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Surface State, Catalytic Activity and Selectivity of Nickel Catalysts in Hydrogenation Reactions

Part 2†.—Surface Characterization of Raney Nickel and Urushibara Nickel Catalysts by X-Ray Photoelectron Spectroscopy

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The X-ray photoelectron spectroscopic study of Raney and Urushibara nickel catalysts activated under various conditions was undertaken to characterize the surface state of the catalysts including the catalysts' structure. Raney nickel catalysts contain both oxidized and metallic aluminium in the activated phase. As for Urushibara nickel catalysts digested with acetic acid or sodium hydroxide, metallic and oxidized zinc were observed in the catalyst surface. Based on the X.p.s. peak intensities for the catalysts, the structure of Urushibara nickel catalysts was found to be that of a supported catalyst, whereas Raney nickel catalysts showed X.p.s. features consistent with those expected for skeletal nickel catalysts.

In our previous paper,[1] nickel boride and nickel phosphide catalysts were investigated by X-ray photoelectron spectroscopy (X.p.s.) in order to characterize the surface state of the catalysts. The surface characterization of nickel catalysts is believed to be the first step in understanding the specific features of these catalysts in catalytic activity and selectivity for hydrogenation reactions. In the present study, Raney and Urushibara nickel catalysts were studied by means of X.p.s. for more precise discussions on the relationship between the surface state of the nickel catalysts and hydrogenation reactions over the catalysts.

With regard to the X.p.s. study of these catalysts, Holm and Storp[2] have reported the surface state of an Al–Ni alloy foil treated with NaOH and they found that aluminium protects the oxidation of nickel by covering the alloy surface. However, their results would provide definite information only on the surface state of Raney nickel catalysts prepared under certain conditions. As for Urushibara nickel catalysts, no X.p.s. results have been published so far.

In this study, the surface structure of these nickel catalysts has been based on the X.p.s. results.

EXPERIMENTAL

CATALYSTS

RANEY NICKEL (R-Ni) CATALYSTS

Three kinds of Ni–Al alloy, 27, 42 and 48 wt% Ni, were employed in this study. They are designated R-Ni(27), R-Ni(42) and R-Ni(48), respectively. The Ni–Al alloy (0.6 g) was activated in 25 cm^3 of an aqueous 20 % NaOH solution for 30 min at the desired tempera-

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ture (30-80°C) by adding the alloy stepwise to maintain the activation temperature within ±1°C. After the activation, the catalyst was washed five times with distilled water and subsequently five times with 99 % ethyl alcohol by decantation.

URUSHIBARA NICKEL (U-Ni) CATALYSTS

U-Ni catalysts were prepared by reducing $NiCl_2$ with zinc dust in the presence of a small amount of water, according to the preparation method described by Hata.[3] The black precipitate (ppt-Ni) produced was subsequently activated in a 20 % acetic acid solution at 50°C for various periods (0-23 min). The prepared catalyst was washed three times with water and then three times with 99 % ethyl alcohol by decantation. The U-Ni catalyst digested with acetic acid is denoted U-Ni(*A*). The ppt-Ni was also treated with a 10 % NaOH aqueous solution at 50°C for 15 min and this catalyst is designated U-Ni(*B*).

B.E.T. surface areas of the catalysts were measured by N_2 adsorption at 77 K as described previously.[1]

X.P.S. MEASUREMENTS

X-ray photoelectron spectra of the catalysts were measured using Al *Kα* radiation without exposing the catalysts to air as described previously in detail.[1] The binding energy values were referenced to the C 1*s* level (285.0 eV) resulting from surface contaminants. The extent of the surface charging of the catalysts thus measured was within a few tenths eV. The accuracy of the binding energy values for the catalysts was ±0.3 eV, judged by the reproducibility of the binding energies for several samples prepared separately.

The peak area intensities were used for (semi-) quantitative purposes and they were measured by planimetry of the graphic displays of the spectra, assuming linear base lines as indicated in fig. 1. The atomic sensitivities of Ni $2p_{\frac{3}{2}}$, Al 2*s* and Zn $2p_{\frac{3}{2}}$ levels used here were

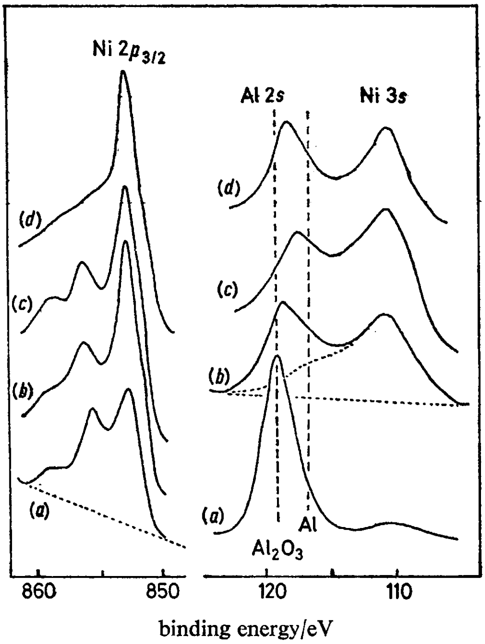

FIG. 1.—X-ray photoelectron spectra of Ni $2p_{\frac{3}{2}}$, Al 2*s* and Ni 3*s* levels for Raney nickel catalysts prepared from 42 % Ni alloy: (*a*) original alloy, (*b*) activated at 30°C for 30 min, (*c*) at 80°C, (*d*) sample (*c*) evacuated at 300°C for 1 h.

3.84,[1] 0.56 and 4.03, respectively, as referenced to N 1*s* level, which was obtained by measuring the spectra for $Ni(NO_3)_2$, $K_2Ni(CN)_4$, $AlPO_4$, $Zn(CN)_2$ and $Ni_3(PO_4)_2$. The values for Al 2*s* and Zn $2p_{3/2}$ levels were consistent with those reported by Wagner [4] (0.56 for Al 2*s* and 4.24 for Zn $2p_{3/2}$).

The peak area intensity ratios of the C 1*s* level due to contaminant carbon to the Ni $2p_{3/2}$ level for the nickel catalysts were almost invariant (C 1*s*/Ni $2p_{3/2}$ = $3 \pm 1 \times 10^{-3}$). Therefore the effect of contaminant carbon on the quantitative results were neglected. Accordingly, the aluminum and zinc concentrations in the catalyst surface would be semi-quantitative. However, the relative values are believed to be correct.

The more precise measurement conditions and treatment procedures of the spectra have been reported in a previous paper.[1]

RESULTS AND DISCUSSION

SURFACE CHARACTERIZATION OF RANEY AND URUSHIBARA NICKEL CATALYSTS

RANEY NICKEL CATALYSTS

Shown in fig. 1 are the X-ray photoelectron spectra of the Ni $2p_{3/2}$, Al 2*s* and Ni 3*s* levels for the R-Ni(42) catalysts. With the original alloy [fig. 1(*a*)], it is shown that the alloy is covered by aluminium oxide or hydroxide (Al 2*s*; 119.1 eV) as evidenced by the much higher Al 2*s*/Ni $2p_{3/2}$ intensity ratio than that expected from the composition and that nickel is protected from oxidation by air by a passive aluminium oxide film. This observation is consistent with that reported by Holm and Storp.[2] The X.p.s. intensity of Al 2*s* diminished with increasing activation temperature as expected. The apparent binding energy of the Al 2*s* level decreased with decreasing aluminium content in the catalyst surface as summarized in table 1 and depicted in fig. 2. The binding energy of the Ni $2p_{3/2}$ band for metallic nickel was 852.2±0.3 eV

TABLE 1.—SURFACE CHARACTERIZATION OF RANEY NICKEL CATALYSTS

catalyst	preparation temperature /°C	surface area/$m^2(g\ cat)^{-1}$	metal[a] /%	binding energy of Al 2*s*/eV	surface content[b] of aluminium (Al/Ni)
R-Ni(48)	30	9.7	77	118.1	0.81
	40	25.4	78	117.7	0.67
	50	43.3	83	117.6	0.56
	60	51.5	79	117.9	0.54
	80	69.2	81	117.5	0.51
R-Ni(42)	30	24.0	79	118.0	0.70
	40	36.1	81	117.7	0.59
	50	49.2	80	117.8	0.54
	60	56.4	77	117.8	0.48
	70	64.9	80	117.5	0.46
	80	63.7	79	117.2	0.38
	—[c]		66	119.1	22.8
R-Ni(27)	30	76.1	71	118.8	1.37
	40	63.9	67	119.0	1.18
	60	71.4	70	118.3	0.81
	80	69.0	81	117.6	0.59

[a] Fraction of Ni metal in the surface Ni. [b] Surface content of aluminium; atomic ratio. [c] Not activated.

for all the R-Ni catalysts examined in this study and consistent with that for bulk nickel metal. The oxidized nickel showed a Ni $2p_{\frac{3}{2}}$ binding energy of 856.0 eV, this being ascribable to nickel hydroxide.[1]

As for the aluminum content in the catalyst surface, only approximate concentrations could be calculated from the intensities of the Al 2*s* and Ni $2p_{\frac{3}{2}}$ levels, since the Al 2*s* spectrum is obscured by the superimposition of the Ni 3*s* level. The Al 2*s* spectrum was obtained by subtracting graphically the Ni 3*s* level corresponding to that for a decomposed-nickel catalyst.[1] The surface content of residual aluminium thus obtained reflects the average composition in the surface layer or in the activated phase of the catalyst. The accuracy of the values in table 1 was estimated to be $\approx \pm 20$ %.

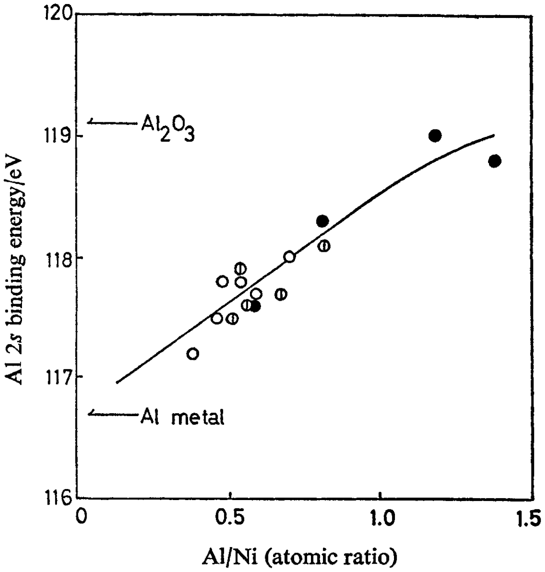

FIG. 2.—Dependence of the apparent Al 2*s* binding energy on the atomic ratio of residual aluminium to nickel in Raney nickel catalysts, ○, R-Ni (42); ◐, R-Ni (48); ●, R-Ni (27).

Although no clear appearance of metallic aluminium was observed with the spectrometer, it is concluded that metallic aluminium is present in the activated phase of R-Ni catalysts as well as aluminium oxide and/or hydroxide, taking into consideration the fact that the f.w.h.m. (full width at half maximum) of the Al 2*s* level increased from 2.7 to $\approx$3.5 eV with the extent of activation, accompanying a decrease in the apparent binding energy of the Al 2*s* band as shown in fig. 2. The aluminium metal/nickel metal ratios were calculated to be 0.4 ± 0.1 by deconvoluting the resultant Al 2*s* spectra into the oxide (119.1 eV) and metal (116.7 eV) assuming a chemical shift of 2.4 eV between the oxide and metal.[5] Taking into account the difference in the escape depths of the photoelectrons, the actual atomic ratio might be smaller than the observed one, since carbon contaminants cover, at least partly, the catalyst surface.

The atomic ratios of residual aluminium to nickel for R-Ni catalysts are plotted as a function of the activation temperature in fig. 3. They approached the same value (Al/Ni = 0.4 under our activation conditions) as the extent of activation increases regardless of the original alloy compositions. Only in the cases of incomplete activation does the aluminium content depend on the composition of the original alloy.

A correlation between the B.E.T. surface area of the catalyst and the surface content of residual aluminium is shown in fig. 4. The surface area approached the same value [$\approx 70\ \mathrm{m^2(g\ cat)^{-1}}$] as the extent of activation increased. The R-Ni(42) and R-Ni(48) catalysts showed identical dependence of the surface area on the surface content of aluminium, while the R-Ni(27) catalysts had considerably higher surface area especially when the catalysts were prepared at relatively low temperatures. In addition, with the R-Ni(42) and R-Ni(48) catalysts the surface areas increased with decreasing residual aluminium content in the surface, whereas for the R-Ni(27) catalysts the surface areas were practically invariant. These findings imply that the surface structures of the R-Ni(42) and R-Ni(48) catalysts are close to each other, while the surface structure of the R-Ni(27) catalysts is considerably different from those of the R-Ni catalysts prepared from the higher nickel content alloys. This is probably due to the presence of a large amount of eutectic phase in the low nickel content alloy.[6] It has been shown by electron microprobe studies[7] that the eutectic phase (5 % Ni) is extracted very rapidly in moderately concentrated alkali, concurrent with the formation of voids formerly occupied by the eutectic. This may explain the specific features of the R-Ni(27) catalysts in fig. 4.

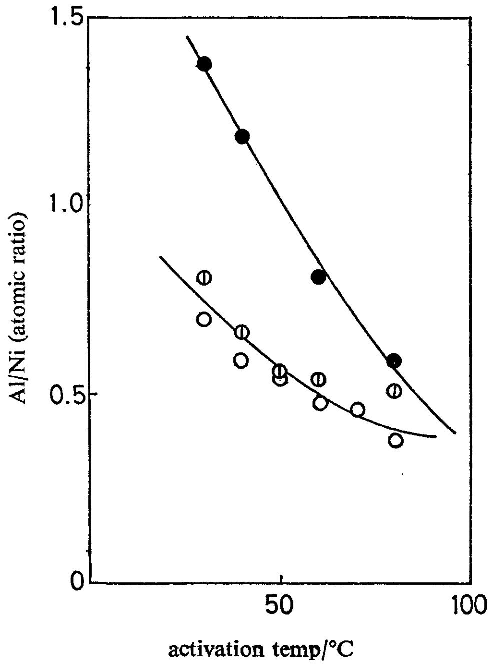

FIG. 3.—Dependence of the atomic ratio of residual aluminium to nickel on the activation temperature; O, R-Ni (42); ⦶, R-Ni (48); ●, R-Ni (27).

Heat treatment (300°C, 1 h in vacuum) of the R-Ni(42) catalyst activated at 80°C resulted in an increase in the aluminium content by ≈50 %, accompanying an increase in the apparent Al 2*s* binding energy and a decrease in the fraction of oxidized nickel as shown in fig. 1. These observations suggest an oxygen transfer from nickel oxide to aluminium metal similar to NiB and NiP catalysts,[1] in which cases boron and phosphorus accept the oxygen of nickel oxide to produce oxidized boron and phosphorus accompanying the reduction of nickel oxide.

URUSHIBARA NICKEL CATALYSTS

In fig. 5, the X-ray photoelectron spectra of the Zn $2p_{\frac{3}{2}}$ level and the Zn *LMM* Auger spectra induced by X-ray radiation are shown for the U-Ni catalysts activated with acetic acid or NaOH. As for the spectra of the Ni $2p_{\frac{3}{2}}$ level, similar spectra were observed to those for R-Ni catalysts. The Ni $2p_{\frac{3}{2}}$ binding energy for the nickel metal was 852.2±0.3 eV. The chemical shift of the Zn $2p_{\frac{3}{2}}$ level between zinc metal (1020.9 ±0.3 eV) and the oxide or hydroxide (1021.3±0.3 eV) was very small (≈0.4 eV) and they were clearly discriminated only by using Zn Auger spectra as reported by Wagner and Biloen.[8] It is evident that metallic zinc is present in the activated phase of the U-Ni catalysts. The fractions of zinc metal and oxide were obtained by deconvoluting Zn Auger spectra into metal (988.9±0.3 eV) and oxide (983.9±0.3 eV) as shown in fig. 5. The zinc content in the catalyst surface was calculated from the Zn $2p_{\frac{3}{2}}$ and Ni $2p_{\frac{3}{2}}$ levels (table 2). With ppt-Ni, the precursor of U-Ni catalysts, it was found that the ppt-Ni was completely covered by zinc hydroxide chloride [3] (O 1*s*; 531.2 eV) as evidenced by the presence of chloride in the surface. However, zinc metal developed gradually with increasing leaching time in acetic acid and the fraction of zinc metal in the surface zinc showed a maximum at ≈7.5 min leaching. The surface properties characterized by X.p.s. are summarized in table 2. Zinc metal in the activated phase would form an alloy with nickel metal, taking into account the Mössbauer spectroscopic study on Urushibara iron catalysts.[9] The atomic ratio of zinc metal to nickel metal was nearly constant (0.5±0.1) similar to that for the R-Ni catalysts where 0.4±0.1 was obtained.

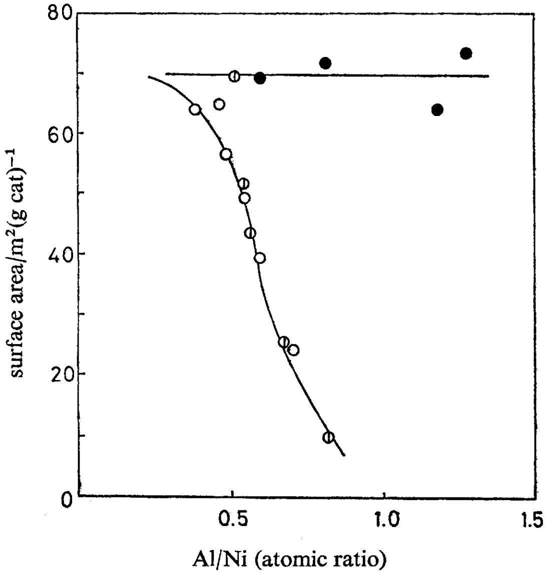

FIG. 4.—Correlation between the surface area of Raney nickel catalyst and the atomic ratio of residual aluminium to nickel.

With regard to the U-Ni(*B*) catalyst, a small fraction of zinc metal was present in the activated phase of the catalyst, judged from the broad Zn Auger spectrum (fig. 5) compared to those of ppt-Ni and ZnO. The intensity of the Ni $2p_{\frac{3}{2}}$ level was very low due to the large surface area of the catalyst (table 2).

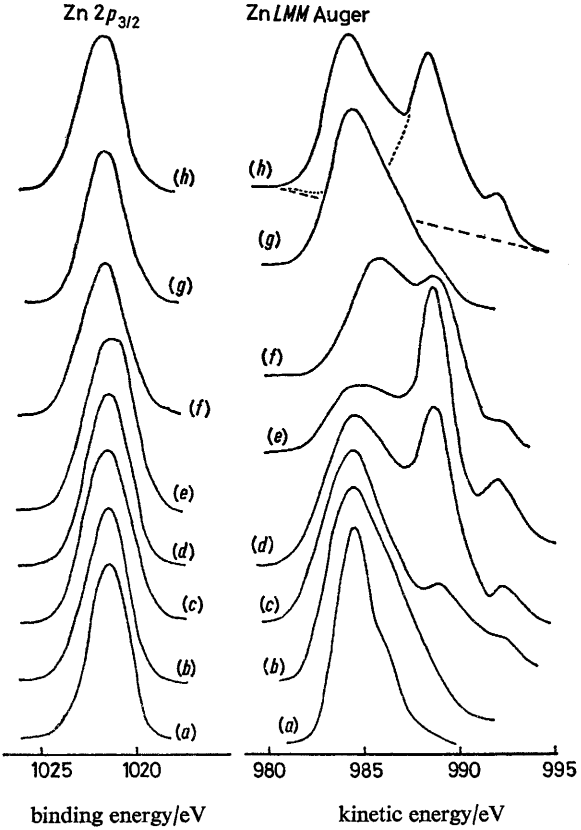

FIG. 5.—X-ray photoelectron spectra of Zn $2p_{\frac{3}{2}}$ level and X-ray induced Zn *LMM* Auger spectra for Urushibara nickel catalysts, (*a*) ppt-Ni, (*b*) U-Ni (*B*), (*c*) U-Ni (*A*) digested for 3 min, (*d*) for 5.5 min, (*e*) for 7.5 min, (*f*) sample (*e*) evacuated at 200°C for 1 h, (*g*) sample (*f*) evacuated at 300°C for 1 h, (*h*) U-Ni (*A*) activated for 23 min.

TABLE 2.—SURFACE CHARACTERIZATION OF URUSHIBARA NICKEL CATALYSTS

catalyst	activation time/min	surface area /$m^2(g\ Ni^{-1})$	Zn/Ni[a]	Ni metal[b] /%	Zn metal[c] /%	Zn metal/[d] Ni metal
ppt-Ni	0		very large		very small	
U-Ni(*A*)	3	30	1.08	56	33	0.64
	5.5	44	0.48	63	59	0.45
	7.5	43	0.44	63	72	0.51
	10	42	0.67	64	68	0.53
	14		0.59	55	47	0.51
	23	43	0.61	64	49	0.47
U-Ni(*B*)	15	104	3.13	23	small	

[a] Atomic ratio of Zn to Ni in the catalyst surface. [b] Fraction of Ni metal in the surface Ni. [c] Fraction of Zn metal in the surface Zn. [d] Atomic ratio of Zn metal to Ni metal in the catalyst surface.

Heat treatment (300°C, 1 h in vacuum) of the U-Ni (*A*) catalyst digested for 7.5 min resulted in the oxidation of both zinc and nickel metal, accompanying an increase in the Zn/Ni ratio. The surface oxidation induced by the heat treatment was completely different from those observed for NiB, NiP[1] and R-Ni catalysts. This is probably due to water and acetic acid adsorbed on zinc oxide or occluded in the bulk of the catalyst.

SURFACE STRUCTURE OF RANEY AND URUSHIBARA NICKEL CATALYSTS

In order to estimate the surface structure of R-Ni and U-Ni catalysts, the Ni $3p$/Ni $2p_{\frac{3}{2}}$ and Zn *LMM* Auger/Zn $2p_{\frac{3}{2}}$ peak intensity ratios of the catalysts were examined. When residual aluminium or zinc even partly covers the nickel surface by a surface enrichment, the Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratio can be expressed as follows for the nickel covered by aluminium or zinc:

$$\left(\frac{\text{Ni } 3p}{\text{Ni } 2p_{\frac{3}{2}}}\right) = \left(\frac{\text{Ni } 3p}{\text{Ni } 2p_{\frac{3}{2}}}\right)_0 \frac{\exp(-d/\lambda_{3p,\text{Ni}})}{\exp(-d/\lambda_{2p,\text{Ni}})} \tag{1}$$

where (Ni $3p$/Ni $2p_{\frac{3}{2}}$)$_0$ is the intensity ratio for bulk nickel metal, d is the thickness of the overlayer of aluminium or zinc and $\lambda_{\text{i,Ni}}$(i $= 2p$ or $3p$) is the escape depth of photoelectrons ejected from the Ni $2p_{\frac{3}{2}}$ or Ni $3p$ level. The kinetic energies of the Ni $2p_{\frac{3}{2}}$ and Ni $3p$ photoelectrons are ≈630 and 1415 eV and hence $\lambda_{2p,\text{Ni}}$ and $\lambda_{3p,\text{Ni}}$ can be calculated to be ≈10 and 20 Å, respectively.[10] Therefore, the Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratios should become larger than the ratio which can be obtained when no surface enrichment of aluminium or zinc occurs, if aluminium or zinc covers, even partly, the nickel metal surface by a surface segregation. As for the zinc constituting the overlayer, the Zn Auger/Zn $2p_{\frac{3}{2}}$ ratio can be represented by the following equation:

$$\left(\frac{\text{Zn Auger}}{\text{Zn } 2p_{\frac{3}{2}}}\right) = \left(\frac{\text{Zn Auger}}{\text{Zn } 2p_{\frac{3}{2}}}\right)_0 \frac{1-\exp(-d/\lambda_{\text{Auger,Zn}})}{1-\exp(-d/\lambda_{2p,\text{Zn}})}. \tag{2}$$

If zinc forms a thin layer over the nickel, a smaller Zn Auger/Zn $2p_{\frac{3}{2}}$ ratio is expected than the ratio for bulk compounds, that is (Zn Auger/Zn $2p_{\frac{3}{2}}$)$_0$, taking into account the fact that $\lambda_{\text{Auger,Zn}} > \lambda_{2p,\text{Zn}}$.

When nickel catalysts are described as supported catalysts over zinc or aluminium, the Ni $3p$/Ni $2p_{\frac{3}{2}}$ intensity ratio is expressed as follows:

$$\left(\frac{\text{Ni } 3p}{\text{Ni } 2p_{\frac{3}{2}}}\right) = \left(\frac{\text{Ni } 3p}{\text{Ni } 2p_{\frac{3}{2}}}\right)_0 \frac{1-\exp(-s/\lambda_{3p,\text{Ni}})}{1-\exp(-s/\lambda_{2p,\text{Ni}})} \tag{3}$$

and with zinc constituting the support eqn (4) can be derived for the zinc covered by the nickel particle:

$$\left(\frac{\text{Zn Auger}}{\text{Zn } 2p_{\frac{3}{2}}}\right) = \left(\frac{\text{Zn Auger}}{\text{Zn } 2p_{\frac{3}{2}}}\right)_0 \frac{\exp(-s/\lambda_{\text{Auger,Zn}})}{\exp(-s/\lambda_{2p,\text{Zn}})} \tag{4}$$

where s denotes the particle size of nickel. In this case the Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratio is expected to be smaller than (Ni $3p$/Ni $2p_{\frac{3}{2}}$)$_0$, while the Zn Auger/Zn $2p_{\frac{3}{2}}$ ratio is anticipated to be larger than (Zn Auger/Zn $2p_{\frac{3}{2}}$)$_0$. Based on eqn (1)-(4), the surface structures of R-Ni and U-Ni catalysts are discussed. Similar applications of the intensity ratios obtained from Auger and X-ray photoelectron spectra were successfully made to the surface segregation phenomena in PtSn alloys by Bouwman and Biloen.[11]

In table 3, Ni $3p$/Ni $2p_{\frac{3}{2}}$ and Zn Auger/Zn$2p_{\frac{3}{2}}$ ratios are summarized for the nickel catalysts, including NiB and NiP catalysts. The extent of carbon contamination is considered to affect these values. However, as stated above, the C $1s$/Ni $2p_{\frac{3}{2}}$ intensity ratio was almost invariant among the nickel catalysts examined here. Taking the ratios for D-Ni(decomposed-nickel)[1] and zinc compounds, which were almost equally contaminated, as (Ni $3p$/Ni $2p_{\frac{3}{2}})_0$ and (Zn Auger/Zn $2p_{\frac{3}{2}})_0$, contamination effects could be neglected within the reproducibility of the intensity ratios (±2 %).

TABLE 3.—Ni $3p$/Ni $2p_{\frac{3}{2}}$ AND Zn *LMM* AUGER/Zn $2p_{\frac{3}{2}}$ RATIOS FOR NICKEL CATALYSTS

	activation conditions			
catalyst	temperature/°C	time/min	Ni $3p$/Ni $2p_{\frac{3}{2}}$	Zn Auger/Zn$2p_{\frac{3}{2}}$
R-Ni(42)	30	30	0.62	
	50	30	0.51	
	80	30	0.47	
			0.65[a]	
	—[b]		1.1	
R-Ni(27)	30	30	0.46	
	60	30	0.47	
	80	30	0.48	
ppt-Ni			—[c]	1.02
U-Ni(*A*)	50	5.5	0.35	1.39
	50	7.5	0.34	1.35
	50	10	0.34	1.35
	50	14	0.40	1.20
	50	23	0.40	1.36
U-Ni(*B*)	50	15	0.22	1.02
NiB(P−1)[d]	30		0.47	
NiP−1[e]	72		0.47	
D-Ni[f]	300	180	0.47	

[a] Evacuated at 300°C for 1 h after preparation. [b] Original alloy. [c] Not determined. [d] Nickel boride catalyst prepared from nickel acetate. [e] Nickel phosphide catalyst. [f] Decomposed-nickel catalyst. Preparation methods of catalysts (*d*)-(*f*) are shown in the previous paper.[1]

Table 3 leads us to conclude that (1) the surface enrichment of residual aluminium is appreciable in the R-Ni(42) catalysts activated at low temperature, while the surface is uniform when prepared at high temperature; (2) with the R-Ni(27) catalysts, Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratios were invariant (≈0.47) regardless of the extent of activation, implying a difference in the surface structure of the R-Ni(27) and R-Ni(42) catalysts, as suggested from fig. 4; (3) as for the original alloy, a considerable surface enrichment of aluminium oxide takes place, as suggested by Holm and Storp;[2] (4) for U-Ni(*A*) catalysts the nickel is supported on zinc, this being verified by the facts that (*a*) the Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratio is smaller than (Ni $3p$/Ni $2p_{\frac{3}{2}})_0$ or 0.47 for bulk nickel and (*b*) the Zn Auger/Zn $2p_{\frac{3}{2}}$ ratio is larger than (Zn Auger/Zn $2p_{\frac{3}{2}})_0$, (5) with U-Ni (*B*) catalyst the nickel particle distribution is better than for the U-Ni(*A*) catalyst, this being consistent with the fact that the U-Ni(*B*) catalyst is much more massive and has a larger surface area than the U-Ni(*A*); and (6) NiB and NiP catalysts have uniform surface structure, that is, no surface enrichment of boron or phosphorus is observed. Therefore, the surface structures of R-Ni and U-Ni catalysts are considerably different; the Ni $3p$/Ni $2p_{\frac{3}{2}}$ ratio for R-Ni catalysts are in good agreement with that expected for the well known skeletal structure,[12] while U-Ni catalysts can be described as supported nickel catalysts.

The surface characterization of R-Ni and U-Ni catalysts by means of X.p.s. leads us to the following conclusions: (1) R-Ni catalysts contain metallic aluminium in the activated phase as well as oxidized aluminium; (2) U-Ni catalysts contain metallic zinc in the activated phase in addition to oxidized zinc; and (3) U-Ni catalysts can be described as supported nickel catalysts, while R-Ni catalysts are shown to have the well known skeletal structure.

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