Electronic Supplementary Information

Propane metathesis and hydrogenolysis over titanium hydride catalysts

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1. Details of gas composition and analysis of catalytic reaction

Table S1. Detailed gas composition and calculated conversion, selectivity, and yield values for propane metathesis and hydrogenolysis reaction over metal hydrides.[a]

Sample	Gas composition [%]							C_3H_8 conversion[c] / %	Metathesis Selectivity[d] / %	Butane yield (Y_{C4H10})[c] / %
	CH_4	C_2H_6	C_3H_8	C_4H_{10} *iso*	C_4H_{10} *n*	C_5H_{12}	C_6H_{14}			
TiH_2	13.6	13.6	71.2	0.8	0.8	0.1	<0.1	28.8	10.4	3.0
ZrH_2	19.4	17.8	62.2	0.3	0.3	n.a.[b]	n.a.[b]	37.8	3.4	1.3
HfH_2	17.6	16.5	65.6	0.1	0.2	n.a.[b]	n.a.[b]	34.4	2.0	0.7
MgH_2	1.3	1.0	97.7	<0.1	<0.1	n.a.[b]	n.a.[b]	2.3	5.0	0.1
CaH_2	1.6	1.5	96.8	0.1	<0.1	n.a.[b]	n.a.[b]	3.2	6.0	0.2
ScH_2	28.5	26.5	44.8	0.1	0.1	n.a.[b]	n.a.[b]	55.2	0.6	0.3
YH_3	9.9	8.2	81.7	0.1	0.1	n.a.[b]	n.a.[b]	18.3	2.7	0.5
LaH_3	4.8	2.0	93.1	<0.1	<0.1	n.a.[b]	n.a.[b]	6.9	1.0	0.1
V_2H	25.2	21.9	52.6	0.2	0.1	n.a.[b]	n.a.[b]	47.4	1.2	0.6

[a]Reaction conditions: 50 mg of catalyst, 1 atm of C_3H_8, 300 ˚C, 24 h. The ball-milled TiH_2 was prepared using a Fritsch P-6 planetary ball mill, and then used for the reactions without exposure to air. [b]Not available. [c]The conversion and yield were calculated based on the gas composition after the reaction using FID-GC. For the details, see Supporting Information. [d]The selectivity for propane metathesis was estimated based on the yield of methane (as hydrogenolysis product) and *iso*/*n*-butane (as main metathesis products).

The compositions (C_n: *n* denotes the kind of gas) of methane ethane, ethylene, propane, propylene, *iso*-/*n*-butane, butene, pentanes, and hexanes were determined on the basis of effective carbon numbers and GC areas. Note that the detailed structures of pentanes and hexanes were not analyzed. The propane conversion, product selectivity, yields of butane (Y_{C4H10}) and methane (Y_{CH4}), were calculated from the gas compositions by the following equations. Coke formation was negligible as indicated by TPO of the used TiH_2 catalyst.

$$C_3H_8\,conversion\ = 1 - C_{C3H8}$$

$$Product\ selectivity\ = \frac{C_n}{(C_{CH4} + C_{C2H6} + C_{iso-C4H10} + C_{n-C4H10} + C_{C5H12} + C_{C6H14})}$$

$$Y_{C4H10} = (1 - C_{C3H8}) \times \frac{C_{iso-C4H10} + C_{n-C4H10}}{(C_{CH4} + C_{C2H6} + C_{iso-C4H10} + C_{n-C4H10} + C_{C5H12} + C_{C6H14})}$$

$$Y_{CH4} = (1 - C_{C3H8}) \times \frac{C_{CH4}}{(C_{CH4} + C_{C2H6} + C_{iso-C4H10} + C_{n-C4H10} + C_{C5H12} + C_{C6H14})}$$

$$Metathesis\ selectivity\ = \frac{Y_{C4H10}}{Y_{C4H10} + Y_{CH4}}$$

The total formation amount of butane was determined by the volume of autoclave, the compositions of *iso*-/*n*-butane, and the amount of catalyst.

2. Figures

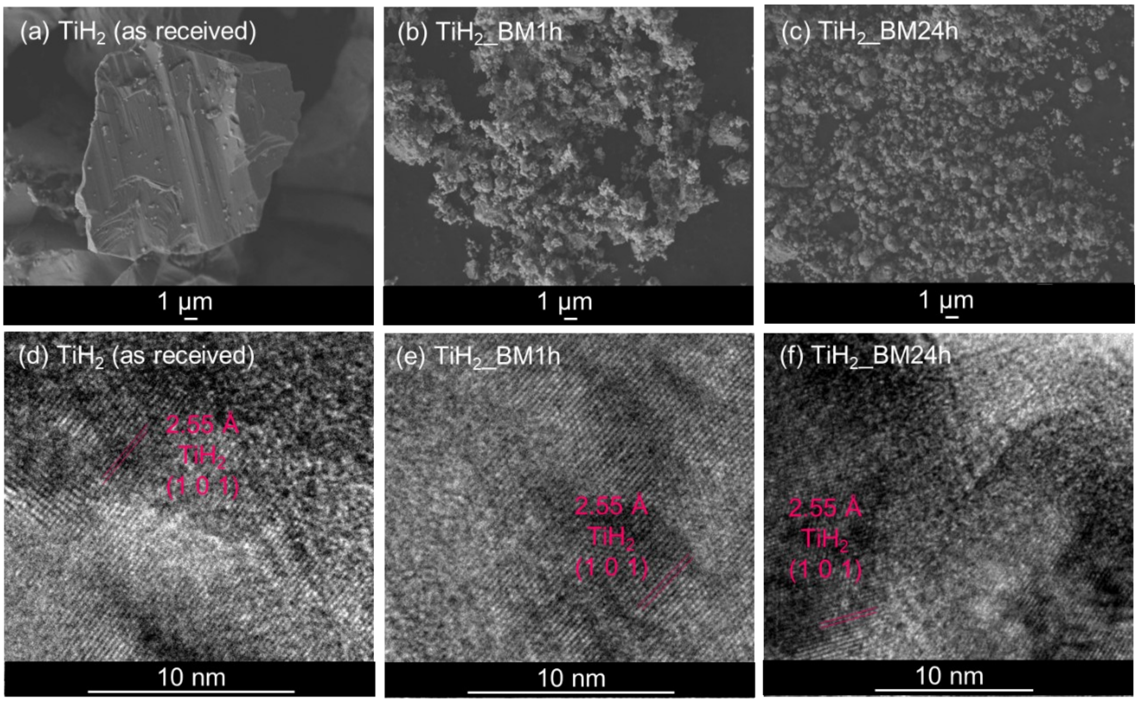

Fig. S1 (a-c) SEM and (d-f) TEM image of a series of TiH_2. (a and d) TiH_2 (as received), (b and e) TiH_2_BM1h, and (c and f) TiH_2_BM24h.

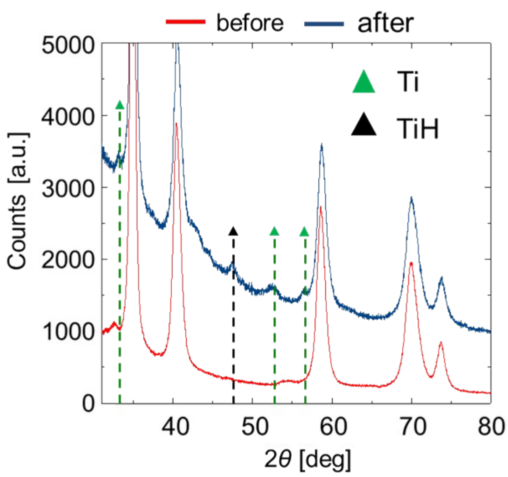

Fig S2. Comparison of XRD pattern of TiH_2_BM1h before and after the reaction with propane at 300 °C for 24 h.

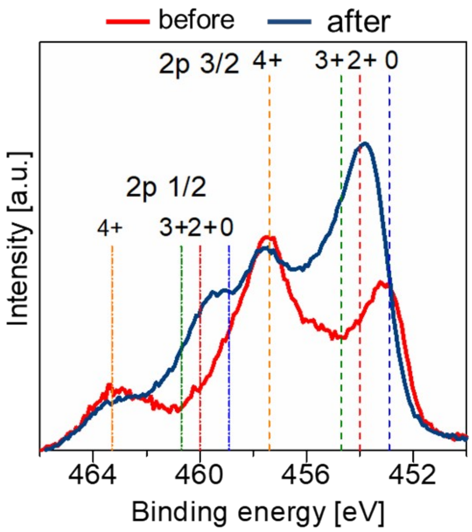

Fig S3. Comparison of XPS spectra for Ti 2p region of TiH_2_BM1h before and after the reaction with propane at 300 °C for 24 h.

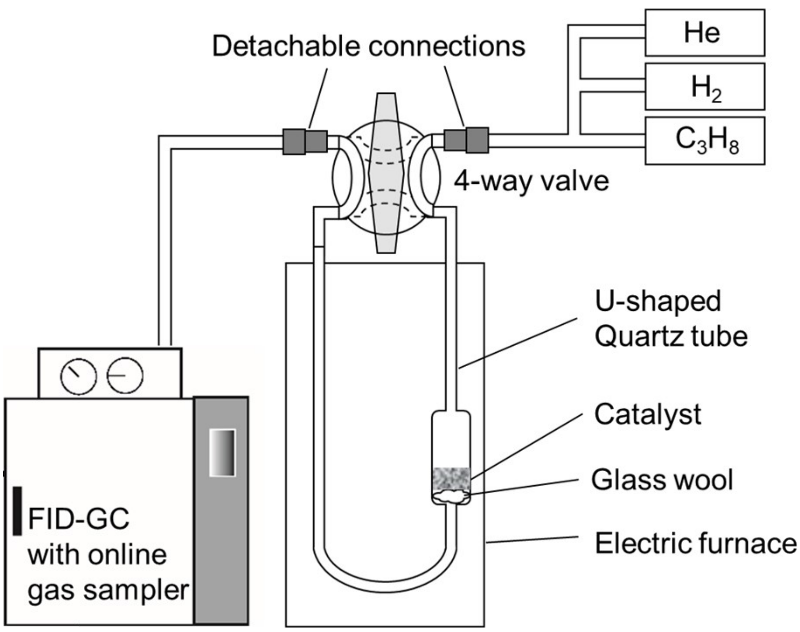

Fig S4. Schematic view of flow-type reactor for propane metathesis and hydrogenolysis reactions using metal hydrides