Ti–Pt intermetallic compound catalysts more active than Pt for hydrogen dissociation and ethylene hydrogenation

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The intermetallic compound, $TiPt_3$, showed much higher catalytic activity than pure Pt catalyst for H_2–D_2 equilibration and ethylene hydrogenation, whereas Ti_3Pt only catalyzed the former reaction with a similar activity to $TiPt_3$.

Intermetallic compounds (IMCs) have unique crystal structures different from those of the component metals. However, the catalytic properties of IMCs have been scarcely studied except for those of so-called hydrogen storage alloys.[1] We have already reported unique catalytic selectivities of some IMCs, such as Co–Ge,[2] Pt–Ge[3,4] and Ni–Sn[5,6] compounds, in hydrogenation and dehydrogenation reactions. For example, Pt_3Ge gives butenes with high selectivity in the hydrogenation of buta-1,3-diene.[3] However, the activity of the above IMCs is always much lower than that of the pure metals, Co, Pt and Ni, because of their very low activity for the dissociation of hydrogen. For example, H_2–D_2 equilibration proceeds on Pt at 298 K, whereas a higher temperature of 523 K is necessary for Pt_3Ge to obtain a similar reaction rate.[3] The low activity of IMC catalysts probably results from their surface structure, that is, the active transition metal atoms are separated by the other element, *e.g.* Ge and Sn, which are almost inert towards the hydrogen dissociation reaction. However, IMCs between two transition metal elements might be expected to be active catalysts for reactions with hydrogen. In this study, we examined the catalytic activity of Ti–Pt IMCs for H_2–D_2 equilibration and the hydrogenation of ethylene and found that they had much higher activity than pure Pt catalyst.

IMC catalysts were prepared by arc melting a mixture of titanium (Soekawa Chemical, 99.9%) and platinum (Tanaka Kikinzoku, 99.95%) under an argon atmosphere. The resultant ingots were crushed in air and filtered into particles with diameters below 25 µm. Powders of pure Ti (Nilaco, 99.98%) and pure Pt (Nilaco, 99.98%) were also filtered into particles with similar diameters. The crystal structure of the IMCs was identified by powder X-ray diffraction (Rigaku, RINT 2400). Single-phase crystals of $TiPt_3$ and Ti_3Pt IMCs were obtained from mixtures with Ti/Pt atomic ratios of 1:3 and 3:1, respectively. The crystallinity of the TiPt IMC obtained from the mixture with Ti:Pt = 1 was not as good as those of $TiPt_3$ and Ti_3Pt. Therefore, we only examined the catalytic properties of $TiPt_3$ and Ti_3Pt as IMC catalysts. H_2–D_2 equilibration was carried out with a glass flow and circulation system connected with a quadrupole mass spectrometer (Spectra International, MICROVISION). Before each reaction, the catalyst was pretreated 'reduced' with flowing hydrogen at a specific temperature for 1 h and evacuated at 298 K for 10 min. A mixture of H_2 (6.6 kPa) and D_2 (6.6 kPa) was then circulated through the catalyst at the reaction temperature of 195 K and the formation of HD was monitored by mass spectrometry. Hydrogenation of ethylene was carried out with the same reaction apparatus. After the same pretreatment of the catalysts, a mixture of ethylene (2.7 kPa) and H_2 (13 kPa) was circulated through the catalyst at the reaction temperature of 251 K. The total pressure was monitored to measure the extent of reaction.

To measure the catalytic activity for the dissociation of hydrogen, the H_2–D_2 equilibration was carried out on $TiPt_3$, Ti_3Pt, Pt and Ti. Fig. 1 shows the fraction of HD in hydrogen as a function of reaction time. On Pt powder catalyst reduced at 573 K, the fraction of HD gradually increased with reaction time. When Pt was reduced at 873 K, the rate of HD formation drastically decreased owing to the agglomeration of the fine powder. It is clear that the surface of the Pt powder is reduced at 573 K and that metallic Pt catalyzed the dissociation of hydrogen at 195 K. On the other hand, Ti powder reduced at 573–1173 K did not catalyze hydrogen dissociation, probably because Ti is not reduced even at 1173 K.

For $TiPt_3$ reduced at 873 K, the rate of HD formation was much higher than that on Pt. SEM images showed that the Pt powder reduced at 573 K consisted of particles with diameters of *ca*. 3–5 µm partially agglomerating to form lumps of 10–25 µm diameter. On the other hand, the reduced $TiPt_3$ consisted of particles with diameters of 10–25 µm. From these observations, the specific surface area of $TiPt_3$ must be lower than that of Pt. Therefore, it is concluded that $TiPt_3$ has higher activity towards hydrogen dissociation than pure Pt. The higher activity of IMC catalysts than their component metals has not previously been reported in the H_2–D_2 equilibration.[2,3,5] The reduction temperature affected the activity of $TiPt_3$ *i.e.* a lower reaction rate was observed when $TiPt_3$ was reduced at 573 or 1173 K. At 573 K, Ti atoms on the surface of $TiPt_3$ would not be reduced completely. XPS measurements would clarify the oxidation state of surface Ti atoms. At 1173 K, $TiPt_3$ particles agglomerated to form large lumps, resulting in lower activity.

The other IMC, Ti_3Pt, reduced at 873 K, also exhibited a higher rate of HD formation than Pt. Its activity was similar to that of $TiPt_3$ reduced at 873 K. It is clear that Ti_3Pt also has a higher activity than Pt towards the dissociation of hydrogen. For Pt–Ge[3] and Ni–Sn[5] IMCs, the activity for the H_2–D_2 equilibration decreases with a decrease in content of Pt and Ni *i.e.* PtGe
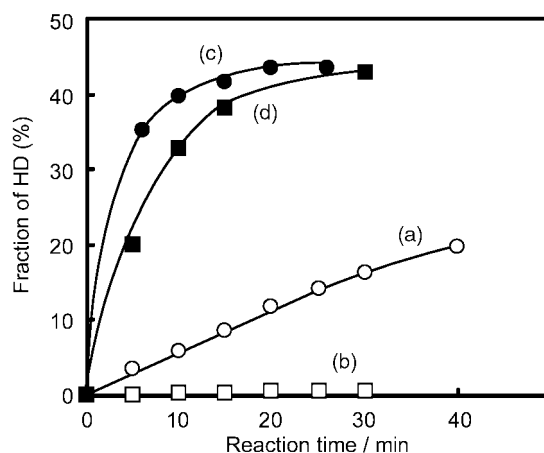

Fig. 1 H_2–D_2 equilibration at 195 K on Pt (a), Ti (b), $TiPt_3$ (c) and Ti_3Pt (d) reduced at 573 K (Pt), 873 K ($TiPt_3$ and Ti_3Pt) and 1173 K (Ti).
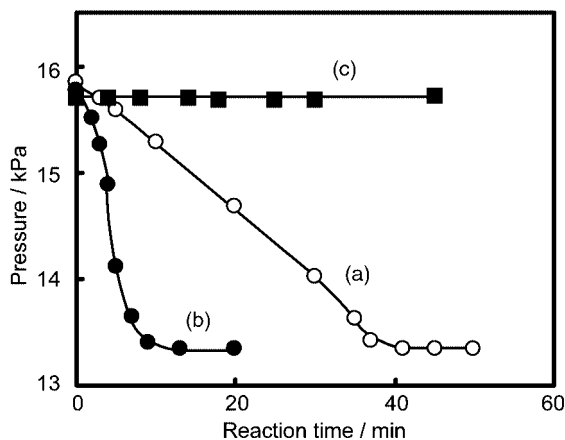
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Fig. 2 Hydrogenation of ethylene at 251 K on Pt (a), TiPt$_3$ (b) and Ti$_3$Pt (c) reduced at 573 K (Pt) and 873 K (TiPt$_3$ and Ti$_3$Pt).

and Ni$_3$Sn$_4$ have much lower activity than Pt$_3$Ge and Ni$_3$Sn, respectively. Ge and Sn would retard the activity by reducing the number of adjacent Pt or Ni atoms. The comparable activity of Ti$_3$Pt to that of TiPt$_3$, which has a nine times larger Pt:Ti atomic ratio, suggests that a pair of Ti and Pt atoms constitutes an active site for the hydrogen dissociation. Reduction of Ti$_3$Pt at 573 and 1173 K resulted in low activity probably because of the same reasons as for TiPt$_3$.

On the basis of the above it is expected that TiPt$_3$ and Ti$_3$Pt would have higher activity than Pt for the hydrogenation of ethylene. Fig. 2 shows the change in total pressure with reaction time during the hydrogenation of ethylene at 251 K. On Pt reduced at 573 K, the pressure decreased with reaction time, indicating the consumption of hydrogen to form ethane and reached a steady state after 40 min of reaction. The decrease in pressure (*ca.* 2.5 kPa) suggests the complete conversion of ethylene into ethane. This was confirmed by gas-phase analysis with a gas chromatograph. On TiPt$_3$ reduced at 873 K, the pressure decreased more rapidly than that on Pt and gas-phase analysis revealed that the hydrogenation was complete in 10 min. This indicates that TiPt$_3$ has higher activity than Pt also for the hydrogenation of ethylene, as expected from its higher activity for the dissociation of hydrogen. On the other hand, Ti$_3$Pt reduced at 873 K did not catalyze the hydrogenation of ethylene at all, though it showed similar activity to TiPt$_3$ for the dissociation of hydrogen. In this case, Ti–Pt pair sites are not able to activate both ethylene and hydrogen.

The higher activity of Ti–Pt IMC catalysts than Pt suggests the possibility of other IMCs consisting of two transition metal elements of being highly active catalysts for hydrogenation and dehydrogenation reactions.

Notes and references

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