

Supporting information

Acidic nanomaterials (TiO_2 , ZrO_2 , and Al_2O_3) are coke storage components that reduce deactivation of Pt-Sn/ γ - Al_2O_3 catalyst in propane dehydrogenation

Adisak Guntida ^a, Sippakorn Wannakao ^b, Piyasan Praserthdam ^{a,*} and Joongjai Panpranot ^a

^a Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b SCG Chemicals, Co., Ltd., 1 Siam Cement Road, Bangsue, Bangkok 10800, Thailand

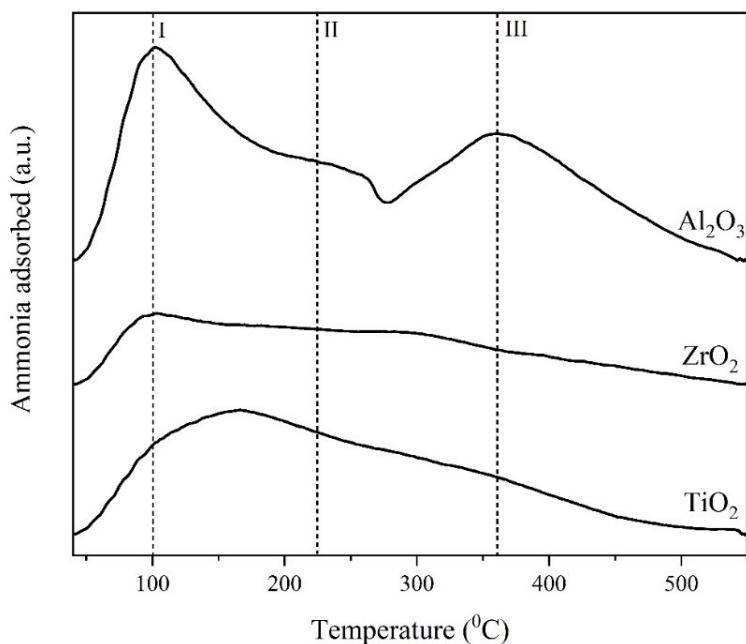


Fig. S1 NH₃-TPD profiles of acidic nanomaterials.

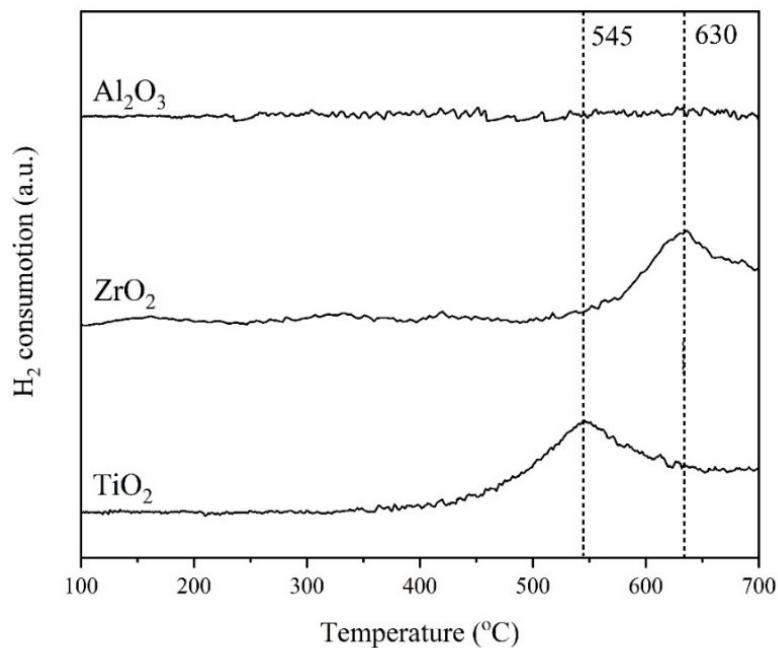


Fig. S2 H_2 -TPR profiles of acidic nanomaterials.

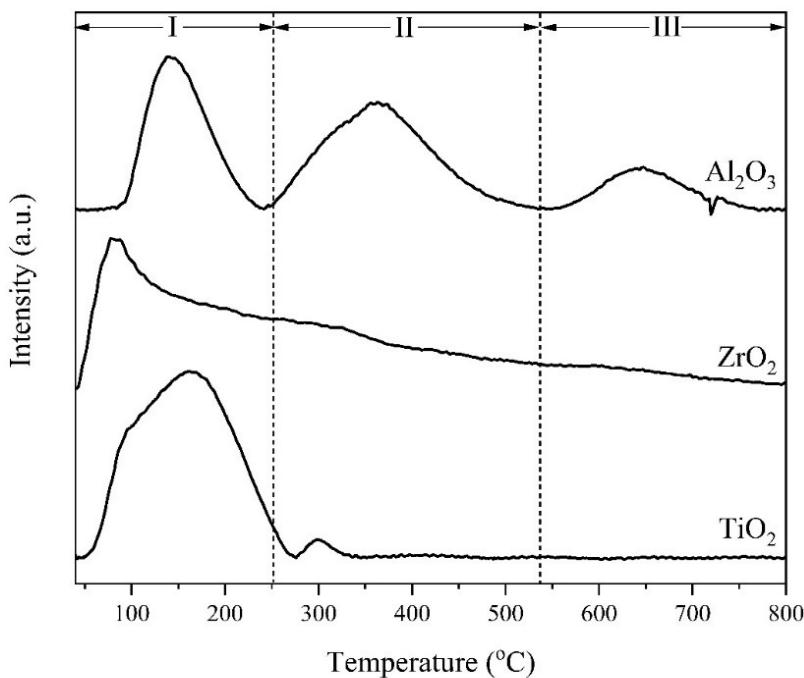


Fig. S3 O_2 -TPD profiles of acidic nanomaterials.

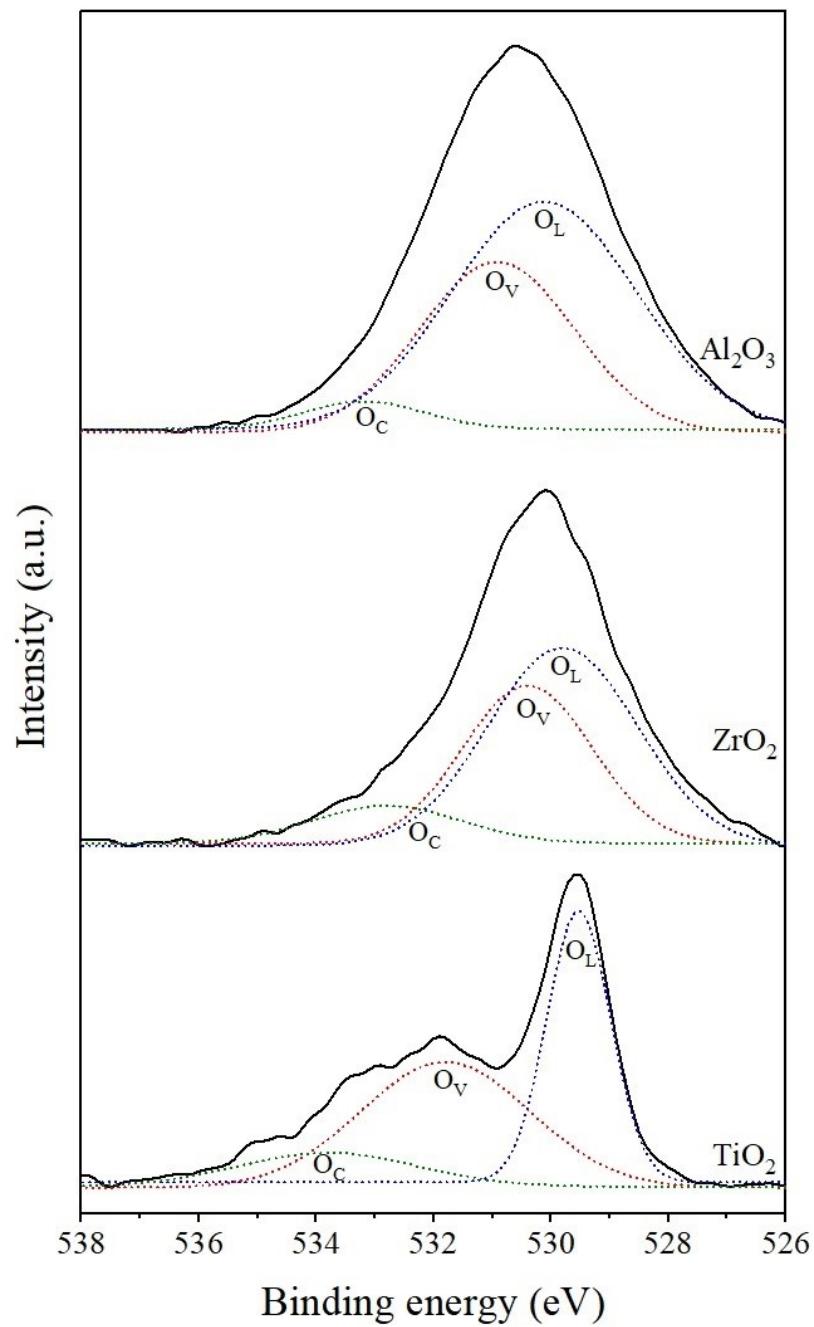


Fig. S4 O1 s peak in the XPS spectrum of acidic nanomaterials.

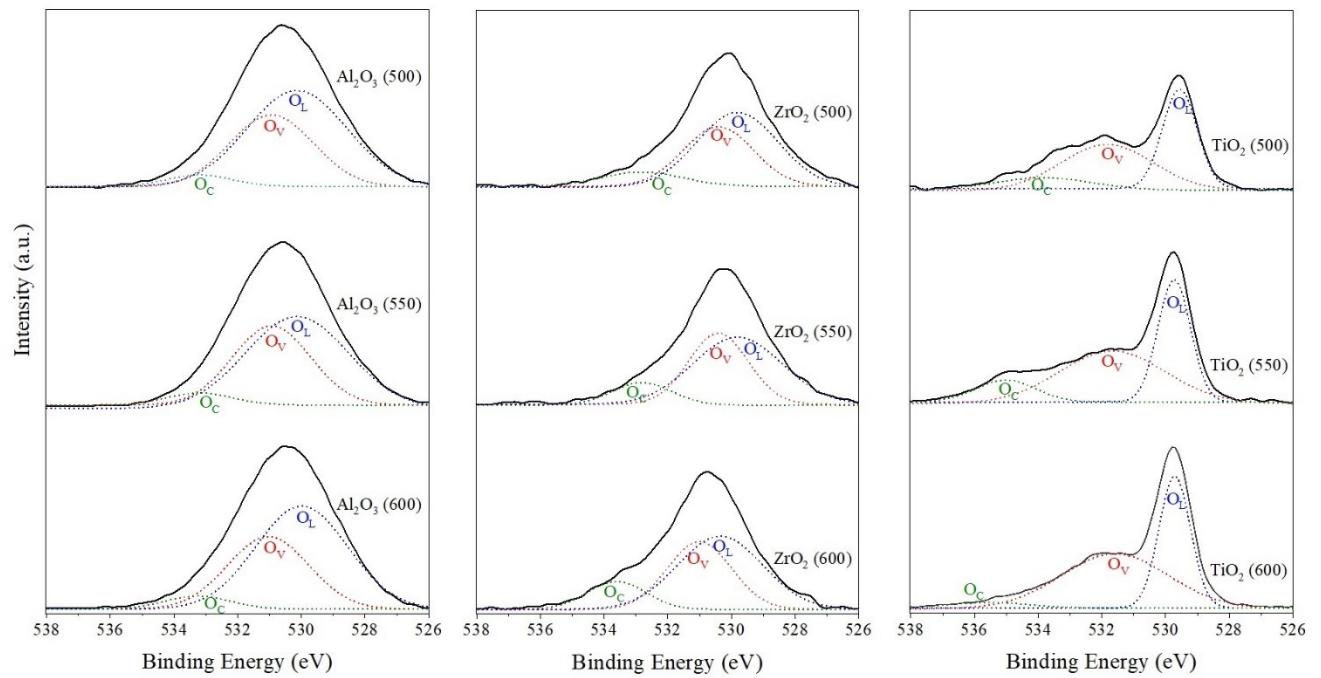


Fig. S5 O1s peak in the XPS spectrum of acidic nanomaterials with different temperature of pretreatment.

Table S1 Summarized conversion and products selectivity during propane dehydrogenation

Initial at 0 h

Catalysts	Conversion (%)	Selectivity (%)					
		C ₁	C ₂	C ₂ [±]	C ₃ [±]	C ₄	C ₄ [±]
inert	0.2	6.8	16.1	11.5	40.9	24.8	0.0
Al ₂ O ₃	0.8	23.1	0.8	35.5	38.5	0.0	2.1
ZrO ₂	1.0	13.9	0.4	16.1	69.7	0.0	0.0
TiO ₂	7.2	2.4	1.2	2.2	93.7	0.1	0.5
Pt-Sn/ γ -Al ₂ O ₃ + inert	26.2	3.4	4.8	0.4	82.9	3.0	4.5
Pt-Sn/ γ -Al ₂ O ₃ + Al ₂ O ₃	27.7	4.3	5.6	0.4	80.5	3.5	4.9
Pt-Sn/ γ -Al ₂ O ₃ + ZrO ₂	30.3	7.0	8.2	0.5	77.8	2.6	3.2
Pt-Sn/ γ -Al ₂ O ₃ + TiO ₂	27.7	6.0	7.1	0.4	75.8	3.0	3.5
							4.2

Final at 5.1 h

Catalysts	Conversion (%)	Selectivity (%)					
		C ₁	C ₂	C ₂ [±]	C ₃ [±]	C ₄	C ₄ [±]
inert	0.3	8.8	10.8	16.4	48.0	16.1	0.0
Al ₂ O ₃	1.1	17.7	0.7	28.8	51.8	0.0	1.0
ZrO ₂	2.7	5.5	0.5	7.2	86.9	0.0	0.0
TiO ₂	2.3	5.5	1.2	8.6	84.7	0.0	0.0
Pt-Sn/ γ -Al ₂ O ₃ + inert	12.2	2.7	1.9	2.0	89.4	0.2	2.7
Pt-Sn/ γ -Al ₂ O ₃ + Al ₂ O ₃	12.5	3.2	1.9	2.3	90.2	0.1	2.0
Pt-Sn/ γ -Al ₂ O ₃ + ZrO ₂	24.1	1.8	2.1	0.5	91.8	0.5	2.0
Pt-Sn/ γ -Al ₂ O ₃ + TiO ₂	19.3	2.1	2.1	0.1	90.6	0.3	2.6
							1.3

Table S2 Textural properties of acidic nanomaterials

Nanomaterials	BET surface area (m ² · g ⁻¹)	Pore size (nm)	Pore volume (cm ³ · g ⁻¹)
Al ₂ O ₃	123.5	12.7	0.54
ZrO ₂	27.1	18.9	0.14
TiO ₂	37.3	26.0	0.30

Table S3 Amount of acidity of nanomaterials

Nanomaterials	Amount of acidity ($\mu\text{mol NH}_3 \cdot \text{g cat}^{-1}$)			
	Weak	Medium	Strong	Total
Al_2O_3	864	1152	1283	3298
ZrO_2	130	181	834	1149
TiO_2	175	1099	916	2191

Table S4 CO-chemisorption of the Pt-Sn/ γ - Al_2O_3 catalyst with acidic nanomaterials

Catalysts	Amount of CO adsorbed ($\mu\text{mol CO} \cdot \text{g cat}^{-1}$)	Pt dispersion (%)
Pt-Sn/ γ - Al_2O_3 + inert	12.3	80.0
Pt-Sn/ γ - Al_2O_3 + Al_2O_3	13.2	85.8
Pt-Sn/ γ - Al_2O_3 + ZrO_2	14.2	92.3
Pt-Sn/ γ - Al_2O_3 + TiO_2	15.0	97.5

Table S5 O_2 -TPD results of acidic nanomaterials

Nanomaterials	O_2 -TPD peaks position ($^{\circ}\text{C}$)	O_2 desorption ($\text{mmol O}_2 \cdot \text{g cat}^{-1}$)
Al_2O_3	146	0.44 (O_v)
	368	0.48
	654	0.13
ZrO_2	87	0.56 (O_v)
	267	0.43
	529	0.30
TiO_2	165	0.93 (O_v)
	307	0.02

Table S6 XPS results of acidic nanomaterials

Nanomaterials	O_v/O_L
Al_2O_3	0.63
ZrO_2	0.69
TiO_2	1.23

Table S7 Adsorption energy of propylene and propadiene on acidic nanomaterials by *in-situ* DSC

Nanomaterials	Propylene (J. g cat ⁻¹)	Propadiene (J. g cat ⁻¹)
Al ₂ O ₃	1.03	5.07
ZrO ₂	1.27	5.33
TiO ₂	1.46	6.50

Table S8 The summarized coke forms during the *in situ* DRIFT study of propadiene at different temperature

Nanomaterials	Temp. (°C)	Area of coke forms			Differentiation ^a		
		C=C	Aliphatics	Aromatics	C=C	Aliphatics	Aromatics
TiO ₂	40	1.22	0.036	0.01	1.00	0.00	0.00
	100	1.02	0.048	0.03	0.84	1.33	3.00
	200	0.32	0.02	0.31	0.26	0.56	31.00
	300	0.07	0.011	4.67	0.06	0.31	467.00
ZrO ₂	40	3.49	0.12	0.08	1.00	0.00	0.00
	100	3.47	0.17	0.11	0.99	1.42	1.38
	200	0.76	0.16	1.56	0.22	1.33	19.50
	300	0.05	0.08	8.5	0.01	0.67	106.25
Al ₂ O ₃	40	3.51	0.009	1.47	1.00	0.00	0.00
	100	1.97	0.016	2.27	0.56	1.78	1.54
	200	1.73	0.062	2.43	0.49	6.89	1.65
	300	1.46	0.152	1.81	0.42	16.89	1.23

^a At 40 °C, there is no differentiation (initial = 1.00).

At elevated temperature, differentiation = area _i at that temperature / area _i at 40 °C

Table S9 The summarized coke deposition and oxygen vacancies of different pretreated acidic nanomaterials

Nanomaterials	O _V /O _L	Coke deposition on nanomaterials (%)
Al ₂ O ₃ 500 °C	0.63	N/A
Al ₂ O ₃ 550 °C	0.64	N/A
Al ₂ O ₃ 600 °C	0.64	N/A
ZrO ₂ 500 °C	0.69	2.5
ZrO ₂ 550 °C	0.71	2.5
ZrO ₂ 600 °C	0.70	2.5
TiO ₂ 500 °C	1.23	3.1
TiO ₂ 550 °C	1.39	3.5
TiO ₂ 600 °C	1.41	3.7