H-Z5(50), (f) Ru/Al_2O_3, (g) Ru/SiO_2.

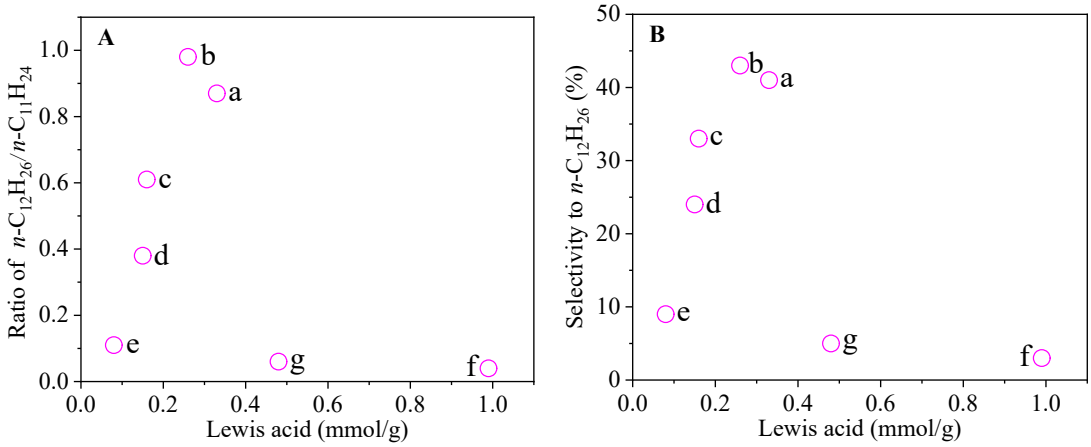

Fig. S7 Relationship between (A) the ratio of n-$C_{12}H_{26}$/n-$C_{11}H_{24}$ or (B) the selectivity to n-$C_{12}H_{26}$ at the conversion levels of 83%-92% and the amount of Lewis acid sites over different catalysts (Data in **Tables 2, 3**). (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), (d) Ru/Na-Z5(27), (e) Ru/H-Z5(50), (f) Ru/Al_2O_3, (g) Ru/SiO_2.

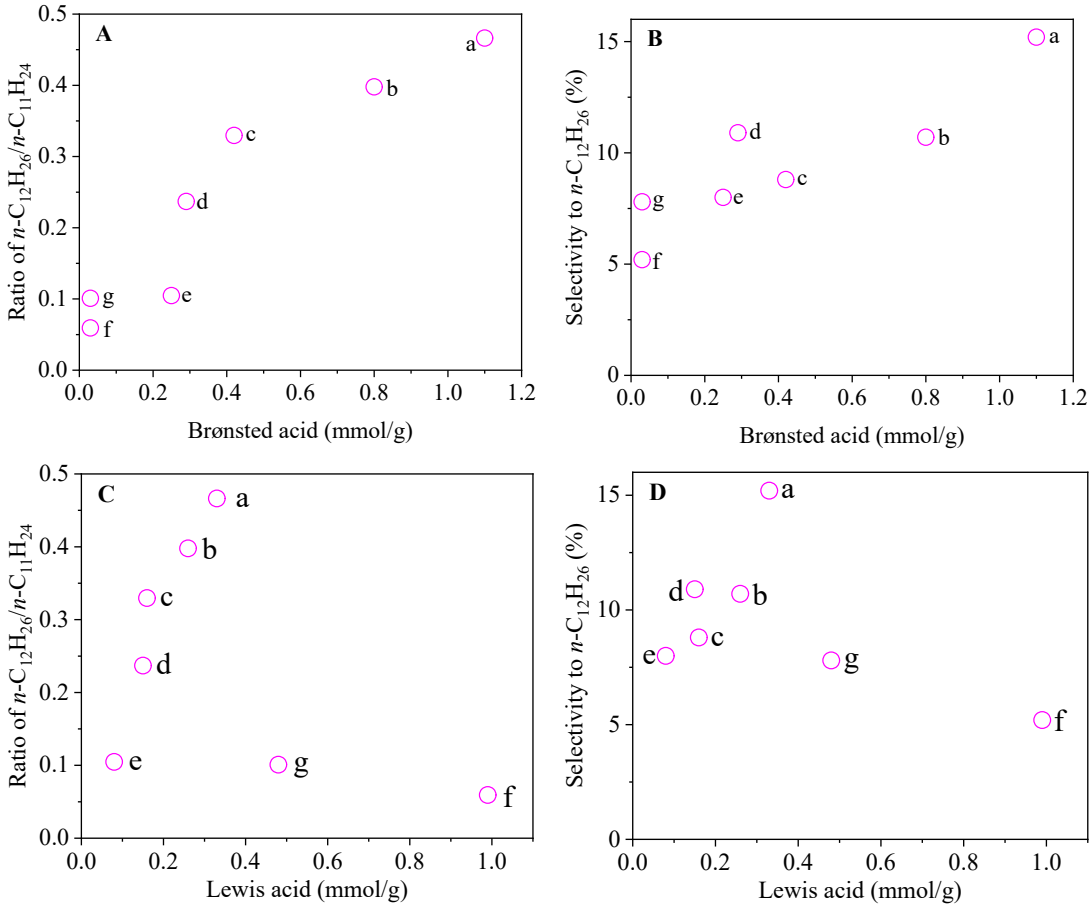

Fig. S8 Relationship of the ratio of n-$C_{12}H_{26}$/n-$C_{11}H_{24}$ or the selectivity to n-$C_{12}H_{26}$ at low conversion levels (<23%) with the amount of Brønsted acid sites (A, B) and Lewis acid sites (C, D) over different catalysts (Data in **Tables 3, S1**). (a) Ru/H-Z5(18), (b) Ru/H-Z5(25), (c) Ru/H-Z5(27), (d) Ru/Na-Z5(27), (e) Ru/H-Z5(50), (f) Ru/Al_2O_3, (g) Ru/SiO_2.

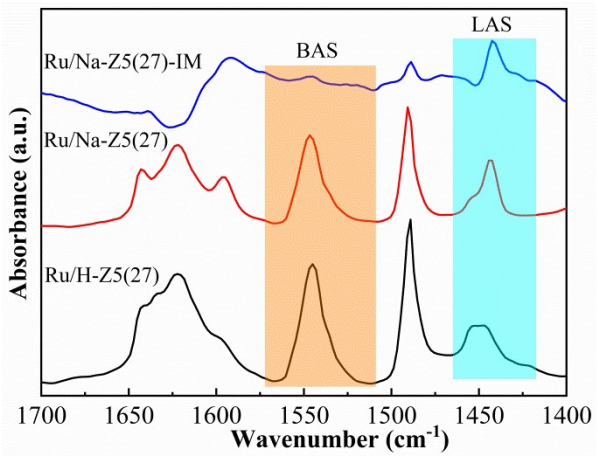

Fig. S9 FTIR spectra of pyridine adsorbed over the Ru/H-Z5(27), Ru/Na-Z5(27) and Ru/Na-Z5(27)-IM catalysts. The labels of 'BAS' and 'LAS' refer to Brønsted and Lewis acid sites, respectively.

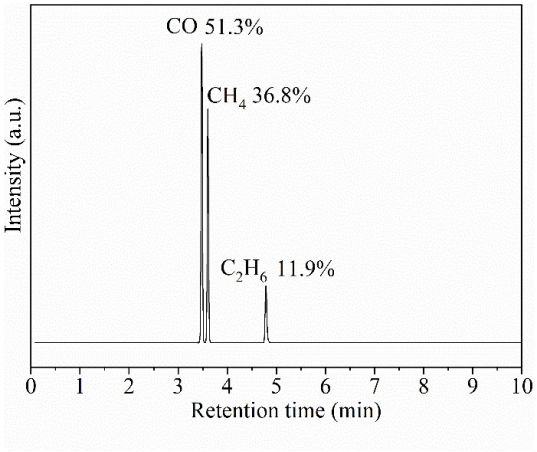

Fig. S10 The relative amounts of gaseous products in the hydroxygenation over Ru/H-Z5(50) catalyst detected by GC/MS. Reaction conditions: 0.5 mmol methyl laurate, 60 mg catalyst, 10 mL *n*-hexane, 3 MPa H_2, 200 ºC, 700 r•min^{-1}. Conversion of methyl laurate is 83%, and selectivity to *n*-$C_{12}H_{26}$ is 9%.

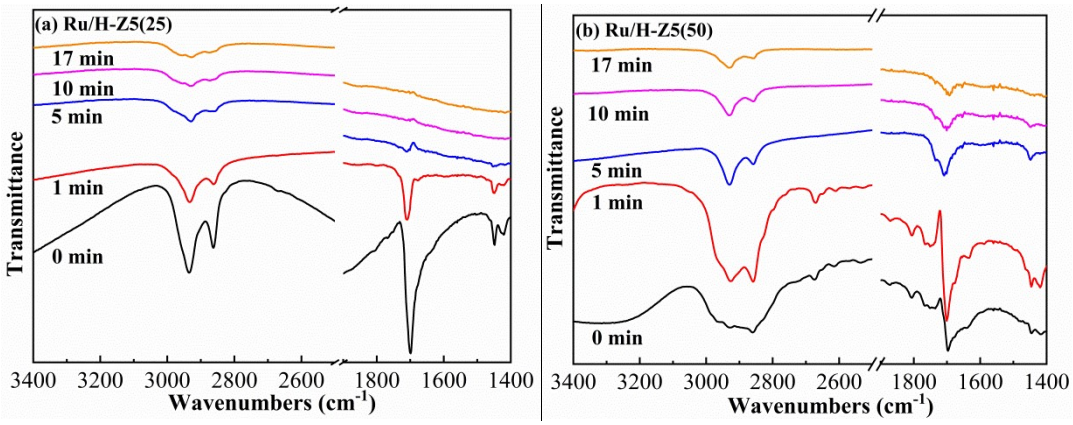

Fig. S11 Fourier Transform Infrared Diffuse Reflection Spectroscopy (DRIFTS) of cyclohexanone desorption over the (a) Ru/H-Z5(25) and (b) Ru/H-Z5(50) catalysts with time extension while purging He (30 mL/min).