Supporting Information

Microstructured Au/Ni-fiber Catalyst for Low-temperature Gas-phase Selective

Oxidation of Alcohols

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Materials and Methods

Catalyst preparation

Sinter-locked three-dimensional microfibrous networks consisting of 5 vol% 8- μ m Ni-fibers and 95 vol% void volume were built using regular papermaking/sintering processes [S1-S5]. Five grams of Ni-fiber chops (8 μ m diameter, 2-3 mm length; manufactured by Western Metal Material Co., Ltd., Xi'an, China) and 1.5 g of cellulose fibers were added to water (1 L) and vigorously stirred to produce a uniform suspension. The resulting suspension was transferred into the head box of a 159 mm diameter circular sheet former (ZCX-159A, Changchun, China), and a 159 mm circular preform was then formed by draining and drying in air. The preform paper was oxidized in air at 500 °C to remove the cellulosic binders and subsequently sintered in hydrogen at 950 °C to create the three-dimensional sinter-locked networks.

Gold was then galvanically deposited on this sinter-locked Ni-fiber by incipiently impregnating it with an aqueous solution containing the specified amount of HAuCl₄ at room temperature. The resulting samples were dried overnight at 80 $^{\circ}$ C and calcined in air at temperatures ranging from 100 to 300 $^{\circ}$ C for 2 h to obtain Au/Ni-fiber catalysts.

Characterization

The catalysts were characterized by X-ray diffraction (XRD; Rigaku Uitima IV diffractometer [Cu K α]), a scanning electron microscope (SEM, Hitachi S-4800), and a transmission electron microscope (TEM, JEOL-JEM-2010 instrument at 200 kV). X-ray photoelectron spectra (XPS) were recorded on a VG EscaLab 220i spectrometer using a standard Al K α X-ray source (300 W) and an analyzer pass energy of 20 eV. All binding energies were referenced to the adventitious C1s line at 284.9 eV. The catalysts were also studied using temperature programmed desorption (TPD) on a Quantachrome ChemBET 3000 chemisorption apparatus with a TCD and an online Mass Spectrometer (Proline Dycor, AMETEK Process Instrument). Gold-loading of the typical Au-4/Ni-fiber (4 wt%) sample was determined to be 3.8 wt% by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo Scientific iCAP 6300 ICP spectrometer.

Reactivity tests

The gas-phase selective oxidation of alcohols on these catalysts with molecular oxygen was performed on a fixed-bed quartz tube reactor (700 mm length by 16 mm inner diameter) under atmospheric pressure as described previously [S5,S6]. Circular chips (16.1 mm diameter) of the microfibrous-structured Au/Ni-fiber catalysts were punched down from their large sheet sample and packed layer-up-layer into the tube reactor. The catalyst used in testing experiments is 0.3 g,

corresponding to a bed thickness of 5 mm. Notice that the 0.1 mm larger diameter than the inner diameter of the tubular reactor was deliberately retained to avoid the appearance of a gap between the reactor wall and the edges of the catalyst chips, thereby preventing gas bypass. Alcohols were continuously fed using a high-performance liquid pump in parallel with O_2 (oxidant) and N_2 (diluted gas of 100 ml/min) feeding using calibrated mass flow controllers into the reactor heated to the desired reaction temperature. Weight hourly space velocity (WHSV) was calculated by dividing the mass flow rate of alcohol feedstock by the catalyst mass. The effluent was cooled using an ice-salt bath (-15 °C) to liquefy the condensable vapors for analysis using an HP 5890 gas chromatography-flame ionization detector (GC-FID) with a 60 m HP-5ms capillary column. The gas-phase products, such as H₂, CO_x, and C1-C3 hydrocarbons, were analyzed using an HP-5890 GC with thermal conductivity detector (TCD) and a 30 m AT-plot 300 capillary column.



Fig. S1. (a) SEM image of the three-dimensional microfibrous-structure of sinter-locked 8- μ m Ni-fiber (SMF-Ni); (b) Optical photographs of the large-area structure of neat SMF_{Ni}; (c) XRD patterns of the Au-4/Ni-fiber (gold loading of 4 wt%) just after undergoing Au galvanic deposition without drying show the metallic gold, indicating the occurrence of the HAuCl₄-Ni galvanic reaction; (d) Optical photographs of the fresh Au-4/Ni-fiber catalyst, a typical sample with 4 wt% Au loading after calcining at 300 °C in air for 2 h; (e) XRD patterns of the fresh Au-4/Ni-fiber catalyst, showing uniform coverage consisting of NiCl₂@Au composites formed along with the Ni-fiber.



Fig. S2. Schematic illustration of the Au galvanic-exchange reaction deposition procedure during the preparation of the fresh catalyst Au-4/Ni-fiber. After calcination at 300 $^{\circ}$ C, the active site precursor NiCl₂@Au composite was formed along with the Ni-fiber.



Fig. S3. The effects of the catalyst preparation conditions on the catalysts Au/Ni-fiber for the gas-phase selective oxidation of benzyl alcohol at 280 °C using O₂/ol ratio of 0.6 and WHSV of 20 h⁻¹. (a, c) Au loading; (b, d) Calcination temperature over the catalyst Au-4/Ni-fiber with the gold loading of 4 wt%. Fresh samples: as-prepared catalysts just after calcining; Pre-activated samples: the catalysts underwent 1 h reaction in gas-phase oxidation of benzyl alcohol at 380 °C with O₂/ol = 0.6 and WHSV = 20 h⁻¹, prior to the tests at low temperatures.



Fig. S4. Longer-term test using a reaction/regeneration cycle for the pre-activated Au-4/Ni-fiber catalyst in the gas-phase selective oxidation of benzyl alcohol. Reaction conditions: 250° C, O_2 /hydroxyl = 0.6, WHSV = 20 h^{-1} . Regeneration conditions: oxidation in air at 380° C for 1 h to burn off carbon deposits.

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Fig. S5. XRD pattern for the pre-activated Au-4/Ni-fiber catalyst showing the formation of NiO nanoparticles. The gold particle size was estimated from the Scherrer equation according to Au[111].



Fig. S6. XPS survey spectra for Au-4/Ni-fiber samples before and after pre-activation. Pre-activation: One hour reaction in benzyl alcohol oxidation at 380 °C using WHSV = 20 h⁻¹ and O₂/hydroxyl = 0.6.



Fig. S7. XRD patterns of the fresh Au-4/Ni-fiber catalyst before drying and calcining (*i.e.*, just after galvanic exchange reaction) with (a) and without (b) removing NiCl₂ by washing the samples for 5 times using deionized water. **Insert-a**: showing no NiCl₂ peak at $2\theta = 16^{\circ}$; **Insert-b**: showing the NiCl₂ peak at $2\theta = 16^{\circ}$).



Fig. S8. XRD patterns of the pre-activated Au-4/Ni-fiber catalyst: (a) The sample with the presence of NiO; (b) with the absence of NiO.



Fig. S9. (a) Reactivity evolution behavior of pre-activated Au-4/Ni-fiber catalyst for benzyl alcohol oxidation with and without the addition of O_2 . (b) O_2 -TPD profiles for (1) pre-activated Au-4/Ni-fiber after 1 h benzyl alcohol oxidation at 250 °C with O_2 and (2) sample 1 followed by another 15 min reaction after switching off O_2 .



Fig. S10. O₂-TPD profiles for (1) pre-activated Au-4/Ti-fiber and (2) pre-activated NiO@Au/Ti-fiber (NiO-doped Au-4/Ti-fiber, NiO loading of 4 wt%) after benzyl alcohol oxidation at 280 °C. Notice that the TPD peak intensity at 510 °C for sample 2 is ~80% of that for Au-4/Ni-fiber (normalized by weight of catalyst sample).



Fig. S11. O₂-TPD profile for (a) the pre-activated Au-4/Ni-fiber sample and (b) the Au-4@NiO/Ni-fiber sample after 1 h reaction in benzyl alcohol oxidation at 280 °C. Notice that the Ni-fiber support was pretreated in air at 600 °C for 2 h to form NiO/Ni-fiber prior to loading Au.

Substrate	Reaction Temp. (°C)	Conv. (%)	Select. (%)
Benzyl alcohol	280	99	99
Benzyl alcohol	230	85	99
1-phenylethanol ^b	300	99	98
2-phenylethanol ^b	340	49	99
1-octanol	300	57	90
2-octanol	340	26	65
Cyclohexanol	340	73	99
Cyclopropyl carbinol	280	92	97
1,2-propanediol ^b	340	99	66

Table S1. Gas-phase selective oxidation of several typical alcohols catalyzed by the pre-activated catalyst $Au-4/Ni-fiber^{a}$

^{*a*} The catalyst Au-4/Ni-fiber was pre-activated before the gas-phase oxidation of benzyl alcohol at 380 °C for 1 h using the molar ratio of O₂ to alcoholic hydroxyl molar ratio (O₂/hydroxyl) = 0.6 and weight hourly space velocity (WHSV) = 20 h⁻¹, and then evaluated at the specified temperature using O₂/hydroxyl = 0.6 and WHSV = 20 h⁻¹ if not otherwise specified. ^{*b*} O₂/hydroxyl = 0.8.

Catalwat	Au loading	NiO loading	Calcination	Reaction	Conv.	Sel.
Catalyst	(wt%)	(wt%)	Temp. (° C)	Temp. (° C)	(%)	(%)
Au/Ni-fiber ^b	4	0	300	280	39	99
NiO/Ni-fiber ^c	0	4	300	280	9	100
NiO@Au/Ni-fiber	4	4	300	280	98.5	98.5
Au@NiO/Ni-fiber	4	N.A. ^d	300	280	39	99
Au/Ti-fiber	4	0	300	280	8	99
NiO/Ti-fiber ^c	0	4	300	280	7	100
NiO@Au/Ti-fiber ^c	4	4	300	280	87	98
Au/SS-fiber ^e	4	0	300	280	17	99
NiO/SS-fiber ^c	0	4	300	280	9	100
NiO@Au/SS-fiber ^c	4	4	300	280	87	99

 Table S2. Gas-phase selective oxidation of benzyl alcohol catalyzed by the various pre-activated catalysts with only Au or NiO NPs, and NiO@Au ensembles.^a

^{*a*} All catalyst samples were prepared similarly to the catalyst Au/Ni-fiber and were pre-activated (i.e., catalysts underwent gas-phase selective oxidation of benzyl alcohol at 380°C for 1 h using O₂/hydroxyl = 0.6 and WHSV = 20 h⁻¹) and then evaluated at the specified temperature while keeping the other reaction parameters unchanged. ^{*b*} The freshly prepared catalyst Au-4/Ni-fiber was washed by deionized water with the temperature of 40 °C for 5 times to remove NiCl₂ completely (AgNO₃ test). ^{*c*} NiO doping: The Ni-fiber, Ti-fiber, Au/Ti-fiber, SS-fiber and Au/SS-fiber were impregnated with aqueous Ni(NO₃)₂ solution followed by calcinations at 300°C. ^{*d*} Not available (N.A.): For this catalyst sample, the Ni-fiber support was deeply oxidized at 600°C in air for 2 h prior to loading Au. ^{*e*} SS-fiber: Stainless steel 316L fiber.

Entry	Microfiber ^b	Catalyst	Au particle	NiO loading by post	Conv.	Sel.
			size (nm) ^c	doping (wt%) ^d	(%)	(%)
1	Ni-8	Au/Ni-fiber ^e	25	0	39	99
2	Ni-8	NiO@Au/Ni-fiber	25	2.3^{f}	98.5	98.5
3	NiO-8 ^g	Au@NiO/Ni-fiber	22	0	39	99
4	NiO-8	NiO@Au@NiO/Ni-fiber	22	4	84	99
5	SS-8 ^{<i>h</i>}	Au/SS-fiber	23	0	17	99
6	SS-8	NiO@Au/SS-fiber	23	4	87	99
7	FeO-8 ^{<i>i</i>}	Au/FeO-fiber	20	0	20	99
8	FeO-8	NiO@Au/FeO-fiber	20	4	85	99
9	Ti-8	Au/Ti-fiber	27	0	8	99
10	Ti-8	NiO@Au/Ti-fiber	27	4	87	98
11	TiO ₂ -16 ^{<i>j</i>}	Au/TiO ₂ -fiber	26	0	27	99
12	TiO ₂ -16	NiO@Au/TiO ₂ -fiber	26	4	90	99

Table S3. The activity of the various pre-activated microfibrous structured Au catalysts (Au loading: 4	4
wt%) catalyzing benzyl alcohol before and after post-doping NiO. ^{a}	

^{*a*} All catalyst samples were prepared similarly to the catalyst Au/Ni-fiber and were pre-activated (i.e., catalysts underwent gas-phase selective oxidation of benzyl alcohol at 380°C for 1 h using O₂/hydroxyl = 0.6 and WHSV = 20 h⁻¹), and then were evaluated at 280 °C using O₂/hydroxyl = 0.6 and WHSV = 20 h⁻¹. ^{*b*} The end number means the diameter (µm) of the microfiber carriers. ^{*c*} Au particle size was estimated from the Scherrer equation according to Au[111] XRD peak. ^{*d*} NiO doping: The Au catalyst was re-impregnated with aqueous Ni(NO₃)₂ solution followed by calcinations at 300°C if not otherwise specified. ^{*e*} The freshly prepared catalyst Au-4/Ni-fiber was washed by deionized water with the temperature of 40 °C for 5 times to remove NiCl₂ completely (AgNO₃ test). ^{*f*} The NiO was transformed from NiCl₂ which was produced from the HAuCl₄-Ni galvanic reaction, and NiO loading (wt%) was calculated according to the equations Ni + HAuCl₄ \rightarrow 2Au + NiCl₂ and NiCl₂ \rightarrow NiO. ^{*g*} The NiO/Ni-fiber was obtained by calcined Ni microfiber at 600 °C in air for 2h. ^{*h*} SS means stainless-steel 316L-fiber. ^{*i*} The FeO microfiber was obtained by calcined SS-316L microfiber at 600 °C in air for 2h. ^{*j*} The TiO₂ microfiber was obtained by calcined Ti microfiber at 650 °C in air for 2h.

Catalyst	Compound type	B. E. (eV)	Peak Area	Fraction (%)
Activated	O-1s			
sample	NiO	529.7	678	42
	Ni ₂ O ₃	531.8	936	58
	Au-4f			
	Au0	84.0	329	68
	Au^+	84.7	150	32
	Au ³⁺	86.2	0	0
	Ni-2p			
	NiO	854.4	2107	56
	Ni ₂ O ₃	856.2	1665	44
After TPD	O-1s			
	NiO	529.7	5109	64
	Ni ₂ O ₃	531.8	2946	36
	Au-4f			
	Au ⁰	84.0	214	100
	Au^+	84.7	0	0
	Au ³⁺	86.3	0	0
	Ni-2p			
	NiO	854.4	8039	73
	Ni ₂ O ₃	856.2	2910	27

Table S4. The XPS results of the pre-activated Au-4/Ni-fiber before and after Temperature-Programmed-Desorption (TPD) at 700 °C for 1h.

Supplementary Discussion 1: The influence of gold particle size

In order to investigate the influence of gold particle size, the gold particle size of the pre-activated catalysts with different gold loading (1 wt% - 5 wt%) was calculated from the Scherrer equation according to Au(111) XRD peak. The particle size and the conversion of benzyl alcohol were showed in **Fig. A**. If the active site is on the gold surface, the gold particle surface area of the catalyst Au-4/Ni-fiber (gold loading is 4 wt%) is 3.2 times as much as that of the catalyst Au-1/Ni-fiber (gold loading is 1 wt%). However, the conversion over Au-4/Ni-fiber is 7 times as high as that of Au-1/Ni-fiber. If the active site is at the particle periphery, the periphery length of Au-4/Ni-fiber is 2.6 times as long as that of Au-1/Ni-fiber. However, the conversion over Au-4/Ni-fiber is 7 times as high as that of Au-1/Ni-fiber. Obviously, the intrinsic activity of Au-4/Ni-fiber is higher than that of Au-1/Ni-fiber, although the particle size of Au-1/Ni-fiber is smaller.



Fig. A. The gold particle size of the pre-activated catalysts with different gold loadings (1 wt% - 5 wt%) and the corresponding benzyl alcohol conversion.

Additionally, another two catalysts with smaller gold particle size were prepared. The first catalyst was prepared with total gold loading is 2 wt% by 8-step wet impregnation method. The previous catalyst Au-2/Ni-fiber was prepared by 1-step wet impregnation. Therefore, the HAuCl₄ concentration in the solution for 8-step wet impregnation is much lower, and the Au-Ni galvanic reaction (Ni + HAuCl₄ = Au + NiCl₂) proceeds incompletely, causing much less NiCl₂ produced than 1-step wet impregnation. Although the particle size is about 16 nm, but the XRD patterns of NiO (transformed from NiCl₂ during pre-activation process) is very weak, and the benzyl alcohol conversion is only 48%, lower than that (conversion ~77%) over the catalyst Au-2/Ni-fiber (gold particle size ~23 nm). In the 8-step wet impregnation method, 7g HAuCl₄ solution with the concentration of 0.0188M was diluted to 56g and the

HAuCl₄ concentration decreased to 0.00235M. For each loading of gold, the Ni-fiber (1.3g) was impregnated with diluted HAuCl₄ solution (7g) and was dried at 80 °C overnight and calcined at 300 °C for 4 h, with the result that 0.25 wt% Au could be placed onto the Ni-fiber. The same procedure was repeated for 8 times in all so as to obtain an Au-2/Ni-fiber catalyst with Au-loading of 2 wt%.

The second catalyst with gold loading is 4% was prepared on the modified Ni-fiber. Ni-fiber was modified by wetness etching method using $Al(NO_3)_3$ solution according to the reference [S4]. After Au-Ni galvanic reaction, the catalyst was washed 5 times to remove the produced NiCl₂. The gold particle size is 12 nm and the conversion is only 49%. This is because the NiCl₂ was washed away and no apparent NiO was formed through the NiCl₂ to NiO transformation during the pre-activation process. Indeed, the same sample without removing NiCl₂ delivered a conversion of 98%. These results indicated that when gold particle size larger than 10 nm in our catalyst system, the Au-NiO interaction in the active site of NiO@Au, not the influence of the gold particle size, is the key role for the catalyst performance, which is consistent with the reported results.^[S7-S9]

Supplementary Discussion 2: The support effect

Many reported results showed that the support effect plays an important, sometimes a crucial role in determining the catalyst performance. In order to investigate the support effect, we prepared a series of contrastive catalysts supported on several other microfibers (SS, FeO, Ti, TiO₂, NiO; SS: Stainless steel 316L fiber). The metal oxide microfiber (FeO, TiO₂, NiO) were obtained by calcined the corresponding metal microfibers at needed temperature in air for 2 h (Table S3). XRD patterns (not shown) indicated that apparent metal oxide phase came into being and the gold particle size was in the range of 20-30nm (Table S3). However, all the catalysts delivered a low benzyl alcohol conversion of <40% (Table S3, entries 1, 3, 5, 7, 9, 11). Even through the catalyst Au-4/Ni-fiber delivered a high benzyl alcohol conversion of >98% (Table S3, entry 2), the conversion decreased dramatically to 39% (Table S3, entry 1), if the freshly prepared catalyst Au-4/Ni-fiber was washed by deionized water for 5 times to remove the produced NiCl₂. This is because the NiCl₂ is washed away (Fig. S7) and no apparent NiO was formed through the NiCl₂ to NiO transformation during the pre-activation process (Fig. S8). Moreover, it was interesting to find all the catalysts activity was enhanced greatly, if the above contrastive catalysts were modified by being added with NiO (Table S3, entries 4, 6, 8, 10, 12). These results indicated that not support effect but the Au-NiO interaction in the active site structure of NiO@Au is the key role for the catalyst performance, which is consistent with other reported results.^[S8-S10]

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Fig. B. XRD patterns of the Au-4/Ni-fiber precursor (**a**) just after undergoing Au galvanic deposition without drying and (**b**) after subsequently calcining at 300°C in air for 2 h (showing NiCl₂ phase formed).



Fig. C. XRD of fresh Au-4/Ni-fiber catalyst sample after gas-phase selective oxidation of benzyl alcohol at 280 $^{\circ}$ C for (a) 1 h and (b) 6 h.

Supplementary Discussion 3: Active-site structure and the NiO-Au NPs interaction

1. Active NiO@Au-NPs ensembles

With the help of XRD, TEM and XPS, the active site was identified as NiO@Au-NPs ensembles, where the Au-NPs must require partial coverage by small NiO segments. The Au-NPs came from the galvanic reaction ($3Ni + 2HAuCl_4 = 2Au + 3NiCl_2 + 2HCl$), meanwhile, NiCl_2 came into being (**Fig. B**). The NiO came from the transformation from NiCl_2 to NiO (Fig. S4; 5 nm particle size, estimated from the Scherrer equation) during the pre-activation process. However, the NiCl_2-to-NiO transformation can proceed only at a high temperature, such as 380 °C, but not after even longer time-on-stream directly at temperatures below 300 °C (**Fig. C**).



Fig. D. XRD pattern of the catalyst Au-4/Ni-fiber before (a) and after (b) pre-activation: showing the disappearance of NiCl₂ (**a-b:** $2\theta = 16.0^{\circ}$) and the formation of NiO nanoparticles (**b:** $2\theta = 37.4^{\circ}$).



Fig. E. XRD patterns of the pre-activated Au/Ni-fiber catalysts with different Au loading (showing NiO phase formed): (a) 1wt%, (b) 2wt%, (c) 3wt%, (d) 4wt%, (e) 5wt%.

Transformation from NiCl₂ to NiO: This transformation can be confirmed by XPS (**Fig. S6**) and XRD (**Fig. D**). XPS result (take the catalyst Au-4/Ni-fiber for example) showed that after pre-activation process, the Cl2p peak disappeared completely and the XRD patterns showed that NiCl₂ disappeared (take the catalyst Au-4/Ni-fiber for example) and NiO was formed after the pre-activated process (**Fig. D**), which is an important process for the active-site formation thereby significantly promoting the catalyst activity, as noted in the manuscript. Other catalysts were observed with a similar NiCl₂-to-NiO transformation process (**Fig. E**). Indeed, Cl ions were found in the initial product during the pre-activation process by AgNO₃ test and no Ni element was found by ICP.

Partial coverage of Au-NPs with NiO segments (NiO@Au-NPs): Firstly, the small NiO segments were visualized by TEM (**Fig. 1a** in the manuscript) to partially cover the large Au NPs to form the active site NiO@Au-NPs ensembles (structurally illustrated in **Fig. 1b** in the manuscript). Moreover, metal element analyses by XPS indicated the coexistence of Au⁰ together with Au⁺ and NiO on the surface of a pre-activated Au-4/Ni-fiber sample (**Fig. F**), further confirming the formation of partial coverage of Au-NPs with small NiO segments (NiO@Au-NPs).



Fig. F. XPS spectra in Au4f and Ni2p regions for the pre-activated Au-4/Ni-fiber sample. Coexistence of Au^0 together with Au^+ , Ni²⁺ (NiO) and Ni³⁺ (Ni₂O₃) supports the NiO@Au-NPs structure.

2. Interaction between Au NPs and NiO segments:

As to the Au-NiO interactions, the results indicated that it plays a crucial role in the catalyst activity. For the catalysts with gold loading of 2-5 wt%, apparent NiO phase was formed and the benzyl alcohol conversion was high (77-98%). For the catalyst with gold loading of 1 wt%, however, very faint NiO XRD peak was observed and the benzyl alcohol conversion was only 14% accordingly (**Fig. A**). Additionally, the results from the contrastive catalysts before and after post-doping NiO provided solid evidences on the fact that the interaction between Au NPs and NiO segments is indispensible for lowtemperature activity of the Au/Ni-fiber catalyst (**Tables S2** and **S3** & Supplementary Discussions 1 and 2).

Supplementary Discussion 4: XPS Data Analysis

For the pre-activated sample Au-4/Ni-fiber, the O(531.8 eV)/Ni(856.2 eV) atom ratio was quantitatively determined using the following calculations. First, the Ni²⁺/Ni³⁺ ratio can be obtained from the Ni2p peak areas of NiO and Ni₂O₃, which are 2107 and 1665, respectively. The Ni²⁺/Ni³⁺ ratio is 56:44 (2107:1665), and the O_{NiO}/O_{Ni2O3} ratio is 42:58 (678:936). The total surface atom ratio of Ni/O is

41.7:49.4, which was given by the XPS total scanning data. Therefore, the O(531.8 eV)/Ni(856.2 eV) atom ratio is quantitatively determined to be $1.56 ([0.58 \times 49.4]/[0.44 \times 41.7] = 1.56)$.

For the same Au-4/Ni-fiber sample after TPD experiment, the O(531.8 eV)/Ni(856.2 eV) atom ratio was quantitatively determined using the same calculation. The Ni²⁺/Ni³⁺ ratio is 73:27 (8039:2910), and the O_{NiO}/O_{Ni2O3} ratio is 64:36 (5109:2946). The total surface atom ratio of Ni/O is 41.7:46.0. Therefore, the O(531.8 eV)/Ni(856.2 eV) atom ratio is quantitatively determined to be 1.47 ([0.36×46.0]/[0.27×41.7] = 1.47). Additionally, the amount of oxygen atoms released from the decomposition of Ni₂O₃ to NiO is 3.55 ([0.44 - 0.28] × 41.6/2 = 3.55), and the amount of total surface oxygen atoms decreased by 3.4 (49.4 - 46.0 = 3.4), which coincided almost stoichiometrically (100% × 3.4/3.55 = 96%).

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