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Characterization of Raney Ru: Effect of Heat Treatment

INTRODUCTION

Raney Ru has been found to be an effective catalyst for ammonia synthesis (*1*), isotopic equilibration reaction (IER) of dinitrogen (*2*, *3*), and CO hydrogenation (*4*). For such reactions, preparation conditions are important because they may affect surface structure. We have studied Raney Ru by XPS, TEM, and other techniques under various conditions. A Raney catalyst has a higher concentration of an active element than a supported catalyst and is more easily studied by XPS. A super high voltage transmission electron microscope (SHV-TEM) enabled us to observe the lattice structures of microcrystals in the metallic block. Although several works have been reported on the surface characterization of Raney Ni or intermetallic catalysts (*5–8*), no such work has been reported on Raney Ru catalyst.

EXPERIMENTAL

$Al_{79}Ru_{21}$ alloy was kindly manufactured by melting Ru and Al metal at around 2100 K under argon atmosphere using an arc furnace by Professor A. Suzuki and Mr. Y. Ohya. XRD analysis (Philips Model PW-1050) shows that $Al_{79}Ru_{21}$ alloy has $Al_{13}Ru_4$ and Al_6Ru phases. Neither Al metal nor Ru metal phase was observed. Raney Ru catalyst was prepared by leaching with 5 *N* KOH solution at 373 K for 2 h (*1–4*). Among several alloy samples with differing Al/Ru ratio, alloy possessing higher Al content than 55 at.% reacted with KOH easily. On the other hand, $Al_{55}Ru_{45}$ alloy, which had AlRu phase mostly, was hardly leached (*3*). Raney Ru leached from $Al_{79}Ru_{21}$ alloy was washed with N_2-saturated water. A part of the sample was examined by SHV-TEM and SEM. A mesh holder was dipped in the storage water which suspended fine particles of the Raney Ru. An ultrasonic generator helped the suspension. The sample mounted on a mesh was evacuated in the TEM equipment and was observed by SHV-TEM at 1000 kV (Hitachi H-1250). The adsorbed water was thought to prevent the sample from oxidation by air. The other wet sample was mounted on the SEM holder with Ag paste and was evacuated in SEM equipment (Hitachi HFS-2) for the SEM and EPMA measurements.

Most of the sample was transferred together with the water to a glass reactor which was connected to a vacuum system. After the storage water was evacuated at 298 K for 10 h, BET area (77 K) and H_2 chemisorption (273 K) were measured. The sample was heated *in vacuo* or under water vapor at varying temperature for 2 h. BET area and H_2 chemisorption were again measured as a function of the treating temperature. At the same time, a part of the sample was transferred to a side arm of the reactor after every heat treatment and it was sealed off to measure the XPS (Shimadzu ESCA 750) and EPMA (Philips EDAX Model 707B) as a function of evacuation temperature.

RESULTS

Nonheated Raney Ru

Figure 1 shows an SEM picture of freshly leached Raney made from $Al_{79}Ru_{21}$ alloy. Cracked units (referred to as third-order particles), several tens of micrometers in width are seen in Fig. 1a. Many fine units

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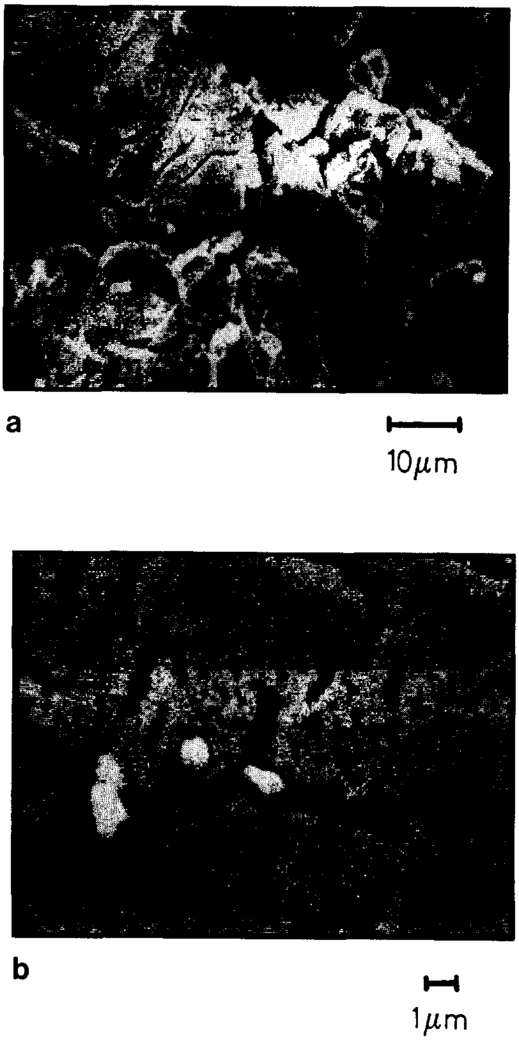

FIG. 1. SEM pictures of Raney Ru from $Al_{79}Ru_{21}$. (a) Blocks (10 μm) divided by cracks are referred to as third-order particles. (b) Blocks (submicrometer) divided by fine pores are referred to as second-order particles.

(referred to as second-order particles), about 1 μm in diameter, and fine pores are seen when the magnification is increased as in Fig. 1b. Such pores are not created in the sample leached at 273 K (*3*). A SHV-TEM picture of the same sample is shown in Fig. 2. Many lattice structures of microcrystals (referred to as first-order particles) are seen. Each microcrystal has a different particle size and lattice width, which are measured and summarized in Table 1 and Fig. 3. These microcrystals are identified to be Ru metal phase although the lattice width values are distributed due to a lattice distortion (Table 1) (*9*). XRD spectra show broad peaks due to Ru metal phase exclusively, which confirms that Raney Ru is composed mainly of Ru microcrystals. The average particle size calculated from data in Fig. 3 is ca. 6 nm, which is close to the value (5 nm) calculated by BET measurement shown in Fig. 5 and to the value (3 nm) by X-ray diffraction line broadening. The particle sizes are calculated by BET data assuming uniform spheres and by XRD data assuming Scherrer's equation. Ru percentage dispersion calculated from H_2 chemisorption (assuming H/Ru = 1) is as high as 18%, which is two orders of magnitute greater than that of metal powder (0.25%) and almost identical to the value for 0.5 wt% Ru/Al_2O_3 (19%) (*10*).

No practical information about Al was obtained by TEM or XRD, but Al could be observed by XPS and EPMA. About 12 at.% of Al (Al/Ru = 12/88 by XPS) is left after leaching, as is shown in Fig. 5. This value is well corresponding to the value by H_2 evolution measurement (*1*). On the other hand, comparison of H_2 chemisorp-

TABLE 1

Lattice Distance of Single Crystals of Nonheated Raney Ru Observed by SHV-TEM

Theoretical lattice distance (nm) Ref. (*9*)	ASTM	Observed lattice distance (nm)
0.192		0.189
0.196		0.194, 0.196, 0.199
0.204 (0.207)	0.2056	0.201, 0.203, 0.203, 0.204, 0.206, 0.206, 0.207, 0.208, 0.208, 0.209
0.218	0.2142	0.213, 0.213, 0.213, 0.214, 0.214, 0.214, 0.217, 0.218, 0.218, 0.220
0.231 (0.226)	0.2343	0.224, 0.226, 0.226, 0.226, 0.227, 0.227
0.237		0.238
0.267		0.273, 0.282
0.308		0.308
0.337		0.341

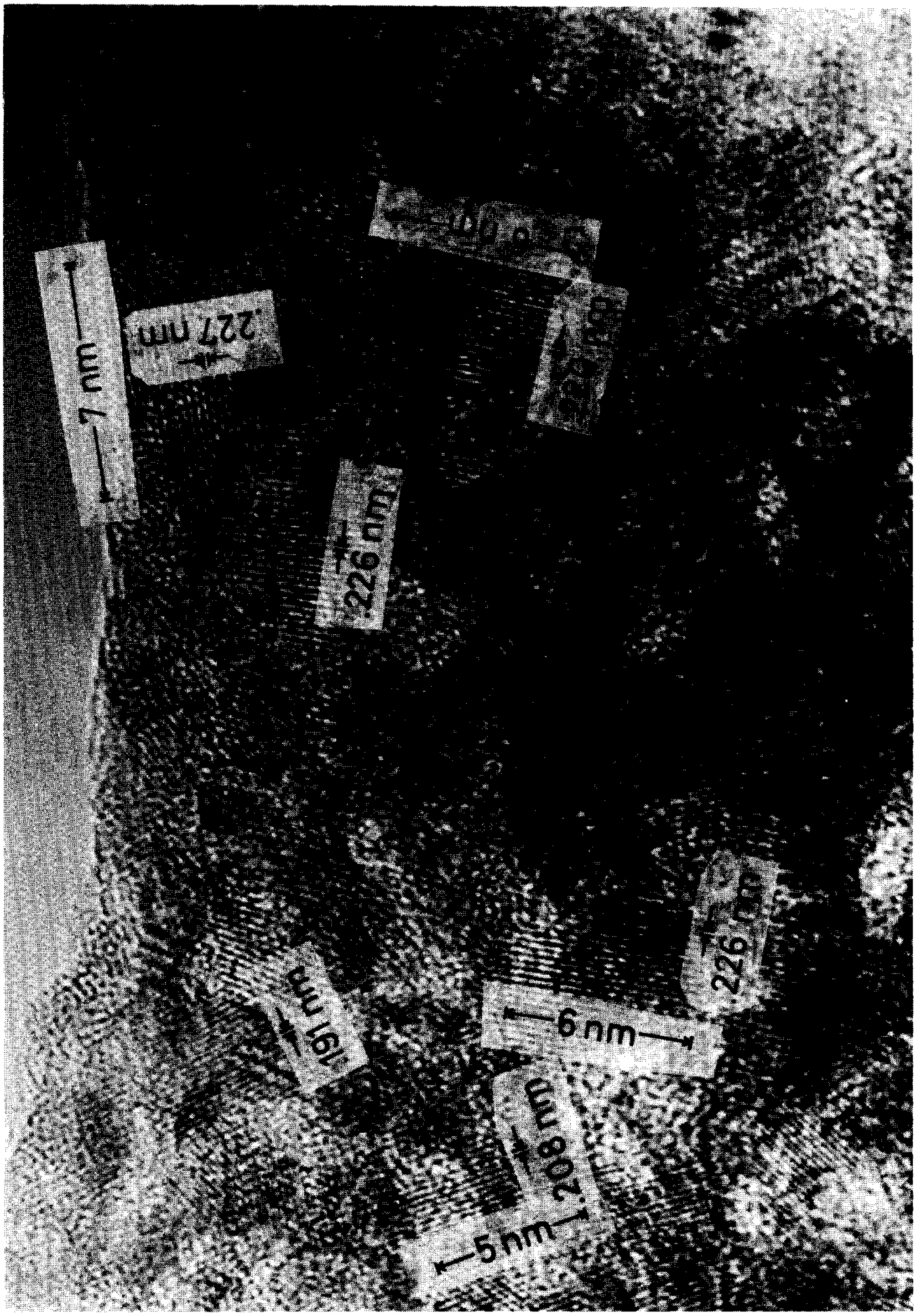

FIG. 2. SHV-TEM picture of Raney Ru made from $Al_{79}Ru_{21}$. Lattice structures of the single crystals are referred to as first-order particles.

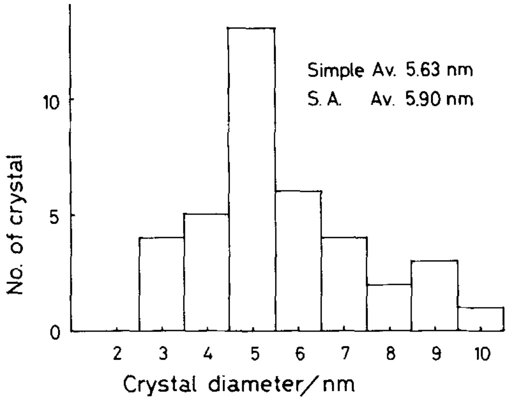

FIG. 3. Crystal size distribution of the single crystals of nonheated Raney Ru. Crystal sizes are measured by using three pictures, one of which is Fig. 2.

tion and BET data shows that about 68% of the surface is occupied by Ru metal, which suggests that 32% of the surface is occupied by other elements such as Al and O. Here, an Ru surface concentration of 1.63×10^{19} m^{-2} (9) and H/Ru = 1 are assumed. Al is inferred to be segregated of the surface; however, the extent seems less prominent on nonheated catalysts than that on heated catalysts. XPS spectra show that Ru is reduced (Ru^0), and most of Al is also reduced (Al^0) before heat treatment, but a part of Al probably at the surface is oxidized as is shown in Fig. 4. Since the escape depth of 1.5 nm is supposed for Al analysis, the major information of XPS comes from the bulk.

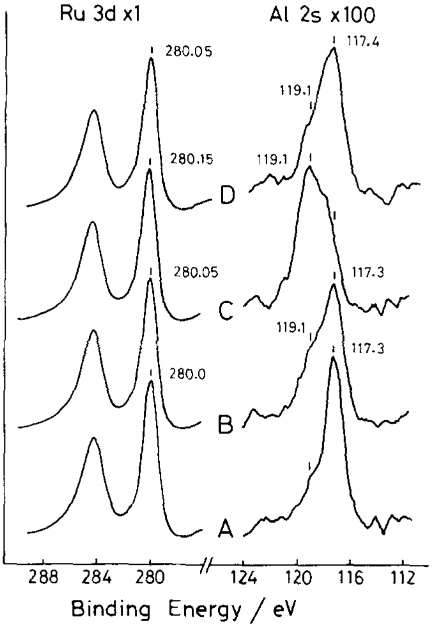

FIG. 4. Al_{2s} and Ru_{3d} XPS spectra of Raney Ru as a function of treated temperature. H_2O–He treatment at 373 K (A), 473 K (B), and 573 K (C). He treatment at 473 K (D) gives the same result as H_2O–He treatment (B). A BE of 280.0 eV corresponds to metallic Ru, and 119.1 and 117.4 eV correspond to Al^{3+} and Al^0, respectively.

Heat-Treated Raney Ru

Figure 5 shows effects of heat treatment on BET surface area, H_2 chemisorption, and XPS measurements. Total (BET) surface area (referred to as S_T) decreases from 98 to 44 $m^2\ g^{-1}$ at 673 K. The sintered particle size calculated by BET (11 nm) is close to the value (10 nm) by X-ray line broadening. The Ru surface area based on H/Ru = 1 (referred to as S_{Ru}) decreases drastically from 66 to 16 m^2g^{-1} at 673 K. Surface Ru percentage S_{Ru}/S_T also decreases 68 to 36%

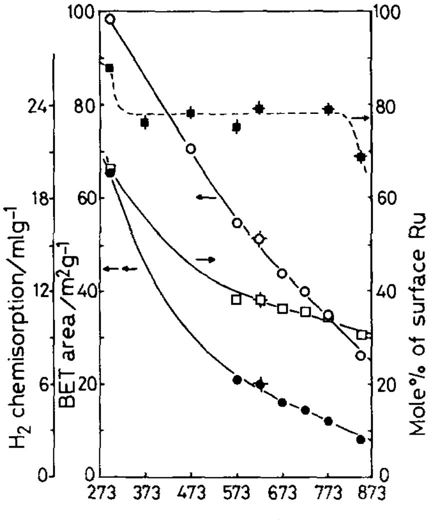

FIG. 5. BET surface area (○, referred to as S_T) and H_2 chemisorption (●, referred to as S_{Ru}) are plotted as a function of treated temperature. Two scales are corresponding on the basis of surface density of Ru (9). □, Surface Ru% (S_{Ru}/S_T). ■, Mole ratio of Ru/(Ru + Al) measured by XPS (MgKα/1254.6 eV).

by heat treatment at 673 K. The rest, 64%, is supposed to be occupied by other elements such as Al and O. Al/Ru ratio by XPS increases from 12/88 to 22/78 at 673 K. These data suggest that surface enrichment of Al occurs during the heating.

XPS spectra of Ru_{3d} after the heat treatment gave very little chemical shift from the metallic state. A part of Ru surface may be oxidized in this state. On the other hand, Al is mostly oxidized by the heat treatment as is seen in Fig. 4. The oxidation occurs in N_2, in He, in H_2O–He, or even in the dynamic vacuum. The oxidation of Al is inferred to be due to water left inside the micropores. A TPD run proved the existence of a water peak at 388 K.

DISCUSSION

Structure of Nonheated Raney Ru

Most of the aluminum in $Al_{13}Ru_4$ or Al_6Ru alloy phase can be dissolved in alkaline solution leaving skeletal Ru metal which is actually composed of microcrystals as are shown in Fig. 2. The microcrystals, having an average diameter of 6 nm (first-order particle), have different lattice directions and are connected with each other forming a skeletal metal particle with a diameter of submicrometer order (second-order particle: Fig. 1b). Furthermore, hundreds of these second-order particles form a cracked metal block as is seen in Fig. 1a (third-order particle: 10 μm in size), and clustered blocks of third-order particles make a visible powder particle. Although the valence state of Al is clear in XPS spectra (mostly reduced before heating), its location cannot be observed by TEM. Reduced Al has been observed in Raney Ni, also (*5*). Aluminium in the bulk phase which is difficult to leach at 373 K is oxidized above 473 K accompanying sintering. The state of metallic Al is supposed in either of the following two cases: (i) unleachable AlRu alloy phase (the lattice structure is too small to be observed by TEM); (ii) interstitial Al dissolved in Ru metal phase as is suggested in the case of Raney Ni (*8*). As is described under Experimental, AlRu phase, if it exists in $Al_{79}Ru_{21}$ alloy, is hard to leach out by the standard condition. Nonsoluble alloy has been observed in Raney Ni, also (*7*). On the other hand, interstitial Al is also probable because lattice imperfections seem to be present in TEM pictures. A small part of Al is inferred to be exposed on the surface. It is oxidized as is shown in Fig. 4.

Structure of Heat-Treated Raney Ru

The crystallite size of Raney Ru, first-order particle, increases from 5 to about 11 nm by heat treatment at 673 K (Fig. 5). A drastic structural change (sintering) is occurring. A slight increase in binding energy of Ru_{3d} might indicate that a small part of Ru itself is oxidized as is shown in the preceding paper (*4*). However, most surface Ru is metallic because (a) hydrogen is chemisorbed and (b) the surface is quite active for IER of dinitrogen (*2*). During the structural change by the heat treatment, Al is oxidized by water left inside the Raney even in a vacuum or N_2 atmosphere, and surface percentage of Ru is decreased. Such a change of Al state is considered to be as follows: (i) Al in AlRu phase is oxidized to Al^{3+} (alumina and/or hydrated alumina) at about 473 K and covers the Ru metal particle; (ii) during the sintering, interstitial Al moves to the surface and is oxidized above 473 K.

CONCLUSIONS

Lattice pictures of TEM show that Raney Ru made from $Al_{79}Ru_{21}$ alloy is composed of microcrystals of Ru metal whose diameter is about 6 nm, which is close to the value (5 nm) by the BET method. Heat treatment at 673 K causes sintering; total (BET) surface area decreases to about 45%; and surface Ru area (assuming $H/Ru = 1$) decreases to about 24%. XPS shows that Al^0 left in the Raney Ru was oxidized to Al^{3+} during the heat treatment, probably due to water left inside the Raney Ru.

These results suggest that a heat treatment causes an enrichment of oxidized Al on the Ru surface during the sintering.

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