Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Dehydra-decyclization of Tetrahydrofurans to Diene Monomers over Metal Oxides

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Total Supp. Pages: 7 **Total Supp. Figures: 6** **Total Supp. Tables: 2**

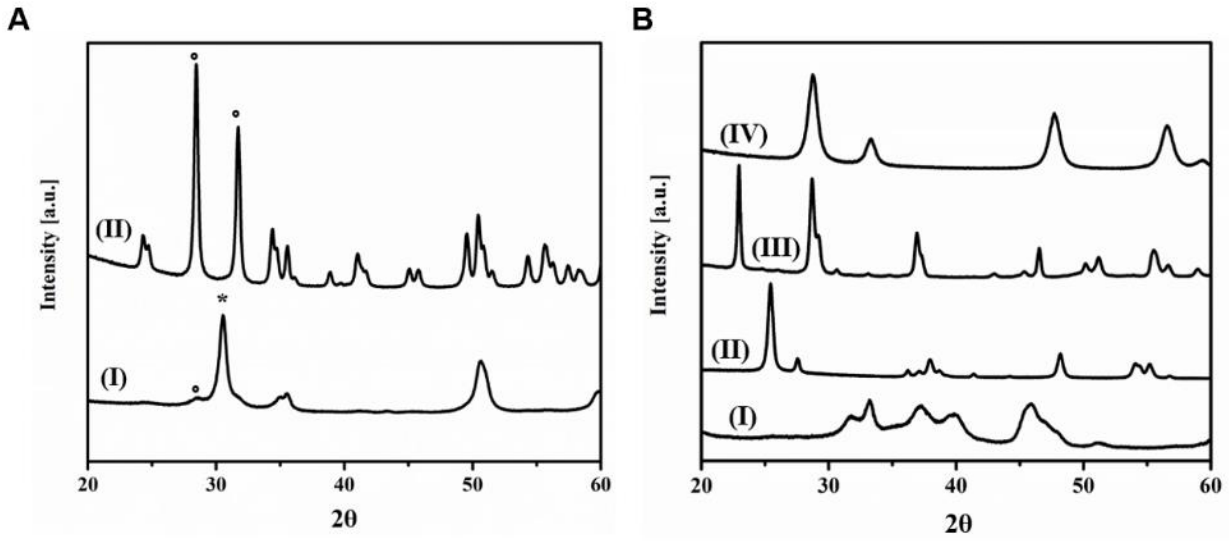

Figure SI. XRD patterns of A. ZrO_2, peaks marked with (*) stand for tetragonal zirconia and peaks marked with (°) stand for monoclinic zirconia **B.** (I) Al_2O_3 (II) TiO_2 (III) Nb_2O_5 (IV) CeO_2.

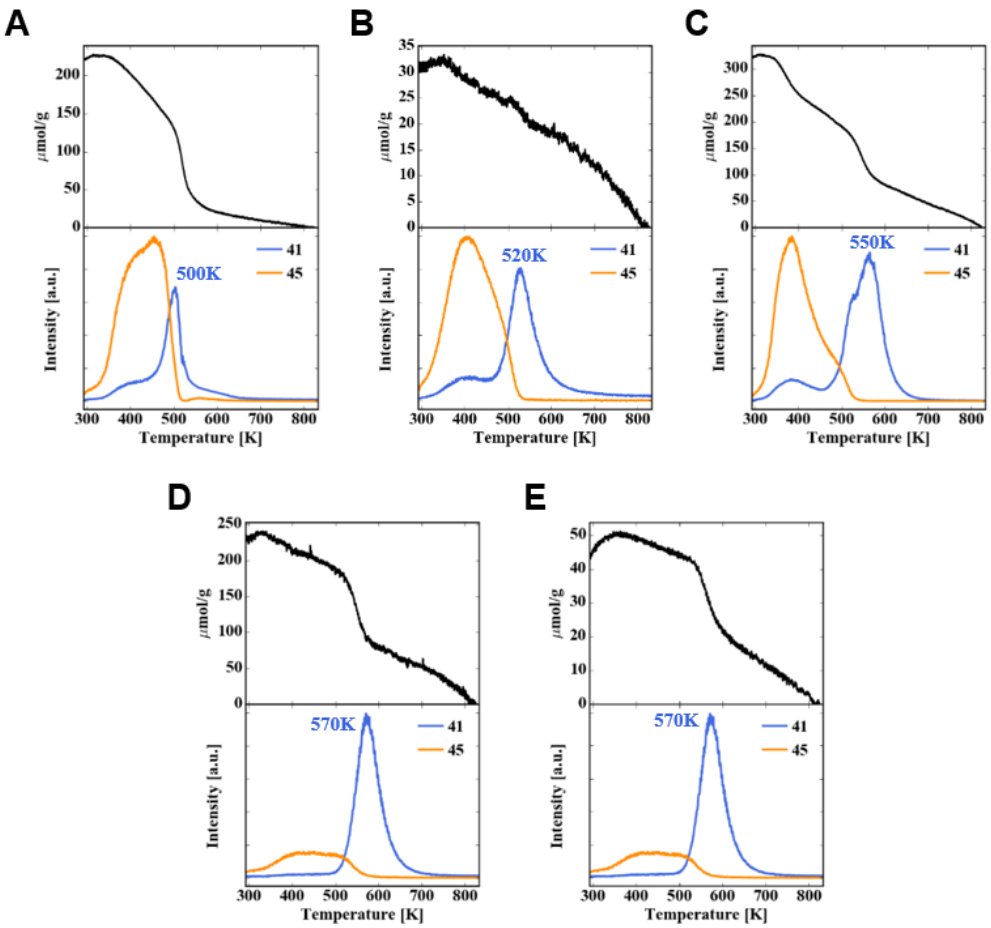

Figure SII. Temperature Programmed Desorption - Thermogravimetric Analysis of isopropanol on A. TiO_2 **B.** Nb_2O_5 **C.** CeO_2 **D.** t-ZrO_2 **E.** m-ZrO_2. The TPD peaks correspond to isopropanol (m/e = 45), propene (m/e = 41). Isopropanol dehydration on Al_2O_3 has been previously demonstrated in our lab[1].

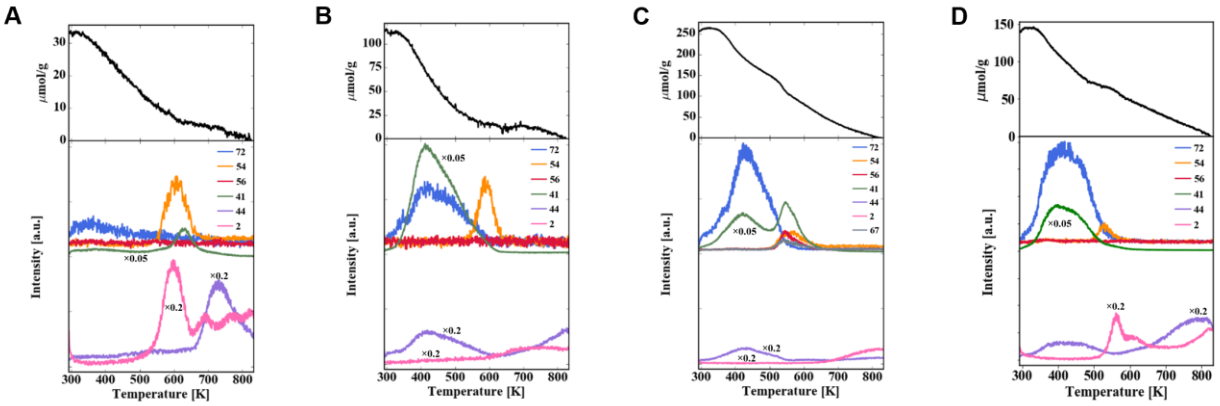

Figure SIII. Temperature Programmed Desorption - Thermogravimetric Analysis of THF on A. m-ZrO_2 **B.** Nb_2O_5 **C.** Al_2O_3 **D.** CeO_2. The TPD peaks correspond to THF (m/e = 72,41), butadiene (m/e = 54), butene (m/e = 56), propene (m/e = 41), CO_2 (m/e = 44), H_2 (m/e = 2), oligomer cracking species (m/e = 41, 54, 56, 67).

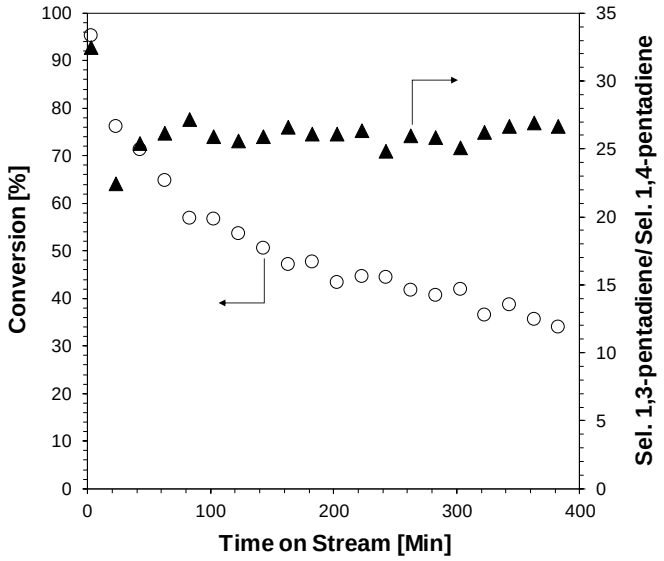

Figure SIV. Selectivity ratio of 1,3-pentadiene to 1,4-pentadiene on t-ZrO_2 with time on stream at 673 K and $P_{2\text{-MTHF}}$ = 10 Torr.

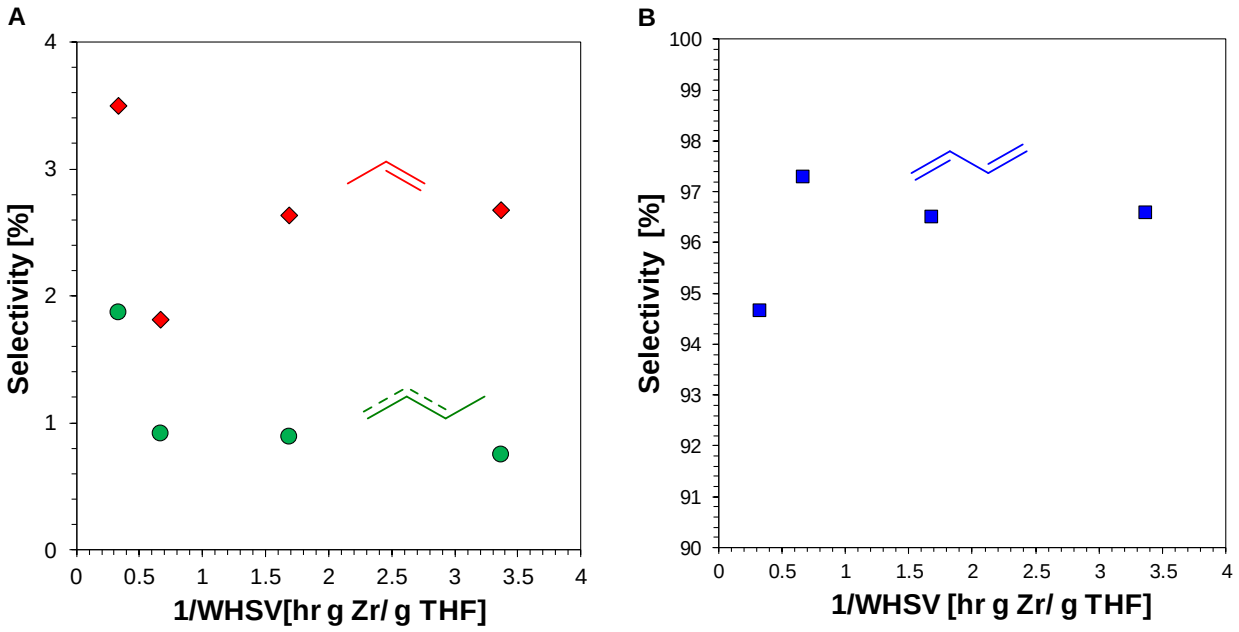

Figure SV. Contact time study of THF Dehydra-decyclization over tetragonal ZrO_2 at 673 K and P_{THF} = 10 Torr. A. Selectivity to propene and butene(s) **B.** Selectivity to butadiene.

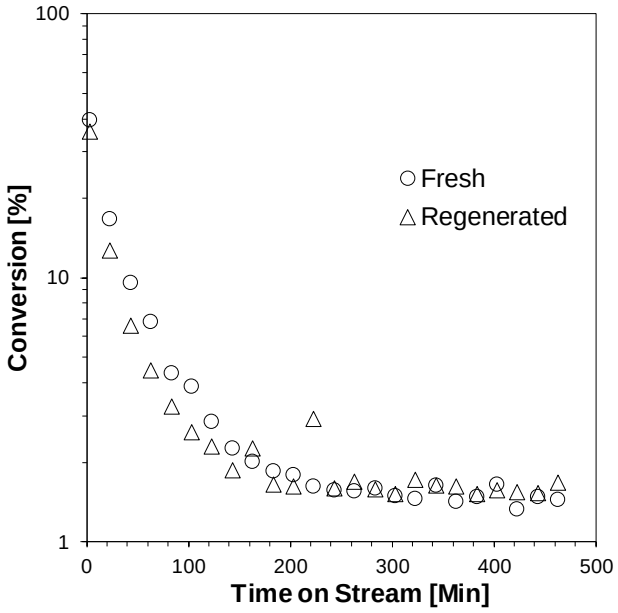

Figure SVI. Dehydra-decyclization of THF on monoclinic ZrO_2 at 673 K and P_{THF} = 10 Torr. Regenerated catalyst calcined in air at 673 K.

Table SI. Successive measurements of selectivity to butadiene as a function of temperature on metal oxides. P_{THF} = 38 Torr, WHSV = 0.93 g THF g-cat^{-1} hr^{-1}.

Temperature (K)	H-ZSM-5	5R WO_x/ZrO_2	CeO_2	Nb_2O_5	TiO_2	Al_2O_3
423	0% 0% 0%					
473	11% 16% 16%					
523	33% 37%	38% 32%				
573	21% 19%	42% 41%	0% 0%		65% 63%	14% 11%
623	19% 19%	44% 48%	36% 40%	19% 19%	43% 45%	9% 9%
673	14% 14%	39% 38%	64% 65%	46% 41%	37% 41%	9% 9%
723			43% 44%	43% 38%	33% 37%	10% 11%
773				39% 39%		

Table SII. Peak desorption temperatures for propene from isopropanol dehydration on metal oxides.

Catalyst	Propene desorption peak temperature (K)
Al_2O_3	440*
TiO_2	500
Nb_2O_5	520
CeO_2	550
t-ZrO_2	570
m-ZrO_2	570

*Isopropanol dehydration on Al_2O_3 has been previously demonstrated in our lab[1].

References:

1. Srinivasan, S. T.; Narayanan, C. R.; Biaglow, A. I.; Gorte, R. J.; Datye, A. K., The role of sodium and structure on the catalytic behavior of alumina: I. Isopropanol dehydration activity. *Applied Catalysis A: General* **1995,** *132* (2), 271-287.