

# Preparation and catalytic properties of single phase Ni–Sn intermetallic compound particles by CVD of Sn(CH<sub>3</sub>)<sub>4</sub> onto Ni/silica

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Particles of each of the single phase Ni–Sn intermetallic compounds Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub> have been formed on silica by chemical vapor deposition (CVD) of Sn(CH<sub>3</sub>)<sub>4</sub> onto Ni/SiO<sub>2</sub> and used as catalysts for cyclohexane dehydrogenation.

We have previously reported unique catalytic selectivities of Co or Pt containing intermetallic compounds (IMCs) for the partial hydrogenation of acetylene<sup>1</sup> or buta-1,3-diene;<sup>2</sup> however, their catalytic activities suffered from low specific surface areas. It was reported that Sn–M (M = Rh, Pt, Pd or Ni) bimetallic catalysts were prepared by CVD of organotin complexes on M/SiO<sub>2</sub>.<sup>3–5</sup> Tin species are deposited by the CVD method preferentially onto the particles of these noble metals. In this study, we applied the CVD method to prepare fine particles of single phase Ni–Sn IMCs on SiO<sub>2</sub>, which were found to have unique catalytic selectivities in the dehydrogenation of cyclohexane.

Ni (5 wt%)/SiO<sub>2</sub> was first prepared by an incipient wetness method using Ni(NO<sub>3</sub>)<sub>2</sub> and silica gel (Fuji-Silysia, Caliact 6), followed by reduction at 723 K in H<sub>2</sub>. The average diameter of the Ni particles measured by TEM, XRD and chemisorption of H<sub>2</sub> was about 7 nm. CVD of Sn(CH<sub>3</sub>)<sub>4</sub> (Soekawa Chemicals) onto Ni/SiO<sub>2</sub> was carried out at 373–523 K with flowing H<sub>2</sub> containing 33 Torr of Sn(CH<sub>3</sub>)<sub>4</sub>, followed by hydrogen treatment at 873–1173 K. The samples were dissolved in hydrochloric acid and the amounts of Ni and Sn were determined by ICP. Unsupported Ni–Sn IMCs were prepared by melting a mixture of Ni and Sn powders in an electric furnace at 1730 K under flowing argon, and the resulting ingot was crushed into 25–38 μm particles. A glass circulation system was used for the pretreatment of catalysts with H<sub>2</sub> and subsequent catalytic reactions.

CVD of Sn(CH<sub>3</sub>)<sub>4</sub> was carried out at various temperatures for 1 h to prepare each Ni–Sn IMC (Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub>). Fig. 1 shows the amount of deposited Sn as a function of CVD temperature on Ni/SiO<sub>2</sub> (a) or SiO<sub>2</sub> (b). The amounts of deposited Sn increased with CVD temperature on both supports.

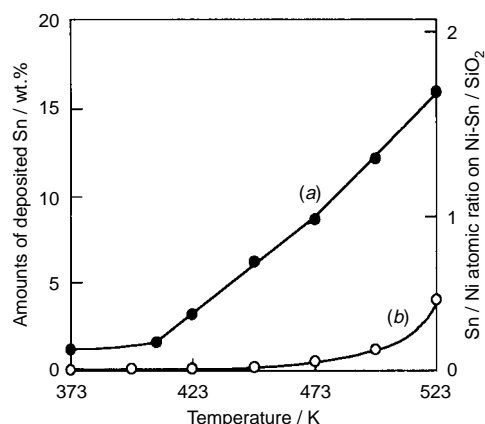


Fig. 1 Effect of CVD temperature on the amount of Sn supported by Sn(CH<sub>3</sub>)<sub>4</sub> on Ni/SiO<sub>2</sub> (a) or SiO<sub>2</sub> (b)

However, the amounts of deposited Sn on Ni/SiO<sub>2</sub> were much larger than those on SiO<sub>2</sub>. In particular, no appreciable deposition of Sn was observed on SiO<sub>2</sub> below 423 K. Sn(CH<sub>3</sub>)<sub>4</sub> was selectively decomposed on Ni particles owing to the high activity of Ni for the hydrogenolysis of Sn(CH<sub>3</sub>)<sub>4</sub>. When CVD of Sn(CH<sub>3</sub>)<sub>4</sub> was carried out onto Ni/SiO<sub>2</sub> at 423, 448 and 498 K, the Ni/Sn atomic ratios of the samples became very close to 3/1, 3/2 and 3/4, respectively. If Sn atoms are deposited on the surface of Ni particles to form a few Sn layers, the Ni/Sn ratio must be much higher than unity. Therefore, during the CVD treatment, some of the deposited Sn atoms will enter into the bulk of the Ni particles after the hydrogenation of Sn(CH<sub>3</sub>)<sub>4</sub> with the evolution of methane. In fact, the X-ray diffraction pattern of Ni–Sn/SiO<sub>2</sub> samples just after CVD included weak peaks of Ni–Sn IMCs in addition to those of Ni metal. Hydrogen treatment after CVD was then performed in order to form single phase Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub> particles.

Fig. 2 shows the X-ray diffraction patterns of the silica-supported Ni–Sn IMC (Ni/Sn = 3/1) after hydrogen treatment at 1173 K for 1 h (a) and of the unsupported Ni<sub>3</sub>Sn powder (b). The supported sample did not show the same diffraction peaks as those of pure Ni supported on SiO<sub>2</sub> (c) and pure Sn supported on SiO<sub>2</sub> (d), but showed almost exclusively peaks at the same positions as those of unsupported Ni<sub>3</sub>Sn. This result confirmed that single phase Ni<sub>3</sub>Sn particles were formed on SiO<sub>2</sub> by the CVD and subsequent hydrogen treatment. Generally, Ni<sub>3</sub>Sn is formed above 1730 K, because the melting points of Ni and Sn are 1730 K and 505 K, respectively. In this study, we succeeded in the formation of single phase Ni<sub>3</sub>Sn particles by hydrogen treatment at much lower temperature after the CVD process.

The XRD measurements showed that single phase Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub> particles were also formed on SiO<sub>2</sub> by hydrogen treatment at 873 and 723 K after CVD at 448 and 498 K, respectively. It is revealed that the lower the Ni/Sn ratio, the

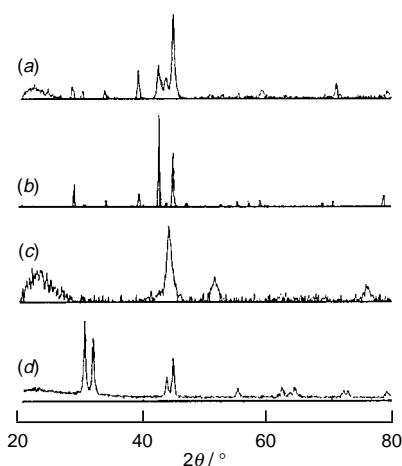
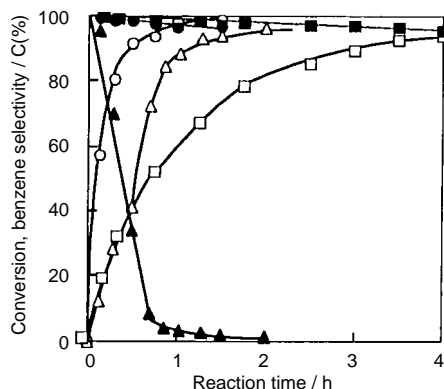


Fig. 2 XRD patterns of supported Ni–Sn IMCs (Ni/Sn = 3/1) on SiO<sub>2</sub> prepared by CVD after hydrogen treatment at 1173 K for 1 h (a), unsupported Ni<sub>3</sub>Sn (b), Ni/SiO<sub>2</sub> prepared by the incipient wetness method after reduction (c) and Sn/SiO<sub>2</sub> prepared by CVD of Sn(CH<sub>3</sub>)<sub>4</sub> on SiO<sub>2</sub> (d)



**Fig. 3** Conversion of cyclohexane (open symbols) and selectivity to benzene (closed symbols) at 823 K on 0.05 g of  $\text{Ni}_3\text{Sn}/\text{SiO}_2$  (O, ●), 0.5 g of unsupported  $\text{Ni}_3\text{Sn}$  (■, □) and 0.5 g of unsupported Ni ( $\Delta$ , ▲)

lower the temperature of hydrogen treatment necessary for the formation of single phase Ni–Sn IMCs. The broad diffraction peaks of supported  $\text{Ni}_3\text{Sn}$  [Fig. 2(a)] suggest that the  $\text{Ni}_3\text{Sn}$  particles have much smaller diameters than those of unsupported  $\text{Ni}_3\text{Sn}$ . The particle sizes of  $\text{Ni}_3\text{Sn}$ ,  $\text{Ni}_3\text{Sn}_2$  and  $\text{Ni}_3\text{Sn}_4$  determined by XRD were about 18, 12 and 12 nm, respectively. These values correspond roughly with the diameters estimated by TEM.  $\text{Ni}_3\text{Sn}$  particles had the largest diameter as these were formed at the highest temperature in the hydrogen treatment. The use of  $\text{Ni}/\text{SiO}_2$  with smaller Ni particles would lead to Ni–Sn IMCs with smaller particles. It is concluded that all kinds of single phase Ni–Sn intermetallic compounds are obtained on silica by the CVD of  $\text{Sn}(\text{CH}_3)_4$  and subsequent hydrogen treatment at temperatures much lower than the melting point of Ni.

The reaction profiles of cyclohexane in hydrogen at 823 K on silica-supported and unsupported  $\text{Ni}_3\text{Sn}$  IMCs and pure Ni catalysts are shown in Fig. 3. The initial molar ratio of hydrogen

to cyclohexane was 6. On the unsupported Ni, benzene was formed as an initial product and was then converted completely into methane in 2 h. On the other hand, the unsupported  $\text{Ni}_3\text{Sn}$  catalyst scarcely converted the initially produced benzene into methane even at higher cyclohexane conversions, though the activity was lower than Ni. The high selectivity to benzene was revealed to be the characteristic catalysis of  $\text{Ni}_3\text{Sn}$  IMC, which would be due to the weaker adsorption of benzene on  $\text{Ni}_3\text{Sn}$  than on Ni. Silica-supported  $\text{Ni}_3\text{Sn}$  showed almost the same selectivity as the unsupported  $\text{Ni}_3\text{Sn}$ . This implies that no pure Ni particles that are too small to be detected by XRD exist on the silica-supported catalyst.  $\text{Ni}_3\text{Sn}$  has the composition richest in Ni among the Ni–Sn IMCs studied. Therefore, it is also indicated that there would be few  $\text{Ni}_3\text{Sn}_2$ ,  $\text{Ni}_3\text{Sn}_4$  or Sn small particles on the silica gel because the Ni/Sn atomic ratio of this sample (3.1/1) was very close to the stoichiometry of  $\text{Ni}_3\text{Sn}$ . Comparing the activity per weight of  $\text{Ni}_3\text{Sn}$ , the supported  $\text{Ni}_3\text{Sn}$  was 500 times more active than the unsupported  $\text{Ni}_3\text{Sn}$ , though the activities of both catalysts per surface area of  $\text{Ni}_3\text{Sn}$  were almost the same. It is clear that the CVD method has resulted in the preparation of silica-supported Ni–Sn IMC catalysts with higher activities than the unsupported ones, owing to the much higher specific surface areas, with retention of the high selectivity to benzene.

#### Notes and References

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