Supporting Information

Dehydrogenation of Isobutane over Ni-P/SiO_2 Catalyst: Effect of P Addition

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Contents

Ni-S/SiO_2 catalyst.

The principle and method of carbometer

1HW(T) HF infrared absorption C/S instrument was applied to measure coke amount. The principle and method are described as follows. The procedure consists of coke combustion, gas purification, quantitative analysis of generated CO_2, and determination of coke amount. $CaCO_3$ is used as a reference sample as it can be decomposed to CaO and CO_2 at high temperature. Fully dried $CaCO_3$ powders (50.0 mg) were loaded in a crucible, and the temperature was rapidly raised to 950 ºC in order to ensure the complete decomposition of $CaCO_3$. The signal of formed CO_2 (22.0 mg) was detected by infrared detector at the same time. The corresponding area of this signal is labeled as S. About 250 mg catalyst (m mg, accurately weighed) was put in another crucible, and it was heated to 950 ºC under O_2 flow. The signal area of generated CO_2 was S_C. The percentage of coke ($\mathbf{w_C}$) in the catalyst can be calculated by the following formula.

$$w_C = \frac{22.0 \times S_C \times 12}{m \times S \times 44} \times 100 wt\% \quad (1)$$

The final coke amount of the catalyst was calculated by the average value for more than three tests.

Figures

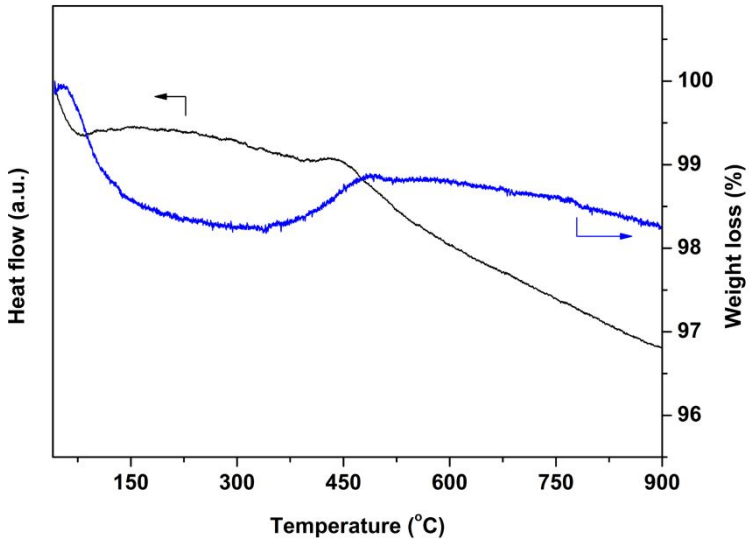

Figure S1. TG-DTA curves of deactivated 5Ni-P/SiO_2-1.0 catalyst.

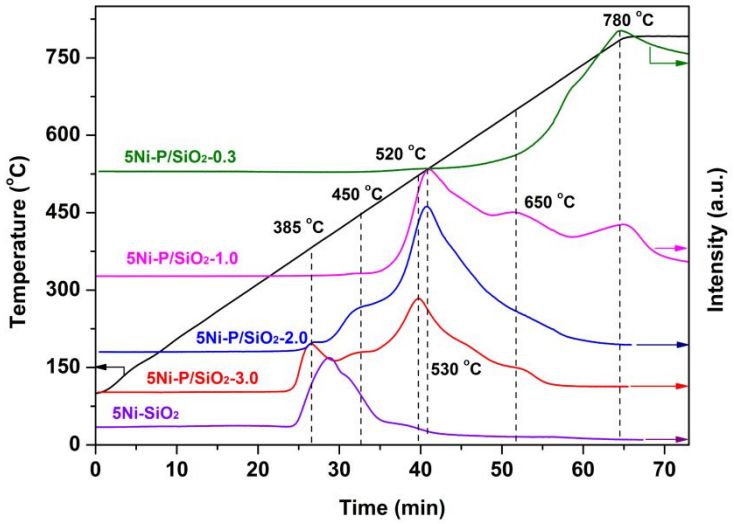

Figure S2. H_2-TPR profiles of the precursors of 5Ni-P/SiO_2-x catalyst.

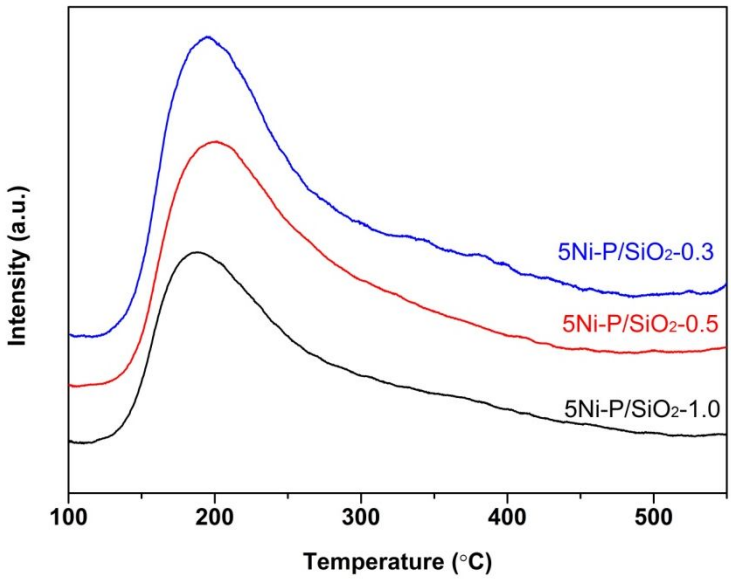

Figure S3. NH_3-TPD curves of 5Ni-P/SiO_2-1.0 catalyst.

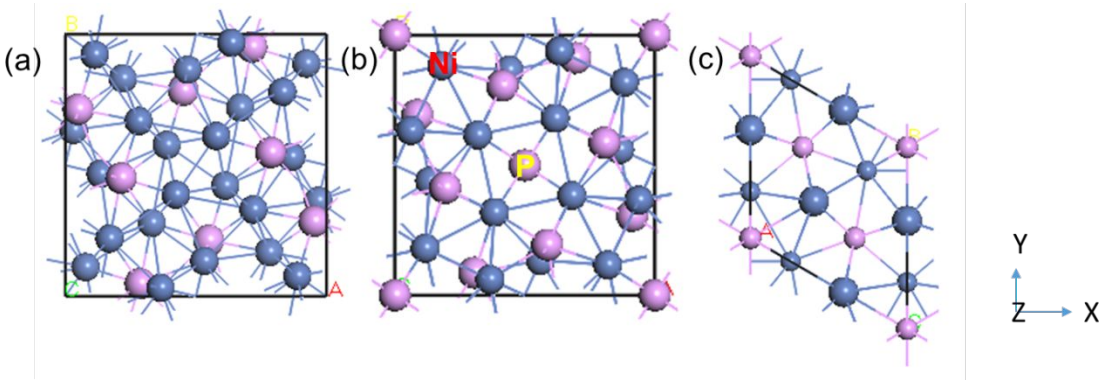

Figure S4. The geometry arrangements of Ni and P atoms in (a) Ni_3P, (b) $Ni_{12}P_5$, and (c) Ni_2P.

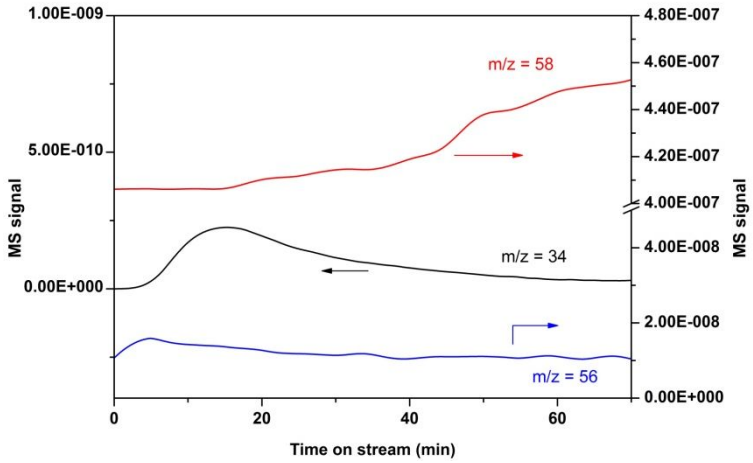

Figure S5. Real time MS spectra of isobutane dehydrogenation over 5Ni-P/SiO_2-1.0 catalyst with time on stream (Reaction conditions: mass of catalyst: 1.0 g; gas flow: 20 mL min^{-1}; isobutane partial pressure: 20 kPa; temperature: 600 ºC).

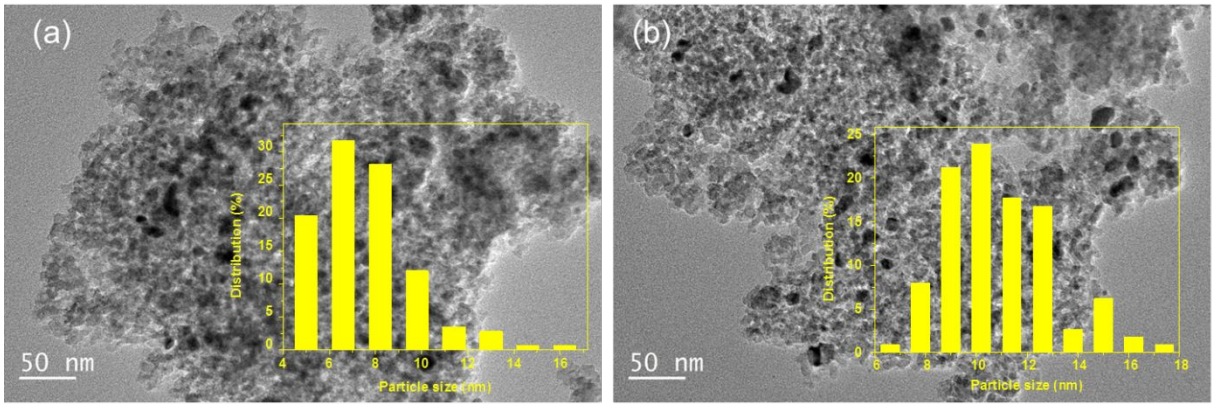

Figure S6. TEM images of fresh (a) and deactivated (b) 5Ni-P/SiO_2-1.0 catalysts

Tables

Table S1 Quantitative results of NH_3-TPD profiles of 5Ni-P/SiO_2-a (a = 1.0, 0.5 and 0.3) catalysts

Catalyst	Total acid sites (mmol g_{cat}^{-1})	Peak temperature (ºC)
5Ni-P/SiO_2-1.0	0.28	188
5Ni-P/SiO_2-0.5	0.41	197
5Ni-P/SiO_2-0.3	0.48	198

Table S2 Reaction results of isobutane on SiO_2 at different temperature.

		Temperature (ºC)			
		560	580	600	620
Conversion (%)		0.7	2.8	6.0	9.6
Selectivity(%)	methane	7.6	15.0	14.8	20.1
	ethane	1.6	0.8	0.3	0.3
	ethene	0.7	0.5	1.0	1.9
	propane	27.5	9.8	3.6	2.7
	propene	19.1	32.2	33.8	37.7
	isobutene	43.6	41.8	46.5	37.3
	n-butenes	0.0	0.0	0.0	0.0
	1,3-butadiene	0.0	0.0	0.0	0.0

Reaction conditions: isobutane flow = 10 mL min^{-1}, mass of SiO_2 = 2.0 g.

Table S3 Gaseous product distribution of isobutane over $5Ni/SiO_2$ catalyst under different GHSV.

		GHSV (h^{-1})	
		150	1200
Conversion (%)		100	20.3
Selectivity (%)	methane	100	98.3
	ethane	0.0	0.3
	ethene	0.0	0.0
	propane	0.0	0.6
	propene	0.0	0.0
	isobutene	0.0	0.9
	n-butenes	0.0	0.0
	1,3-butadiene	0.0	0.0

Reaction conditions: mass of catalyst = 2.0 g, temperature = 600 ºC.

Table S4 Reaction results of isobutane over P/SiO_2 catalyst.

		P/SiO_2
Conversion (%)		6.3
Selectivity(%)	methane	9.2
	ethane	0.3
	ethene	0.7
	propane	3.9
	propene	24.9
	isobutene	55.3
	n-butenes	5.4
	1,3-butadiene	0.2

Reaction conditions: temperature = 600 ºC, mass of catalyst = 2.0 g, GHSV = 150 h^{-1}

Table S5 Reaction results of isobutene passing through 5Ni-P/SiO_2-1.0 catalyst at different temperature.

		Temperature (ºC)		
		560	580	600
Conversion (%)		19.0	21.8	25.2
Percent(%)	C6+	0.1	0.1	0.2
	methane	1.7	2.4	3.2
	ethane	0.2	0.2	0.3
	ethene	0.7	0.8	1.1
	propane	0.1	0.2	0.2
	propene	3.6	4.6	5.7
	isobutane	3.2	3.7	4.4
	n-butane	3.2	3.7	4.4
	n-butenes	0.1	0.1	0.1
	isobutene	81.0	78.2	74.8
	1,3-butadiene	5.5	5.4	5.0
	C5	0.5	0.5	0.6

Reaction conditions: mass of catalyst = 2.0 g, GHSV = 150 h^{-1}.

Table S6 Reaction results of isobutene passing through 5Ni-P/SiO_2-1.0 catalyst under different GHSV.

		GHSV (h^{-1})			
		90	120	150	180
Conversion (%)		37.5	29.3	25.2	20.9
Percent (%)	C6+	0.2	0.1	0.2	0.2
	methane	5.8	4.0	3.2	2.7
	ethane	0.7	0.4	0.3	0.2
	ethene	1.7	1.2	1.1	0.8
	propane	0.7	0.4	0.2	0.1
	propene	8.6	6.4	5.7	4.8
	isobutane	5.8	5.0	4.4	3.6
	n-butane	5.8	5.0	4.4	3.6
	isobutene	0.8	0.3	0.1	0.1
	n-butenes	62.5	70.7	74.8	79.1
	1,3-butadiene	6.6	5.9	5.0	4.2
	C5	0.8	0.6	0.6	0.5

Reaction conditions: Temperature = 600 ºC, mass of catalyst = 2.0 g.

Table S7 Assignment of the infrared spectrum of gaseous isobutane.

Assignment	Wavenumber (cm^{-1})
$\nu_a(CH_3)$	2978, 2966, 2952
$\nu_s(CH_3)$	2879, 2870
$\nu_{(C-H)}$(methylidyne)	2892
$\delta_{as}(CH_3)$	1490, 1477, 1464
$\delta_{sy}(CH_3)$	1395, 1380, 1365
$\delta_{(C-H)}$(methylidyne)	1334
$\nu_{(C-C)}$	1177

Table S8 Assignment of the infrared spectrum of gaseous isobutene.

Assignment	Wavenumber (cm^{-1})
$\nu_{asym(C-H)}(=CH_2)$	3097, 3087, 3077
$\nu_{(C-H)}(-CH_3)$	2990, 2979, 2968, 2944, 2927, 2893, 2865
ν(C=C)	1660
$\delta_{(C-H)}(-CH_3)$	1469, 1459, 1446, 1393, 1380, 1373
$=CH_2$ in plane bend	1291, 1281, 1271
ν(C-C)	1067, 1054
$=CH_2$ twist	990

Table S9 Pore properties of fresh and deactivated (after 120 min reaction) 5Ni-P/SiO_2-1.0 catalyst.

Catalyst	BET surface area ($m^2\ g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3\ g^{-1}$)
Fresh 5Ni-P/SiO_2-1.0	265.5	7.1	0.7
Deactivated 5Ni-P/SiO_2-1.0	263.7	7.5	0.7

Table S10 The conversion of isobutane and selectivity to isobutene over 5Ni-P/SiO_2, 5Ni-Sn/SiO_2 and Ni-S/SiO_2 catalyst.

Catalyst	Isobutane conversion (%)	Isobutene selectivity (%)
Ni-S/SiO_2[a]	67.0	87.6
5Ni-P/SiO_2[b]	11.6	86.2
5Ni-Sn/SiO_2[b]	10.1	94.2

Reaction conditions: [a] mass of catalyst: 4.0 g; 14.3 vol % isobutane in N_2 at a total flow rate of 14 mL min^{-1}; [b] mass of catalyst: 2.0 g, isobutane flow rate of 10 mL min^{-1} without N_2.