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# Preparation and catalytic properties of fine particles of Pt-Ge intermetallic compound formed inside the mesopores of MCM-41

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ABSTRACT

Fine particles of Pt-Ge intermetallic compound were prepared by using mesoporous silica MCM-41 as a support and examined as a catalyst for $H_2$–$D_2$ equilibration and the hydrogenation of acetylene to clarify the catalytic properties of single-phase intermetallic compound with nano-order particle size. The mesopore structure of MCM-41 was not affected extensively by the introduction of Pt and Ge. Pt-Ge particles on MCM-41 gave very narrow particle-size distribution around 1.5 nm, suggesting the presence of Pt-Ge particles inside the mesopores of MCM-41, whereas those prepared on silica gel had the wide distribution of 1–6 nm. Though the Pt-Ge particles on MCM-41 were too small to identify their crystal phase by XRD, IR spectra of adsorbed CO indicated the presence of intermetallic phase, probably PtGe. Pt-Ge/MCM-41 showed lower catalytic activity than PtGe/$SiO_2$ for $H_2$–$D_2$ equilibration at 77 K and an induction period was observed for the former catalyst. The physically adsorbed hydrogen molecules may hinder the diffusion of HD through the mesopores. Pt-Ge/MCM-41 showed higher selectivity to ethylene than Pt/MCM-41 in the hydrogenation of acetylene, which again indicates the formation of PtGe intermetallic compound.

## 1. Introduction

Intermetallic compounds (IMCs) are the stoichiometric compounds between two or more metal elements. As compared with usual alloy, which is a solid solution having the same crystal structure as that of either component metal, various IMCs have their specific crystal structures different from those of their component metals. The specific crystal structure and the combination of two elements sometimes give IMCs unique bulk properties, such as super conductivity, hydrogen storage ability, shape memory effect, etc. However, their catalytic properties, one of the important surface natures, have never been studied sufficiently. We have studied the catalytic properties of single-phase IMCs as compared with those of pure metals [1]. In the hydrogenation of acetylene, CoGe [2], $Ni_3Sn$ and $Ni_3Sn_2$ [3] have higher selectivity to ethylene than Co and Ni. Recently, Studt et al. [4] explained the higher ethylene selectivity of NiZn than Ni by the change in heats of adsorption of hydrocarbons. Kovnir et al. [5] have reported that the high ethylene selectivity of PdGa is attributable to the isolation of surface Pd atoms by the formation of IMC with Ga. We have also reported that $Pt_3Ge$ has higher selectivity to butenes than Pt in the hydrogenation of 1,3-butadiene [6]. $Pt_3Ti$ shows higher activity than Pt for $H_2$–$D_2$ equilibration and the hydrogenation of ethylene [7]. $CoHf_2$ shows high activity and stability in the $CO_2$ reforming of methane [8]. Tsai et al. [9] reported the similarity in catalytic activity of PdZn to that of pure Cu in the steam reforming of methanol. However, these catalysts, which consisted of large grains of IMCs with the size of 10–50 μm, showed very low specific activity compared with supported metal catalysts containing nano-order metal particles.

To obtain highly active IMC catalysts, fine particles of IMC have to be prepared by fixing them on supports. Though many researchers have already reported that Pt-Sn IMC phases, for example, $PtSn_4$, PtSn, and $Pt_2Sn$ [10], are present in supported Pt-Sn bimetallic catalysts used for petroleum reforming, metallic species are always the mixture of two or more metals, alloys, IMCs and even oxidized species. Therefore, the intrinsic catalytic properties of the specific Pt-Sn IMC have never been clarified. Some researchers have tried to prepare single-phase IMC particles on oxide supports. Iwasa et al. formed PdZn particles by reducing Pd/ZnO and found them active for the steam reforming of methanol [11]. Llorca et al. have prepared PtSn on $SiO_2$ by successive impregnation method [12]. We have prepared single-phase IMCs on the surface of silica gel [1]. First, each single-phase Ni-Sn IMC, $Ni_3Sn$, $Ni_3Sn_2$ and $Ni_3Sn_4$, was prepared by chemical vapor deposition (CVD) of $Sn(CH_3)_4$ onto Ni/$SiO_2$ under various conditions [13]. A similar CVD method has been applied to obtain RuTi/$SiO_2$ [14,15], $Pd_3Bi$/$SiO_2$ [16] and $Pt_3Sn$/H-SAPO-11 [17]. However, the particle size of these IMCs was not uniform. For the definite characterization and assignment of

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active sites, it will be better to obtain single-phase IMC particles with a uniform diameter. Moreover, the metal particles in uniform size would prove the relationship between the coordination number and catalytic properties, especially in so-called structure sensitive reactions. The role of corner and edge atoms has been reported for pure metal catalysts, such as Ni [18], Pt [19,20] and Rh [21].

We have previously reported [22] the preparation of Ni-Ge IMC particles inside the mesopores of MCM-41, which is a mesoporous silica having orderly hexagonal structure with a homogeneous pore diameter. Fine particles of single-phase $Ni_3Ge$ were formed predominantly inside the mesopores through the successive loadings of Ni by template ion-exchange [23] and Ge by CVD. $Ni_3Ge$/MCM-41 thus prepared gave higher intrinsic activity than Ni/MCM-41 and $Ni_3Ge/SiO_2$ for $H_2$–$D_2$ equilibration and acetylene hydrogenation. In this study, we applied the above strategy to Pt-Ge IMCs because Pt is known to be extremely active compared with Ni for many reactions. The objectives of this study are to obtain uniform particles of Pt-Ge IMC inside the orderly mesopores of MCM-41 and clarify their catalytic properties.

## 2. Experimental

### 2.1. Catalyst preparation

MCM-41 mesoporous silica was synthesized hydrothermally [24]. The surfactant of cetyltrimethylammmonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, 27 g) was dissolved into 270 g of pure water at 313 K. Coloidal silica (Nissan Chemical Ind., Snowtex 20, 159 g) and a 4.2% aqueous solution of sodium hydroxide (142 g) were dropped into the surfactant solution and the mixture was stirred for 1 h. The mixture was transferred into an autoclave and heated at 413 K for 48 h without stirring. The solid obtained was filtered, washed with pure water, dried at 353 K and calcined in air at 813 K for 10 h to obtain MCM-41.

Platinum was introduced by an ion-exchange technique [25] into MCM-41. MCM-41 (2.0 g) was put into an aqueous solution of ammonia ($3 \times 10^{-4}$ M) and the mixture was stirred for 1 h to transform SiOH into $SiONH_4$. The solid was filtered, washed with pure water and dried at 353 K to obtain $NH_4^+$-MCM-41. Tetraammineplatinum(II) acetate (N.E. Chemcat Corp., 0.047 g) was dissolved into 100 g of pure water and the solution was added to $NH_4^+$-MCM-41. After stirring it at 298 K for 1 h, the solid was filtered, washed with pure water, dried at 353 K and calcined in air at 473 K for 8 h to obtain $PtO_x$/MCM-41. The ammonium ion-exchange and Pt loading were repeated similarly onto $PtO_x$/MCM-41. Finally, Pt/MCM-41 was obtained through the reduction with flowing hydrogen (60 ml $min^{-1}$) at 473 K for 1 h.

Introduction of germanium was carried out by the CVD method in a similar manner to the preparation of $Ni_3Ge$/MCM-41 [22]. Pt/MCM-41 (0.40 g) was put into a quartz reactor (17 mm ID) and reduced in flowing hydrogen (60 ml $min^{-1}$) at 473 K for 1 h. After the temperature was set to 423 K, the vapor of $Ge(CH_3)_4$ saturated at 273 K in flowing hydrogen (30 ml $min^{-1}$) was introduced onto Pt/MCM-41 for 1 h as CVD treatment. The sample was further treated with flowing hydrogen (60 ml $min^{-1}$) at 873 K for 1 h to give Pt-Ge/MCM-41.

As a reference catalyst, Pt-Ge/$SiO_2$ was prepared stepwise through Pt/$SiO_2$ using silica gel (Caliact G6, Fuji Silysia). First, Pt(1 wt%)/$SiO_2$ was prepared by a usual pore-filling impregnation with an aqueous solution of tetraammineplatinum(II) acetate, followed by the calcination in air at 673 K and the reduction with flowing hydrogen at 773 K. Ge was then introduced by the CVD method in a similar manner to the Pt-Ge/MCM-41 preparation. The temperature of Pt/$SiO_2$ was set to 553 K during the CVD for 1 h.

### 2.2. Characterization

The structural information on MCM-41-supported catalysts was obtained by powder X-ray diffraction (XRD, Rigaku, RINT2400) and small angle X-ray scattering (SAXS, Rigaku, NANO-Viewer system) with Cu Kα X-ray. Nitrogen adsorption measurements were also conducted using Coulter SA-3100. The crystal structure of supported metal particles was examined also by XRD. TEM images were obtained by a Jeol JEM-2010F microscope. The bulk composition of prepared catalysts was determined by ICP (Rigaku, JY38) after dissolving samples with HF solution and aqua regia.

The amount of hydrogen adsorbed at 195 K was measured in a similar manner to the method reported by Freni et al. [26]. The sample (50 mg) was put into a quartz tube and reduced by flowing hydrogen (60 ml $min^{-1}$) for 1 h at 473 K for Pt/MCM-41, 773 K for Pt/$SiO_2$ and 873 K for Pt-Ge/MCM-41 and Pt-Ge/$SiO_2$. After hydrogen was purged by flowing argon for 10 min, the sample was cooled to 195 K. A pulse of $H_2$ ($5.0 \times 10^{-9}$ mol) diluted by argon was introduced with the outlet gas monitored by a thermal conductivity detector (TCD). The pulses were repeatedly introduced onto the sample to reach the adsorption equilibrium. Then, the sample was heated abruptly by a heating gun and the total amount of evolved $H_2$ was measured by the TCD. The amount of CO adsorbed at 298 K was measured by a usual pulse technique. Samples were pretreated by hydrogen at the same temperatures as those for the pretreatment for $H_2$ adsorption measurements. Then hydrogen was purged by flowing helium. A pulse of CO ($5.0 \times 10^{-9}$ mol) diluted by helium was introduced repeatedly at 298 K to reach the equilibrium to obtain the amount of irreversibly adsorbed CO.

IR spectra of adsorbed CO were measured with a JASCO FT/IR-430 spectrometer in its transmission mode. A self-supporting wafer (ca. 10 mg $cm^{-2}$) of catalyst was put in a quartz cell having $CaF_2$ windows. After the reduction in circulating hydrogen (15 kPa) at 673 K (473 K for Pt/MCM-41) for 1 h and the evacuation at the same temperature, the sample was cooled in vacuo to 298 K. CO (1.5 kPa) was introduced at 298 K and a spectrum was recorded with 0.5 $cm^{-1}$ resolution and 50 scans. Spectra were further obtained after the evacuation at various temperatures.

### 2.3. Catalytic reactions

$H_2$–$D_2$ equilibration was carried out using a glass circulation system connected to a quadrupole mass-spectrometer (Canon Anelva, M-101QA-TDM). Before each reaction, 20 mg of catalyst was reduced with 15 kPa of circulating $H_2$ for 1 h at 473 K for Pt/MCM-41, 773 K for Pt/$SiO_2$ and 873 K for Pt-Ge/MCM-41 and PtGe/$SiO_2$, followed by the evacuation at the reduction temperature. A mixture of $H_2$ (6.7 kPa) and $D_2$ (99 atom%, 6.7 kPa) was circulated through the catalyst at 77 K. The extent of the equilibration reaction was monitored by the change in the fraction of HD in hydrogen, $HD/(H_2 + HD + D_2)$.

The hydrogenation of acetylene was carried out using a continuous flow reaction system under atmospheric pressure. The catalyst (20 mg) was placed in a tubular quartz reactor of 17 mm ID. Prior to the catalytic run, the catalyst was reduced with flowing hydrogen for 1 h at the same temperatures as those in $H_2$–$D_2$ equilibration. The reaction was started at 473 or 573 K by supplying a reactant gas composed of $C_2H_2$ (14 kPa), $H_2$ (29 kPa) and He (balance) with a total flow rate of 28 ml $min^{-1}$. Gaseous products were analyzed by using an FID gas chromatograph (Shimadzu, GC-14B) with a column of CP8567 (Varian). The selectivity to ethylene was calculated based on the total amount of carbon in acetylene converted into ethylene.