Supporting Information

One-pot Hydrodeoxygenation (HDO) of Lignin Monomers to C9 Hydrocarbons co-catalysed by Ru/C and Nb_2O_5

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Tables

Table S-1. Time profile of co-catalyst system

Entry	Time (h)	Conv. (%)	Product Distribution (%)				
			1	**2**	**3**	**4**	**5**
1[a]	2	14	-	-	-	100	-
2[b]	2	41	-	-	-	18	82
3	2	36	4	5.9	9.4	65	16
4	4	100	35	33	31	-	-
5	8	100	94	6.4	-	-	-
6[c]	12	100	100	-	-	-	-

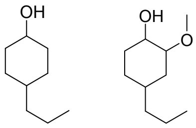
Reaction condition: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, methanol 0.8 mL, P(H_2) = 6 bar, 250 ℃, 12h. [a] Reaction with Ru/C only. [b] Reaction with Nb_2O_5 only. [c] The same experiment as entry 4 in Table 2.

Table S-2. Catalyst recyclability test

Run	Conv. (%)	Product Distribution (%)					Material balance (mol%)
		1	**2**	**3**	**4**	**5**	
1	100	81	19	-	-	-	92
2	100	81	19	-	-	-	94
3	78.6	14	10	12	56	8	94
4[a]	56.3	27	4	18	46	6	88
5[b]	47	17	3	21	55	3	88
6[c]	80	31	4	7	38	20	90

Reaction condition: DHE 1 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, methanol 1 mL, P(H_2) = 6 bar, 250 ℃, 16 h. Unless noted, the catalyst was washed using ethanol twice, dried in vacuum chamber at room temperature for 24 h and in oven at 120 ℃ for 1 h before using for next run. [a] Catalyst was calcinated under N_2 at 450 ℃ for another 45 min before use. [b] Catalyst was reduced under H_2(5%)/Ar at 350 ℃ for another 3 h before use. [c] Fresh Nb_2O_5 0.1 g was added into the reused catalyst mixture (0.2 g left after five runs) for the Run 6.

Table S-3. Reaction with cyclohexanol feedstock over Ru/C or Nb_2O_5 alone.

Entry	Substrate	Conv. (%)	Product Distribution (%)	
			1	**other**
1		99	100	0
2		62	14.5	85.5

Reaction condition: propyl cyclohexanol and 2-methoxy-4-propycyclohexanol mixture (1:1) 0.4 mL, Ru/C 100 mg (entry 1) or Nb_2O_5 200 mg (entry 2), H_2O 12 mL, methanol 0.8 mL, initial $P(H_2)$ = 6 bar, 250 °C, 12 h.

Figures and Schemes

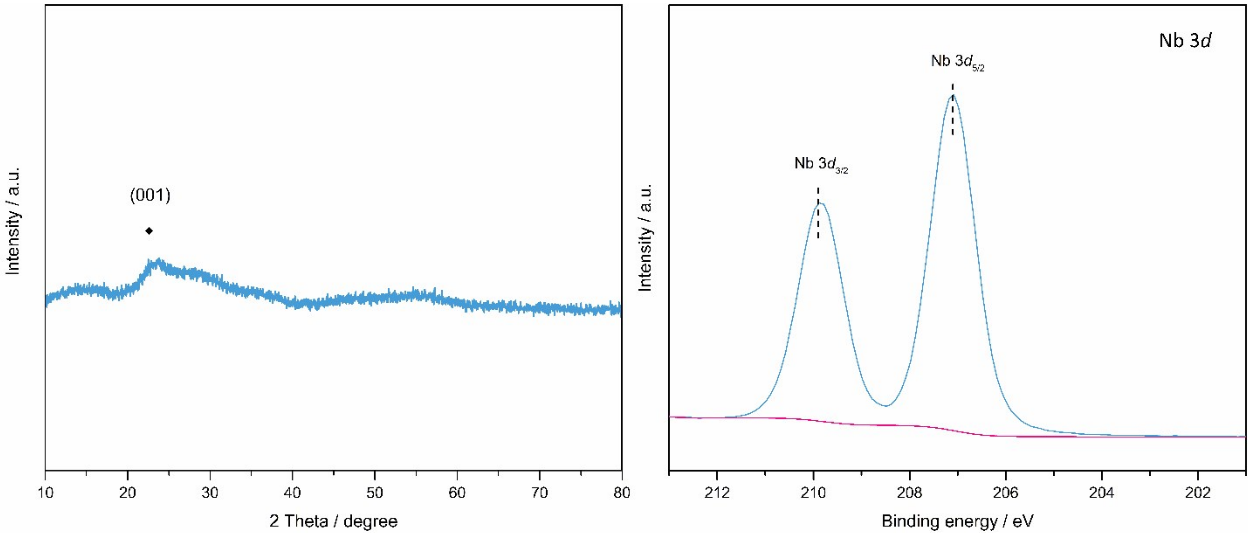


Figure S-1. XRD pattern (left) and XPS analysis (right) of Nb_2O_5 catalyst. According to XRD pattern of Nb_2O_5 (left), only one broad diffraction peak located at about 22.7° is observed, which corresponds to the facet (001). No sharp peak is observed, which suggests that the synthesized Nb_2O_5 has the amorphous structure. XPS analysis was also performed to obtain the oxidation state (right). The catalyst shows the typical Nb $3d_{3/2}$ (209.9 eV) and Nb $3d_{5/2}$ (207.1 eV) peaks of Nb^{5+}. [1] No other peaks were obtained.

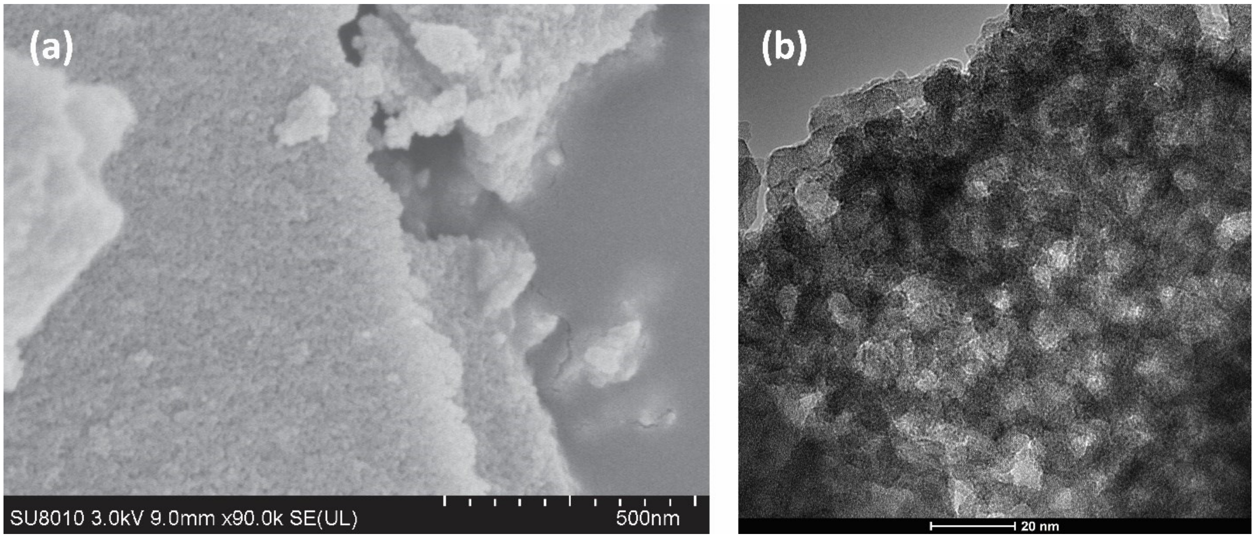


Figure S-2. SEM (a) and TEM (b) images of Nb_2O_5 catalyst. According to the SEM image, the bulk-shape particles of synthesized Nb_2O_5 are not the crystalline form. Numerous pores are evenly distributed on the top and cross section of the catalyst evenly. From the TEM image, the inner pores of Nb_2O_5 can be observed more clearly. The pores are not regular but has relatively consistent pore size that is around 5 nm. Combining with the XRD result, the synthesized Nb_2O_5 is an amorphous mesoporous solid.

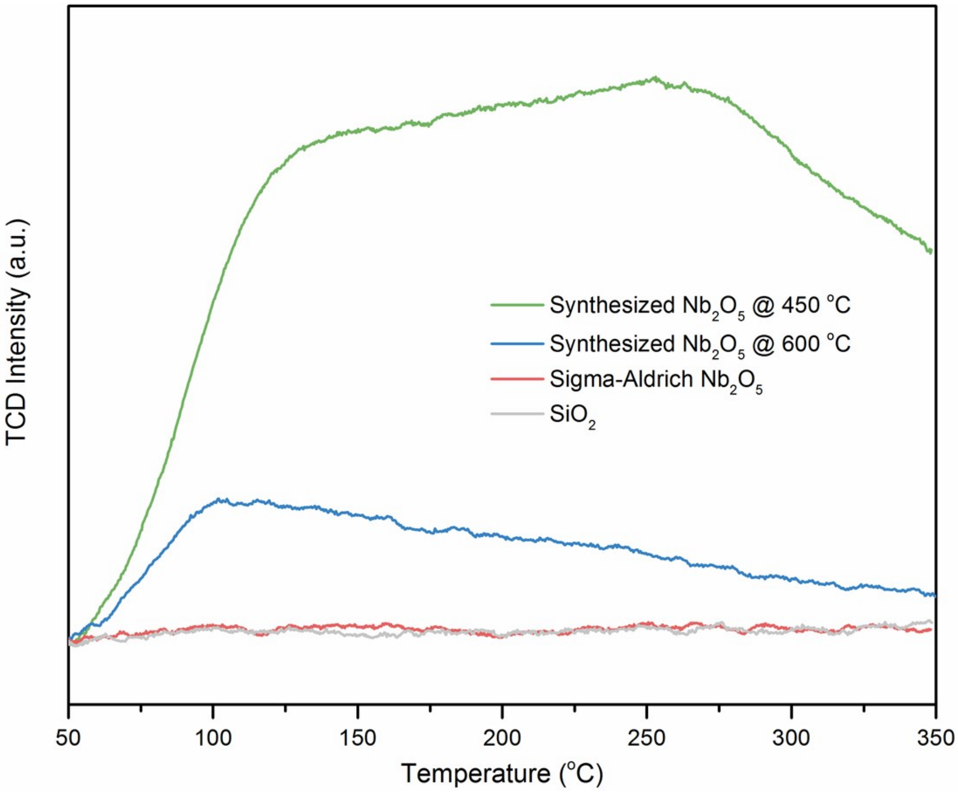


Figure S-3. NH_3-TPD profiles of different Nb_2O_5 catalysts. The Nb_2O_5 was prepared by using niobium (V) chloride and CTAB in a Teflon lined autoclave and calcinated at 450 ℃ and 600 ℃, respectively. Nb_2O_5 purchased from Sigma-Aldrich used as is. SiO_2 has no acid sites and was analyzed for comparison. 0.2600 g Nb_2O_5 prepared at 450℃, 0.1964 g Nb_2O_5 prepared at 600℃, 0.2210 g purchased Nb_2O_5, and 0.2173 g SiO_2 samples were loaded for NH_3-TPD analysis. The ammonia adsorption was determined in term of mmol of NH_3 per gram of loaded sample.

The acid property of Nb_2O_5 catalyst is sensitive to the calcination temperature. According to the figure, Nb_2O_5 calcinated at 450 ℃ adsorbs the largest amount of ammonia among other samples which indicates the 450 ℃ Nb_2O_5 has the most abundant acid sites. When the calcination temperature increased to 600 ℃, the acid sites reduced dramatically. And the purchased Nb_2O_5 from Sigma-Aldrich has been reported to be calcinated at 1000 ℃ almost has no acid sites comparing to SiO_2.[2] According to our results, abundant acid sites of Nb_2O_5 are vital to our HDO reactions. From entries 1 and 2 in Table 3, Nb_2O_5 calcinated at 450 ℃ promotes the hydrolysis to catechol (**5**) and dehydroxylation to phenol (**4**) but the purchased Nb_2O_5 shows no activity.

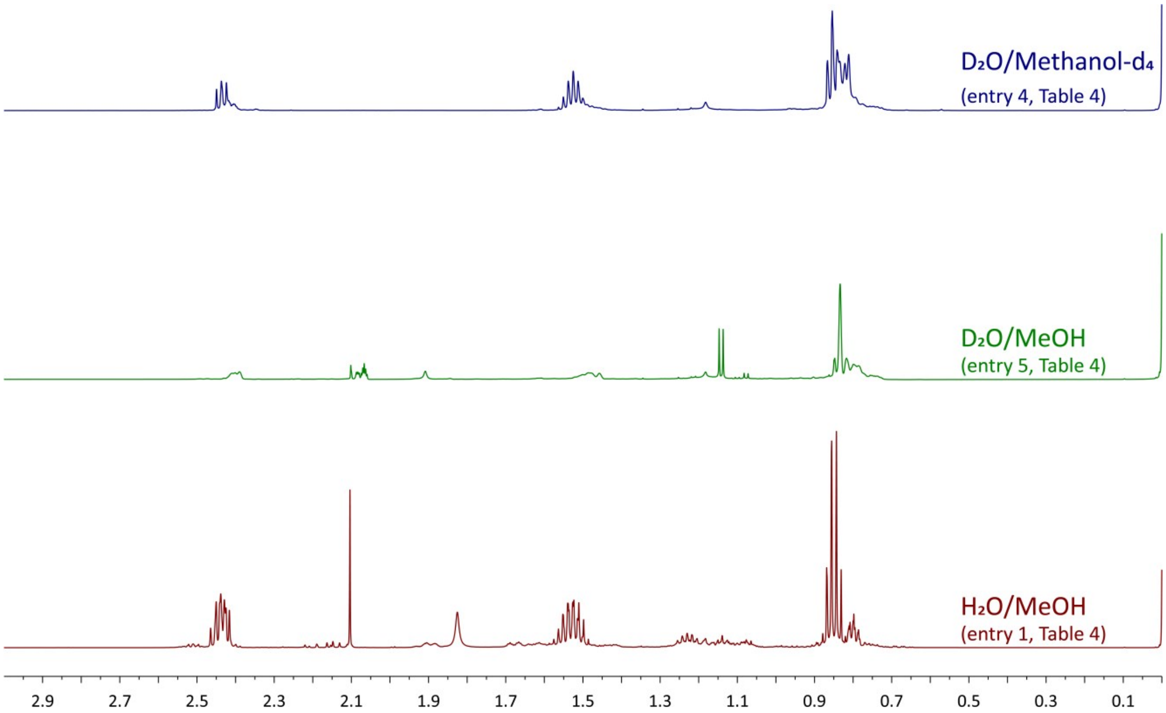


Figure S-4. ^1H NMR in the aliphatic region of the products obtained after DHE reactions in D_2O/methanol-d_4 (top, entry 4 in Table 4) D_2O/MeOH (middle, entry 5 in Table 4) and H_2O/MeOH (bottom, entry 2 in Table 4). Conditions: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, water 12 mL, methanol 0.8 mL, purged with H_2 and vented to $P(H_2)$ = 1 bar, 250 ℃, 12 h reaction time. For the entry 4 in Table 4 (top), the reaction time was 24 h; for the entry 1 in Table 4 (bottom), 0.4 mL MeOH was used.

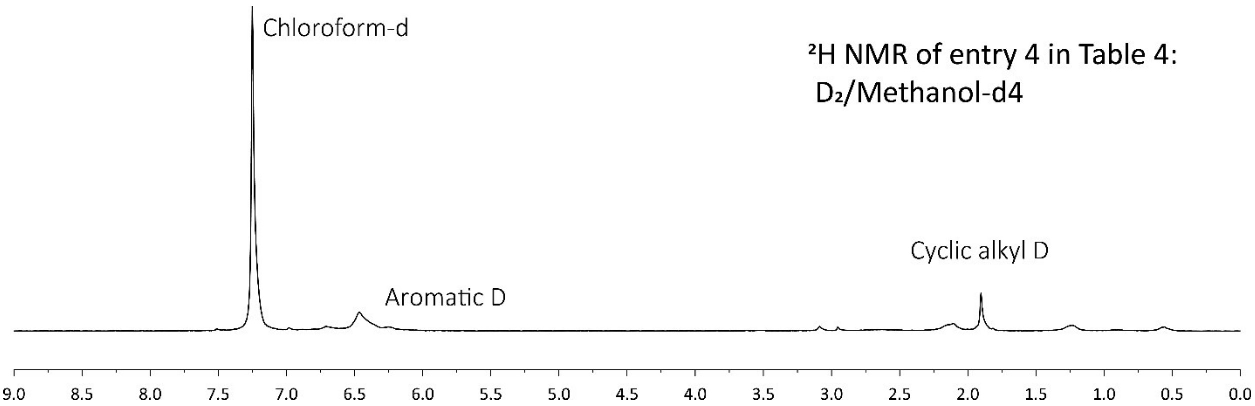


Figure S-5. ^2H NMR spectrum of products obtained from the reaction of DHE in D_2O and methanol-d_4. Conditions: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, D_2O 12 mL, methanol-d_4 0.8 mL, purged with H_2 and vented to $P(H_2)$ = 1 bar, 250 ℃, 24 h reaction time.

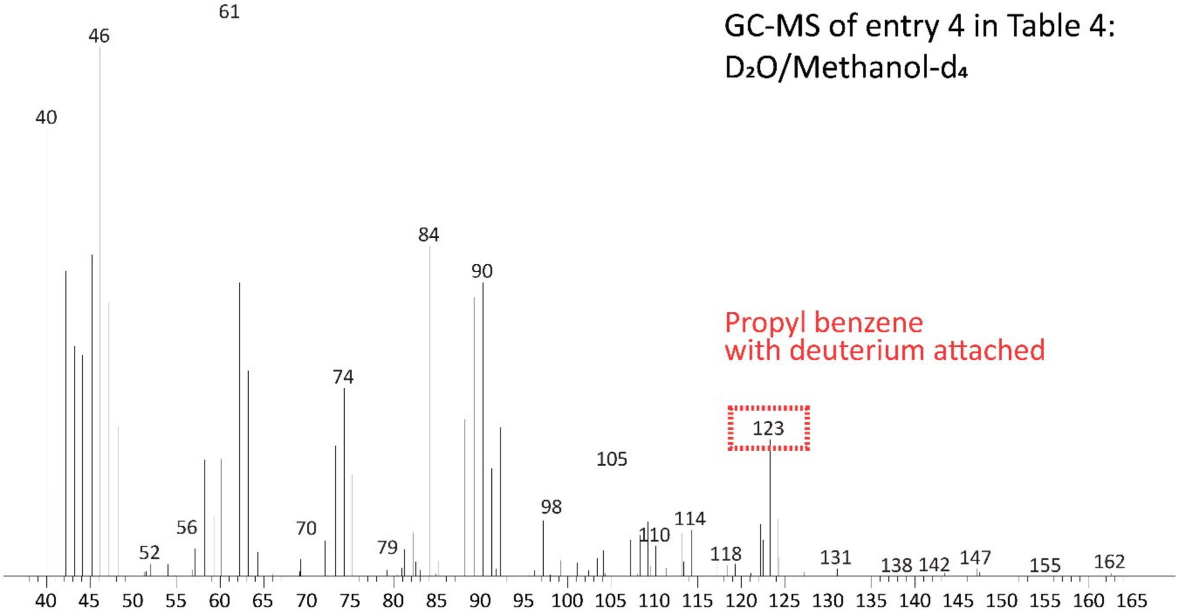


Figure S-6. GC-MS of propyl benzene obtained from the reaction of DHE in D_2O and methanol-d_4. Conditions: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, D_2O 12 mL, methanol-d_4 0.8 mL, purged with H_2 and vented to $P(H_2)$ = 1 bar, 250 ℃, 24 h reaction time.

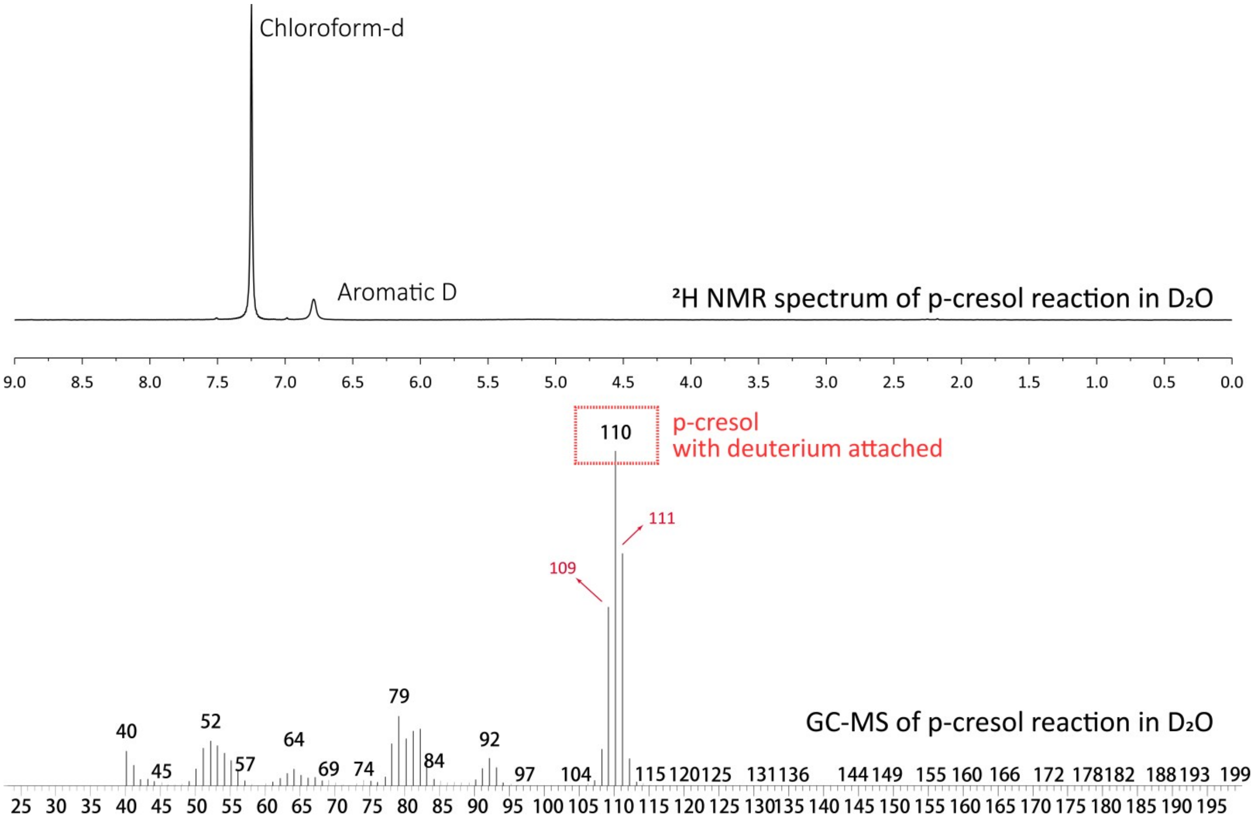
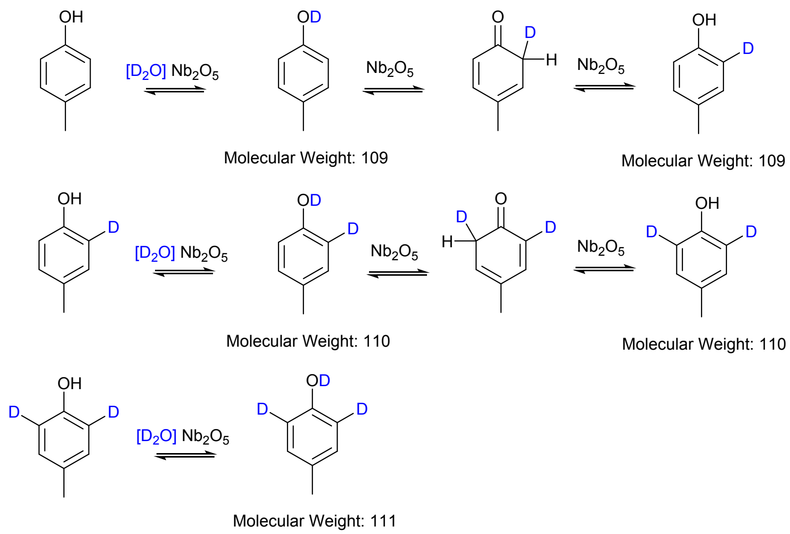


Figure S-7. ^{2}H NMR (above) and GC-MS (bottom) spectra of p-cresol after reaction with Nb_2O_5 in D_2O. Conditions: p-cresol 0.2 mL, Nb_2O_5 200 mg, D_2O 12 mL, P(H_2) = 6 bar, 250 ℃, 12 h reaction time. No HDO product was observed after reaction. However, the molecular weight of p-cresol was detected to be M/e 109, 110, and 111 by GC-MS. This suggests that up to three aromatic hydrogens on p-cresol exchanged with the solvent D_2O during the reaction. The aromatic deuteriums detected upon recording the ^{2}H NMR spectrum of the p-cresol after reaction, can be explained by the tautomerization mechanism (Scheme S-1).



Scheme S-1. The mechanism of p-cresol reaction with Nb_2O_5 in D_2O. The deuterium from D_2O could transfer to aromatic ring through tautomerization catalysed by Nb_2O_5. This Scheme shows the possible structures and molecular weight of p-cresol after isotopic reaction with Nb_2O_5 in D_2O in agreement with the GC/MS and ^{2}H NMR results.

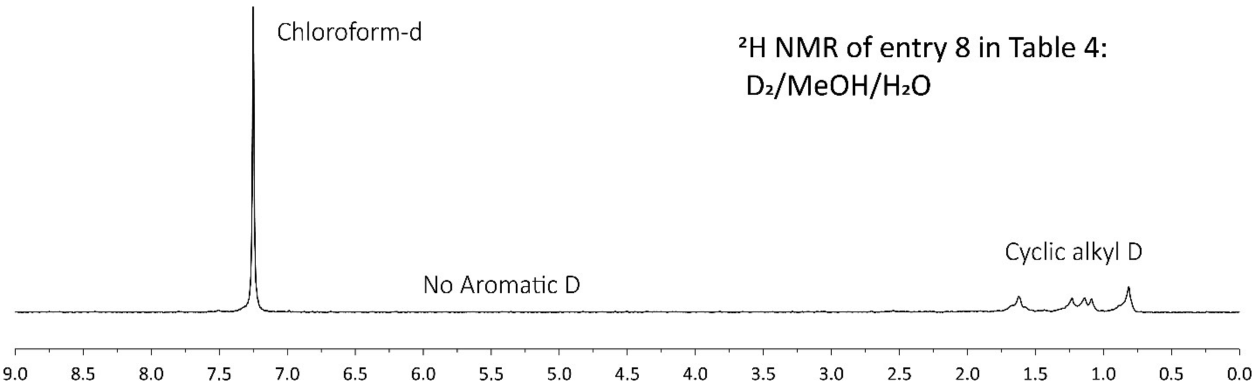


Figure S-8. ^{2}H NMR spectrum of the products from the catalysed reaction of DHE with D_2 in H_2O and MeOH. Conditions: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, MeOH 0.8 mL, P(D_2) at RT = 6 bar, 250 ℃, 24 h reaction time.

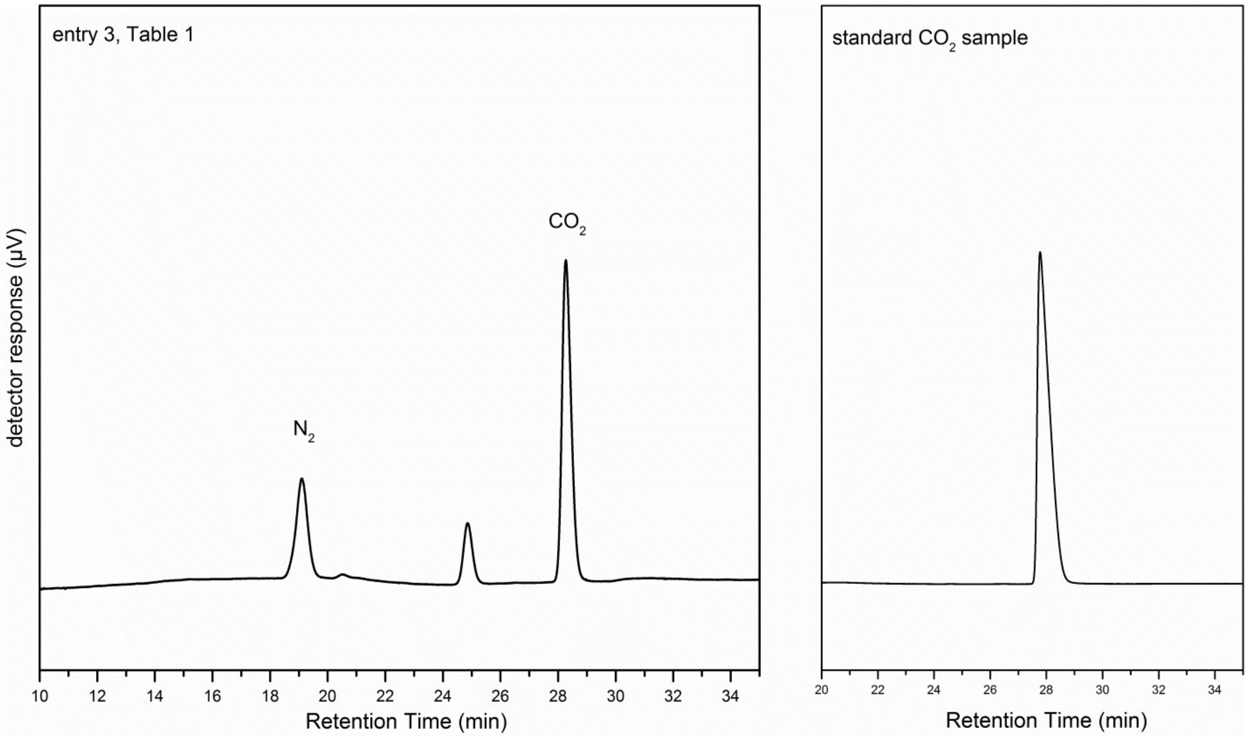


Figure S-9. GC-TCD analysis of a typical reaction in the co-catalyst system (entry 3, Table 1). The gas phase products were collected after reaction (left). A standard CO_2 sample was obtained and analyzed for peak assignment by its retention time at 28.2 to 28. 5 min (right). Reaction condition: DHE 0.2 mL, Ru/C 100 mg, Nb_2O_5 200 mg, H_2O 12 mL, methanol 0.8 mL, $P(H_2)$ = 1 bar, 250 ℃, 12 h. CO_2 gas was detected as the main product in gas phase after the HDO reaction. It was evident that catalytic reforming of methanol occurs in this co-catalyst system.

References

1. Özer, N.; Rubin, M. D.; Lampert, C. M., Optical and electrochemical characteristics of niobium oxide films prepared by sol-gel process and magnetron sputtering A comparison. *Solar Energy Materials and Solar Cells* **1996,** *40* (4), 285-296.

2. Chan, X. J.; Pu, T. C.; Chen, X. Y.; James, A.; Lee, J.; Parise, J. B.; Kim, D. H.; Kim, T., Effect of niobium oxide phase on the furfuryl alcohol dehydration. *Catal Commun* **2017,** *97*, 65-69.