Preparation of Metal-Oxide Composite Catalysts from Homogeneous Phase

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Supported metal catalysts have been used for various chemical processes. Catalytic combustion has been considered as clean emission less method to burn fuel and ha Pd/Al_2O_3 is the most standard catalyst for combustion of methane where the alumina support provides large surface area for deposition of fine metal particles. Pd/SnO_2 was found to be more active than the conventional catalyst, though the specific surface area of SnO_2 is lower than that of alumina. The microstructure of metal-oxide was quite different between the Pd/Al_2O_3 and Pd/SnO_2 catalysts. The X-ray diffraction pattern and chemisorption behavior of CO and oxygen was also contrasting between the two catalysts. This implies that strong chemical interaction between support and Pd for the Pd/SnO₂. Deposition of metallic component from homogeneous phase was also effective for preparation of Ni catalyst from a hexaaluminate type oxide and that of Cu catalyst from a spinel type oxide. The investigation on the process of formation of metal deposits fro the homogeneous phase should be important for improving catalytic performance via metal-support interaction.

Key words: supported metal catalyst, catalytic combustion, partial oxidation, shift reaction

1. Introduction

Supported metal catalysts have been used for environmental protection and energy conversion processes. For example, catalytic combustion is free from NO_x emission because of the replacement of flameless combustion with surface catalytic oxidation for radical flame reaction [1-3]. Thermal NO_x which is formed via radical chain reaction in the high temperature flame is not produced during surface catalytic oxidation. Catalytic combustion has been employed not only for combustors but also removal of dilute volatile organic compounds in the vapor phase. The low temperature combustion can be initiated by the surface reaction over supported noble metal catalysts such as Pd/alumina.

The fuel cells have been considered as efficient power generation system in the near future. The system consists of hydrogen production, purification, and electrochemical reaction processes by using variety of catalytic reactions; i.e., steam reforming of hydrocarbons and alcohols, shift reaction to reduce CO, selective CO removal, and electrode catalysts. All these catalytic reactions have been carried out by use of supported metal catalysts.

Porous oxide support has been employed to attain high dispersion of fine metallic deposits of the active components in the catalysts. The oxide supports possess large surface areas to provide large reaction

surface of the active component. In addition to this physical effect to disperse metal particles, the chemical interaction with support often affects the activity and selectivity in the catalytic reaction. The supported catalysts have been generally produced via impregnation process in which solid support oxide is immersed in the solution of metal component. The catalysts were produced by drying and calcination after the impregnation. Alternative preparation route for metal catalysts is to starts from homogeneous oxide phase followed by phase separation and deposition of metal by reduction of active component. At the initial stage of metal deposition, strong chemical interaction between metal and support is expected. In this article, several examples of the preparation of metal catalysts from homogeneous oxide phase have been demonstrated. The interaction affects the activity of the catalysts.

2. Experimental - Sample preparation

 SnO_2 powders were obtained from commercial powder and hydrolysis of $SnCl_4$ and subsequent heating. The powders of oxides were precalcined at 500-1400°C for 5 h in air unless otherwise noted [4]. Palladium catalysts were prepared by the impregnation method using the SnO_2 powder and a Pd salt; Pd(CH₃COO)₂. The loading of Pd in its metallic state was 1-10wt% of the catalysts. The catalysts were dried and subsequently calcined in air at 600-1000°C for 5 h. Specific surface area of catalysts was determined by the BET method using nitrogen adsorption.

The BaNiAl₁₁O_{19- α} catalyst was prepared by the alkoxide method. The calculated amounts of barium and Al[OCH(CH₃)₂]₃ were added to 2-propanol and the

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mixture was stirred at 80°C in N₂ flow to avoid contact with moisture. A precipitate was obtained by adding the calculated amount of aqueous Ni(NO₃)₂ solution. The precipitate was dried at 120°C for 12 h, pre-calcined at 500°C for 1h, and then finally calcined at 1200°C or 1400°C for 5 h in air.

Copper manganese oxide catalysts were prepared by the coprecipitation method., In the preparation of Cu-Mn spinel oxides, aqueous ammonia and a solution of nitrates were added. The resultant gel was dried in air at 100°C for 12 h and precalcined at 400°C for 1 h to remove nitrate residue. Then the dried powder was calcined at 900°C or other temperatures for 10 h.

3. Results and discussion

3.1. Catalytic combustion of methane over supported Pd catalysts

Many studies have dealt with low-temperature methane combustion based on Pd/Al₂O₃ [1,2], since alumina has been regarded as the most popular support material for precious metals because of its high surface area and chemical stability. Table 1 summarizes the catalytic oxidation of methane over Pd/ SnO2 and conventional supported Pd catalysts [3-7]. A Pd/SnO₂ catalyst was found to have an excellent activity for the complete oxidation of methane, though the BET surface area of the SnO₂ support was far smaller than that of Al₂O₃ as shown in Table 1. Our previous study has revealed that the PdO phase was well-dispersed on the SnO₂ support, and that the PdO phase was stabilized at higher temperatures than bulk PdO without support materials. Therefore, it is desirable to further enhance the catalytic activity bv optimizing the preparation procedures of Pd/SnO₂ after clarifying the effects of the starting materials and heat treatment.

The X-ray diffraction pattern of Pd/ SnO_2 prepared by the coprecipitation process is shown in Fig. 1. The width of the SnO_2 line suggests that the crystallite size of SnO_2 became smaller with an increase in Pd content. Another explanation of the line broadening is the poor crystallinity of SnO_2 due to strong chemical interactions with Pd. Partial dissolution of the Pd species in the SnO_2 lattice may introduce a number of defects. Because of the defective structure, small particle size, and well mixed Pd and SnO_2 . The microstructure of metal-oxide was quite different between the Pd/Al₂O₃ and

 Pd/SnO_2 catalysts. TEM observation of the Pd/SnO_2 suggested that a core of crystalline Pd/SnO_2 was covered with a surface Pd layer for the Pd/SnO_2 catalyst.

As shown in Table 2, Pd/SnO_2 adsorbed very little CO. These phenomena had been interpreted as the formation of Pd-Sn alloy of surface of Pd particles or as the strong interaction between dispersed Pd and SnO_2 [2]. Therefore, it is concluded that the metallic Pd on SnO_2 hardly adsorbs CO when they are in a strong interacting state. As mentioned above, microstructure and

Table 1 Surface area and catalytic activity of $1wt\% Pd/Al_2O_3$ and $1wt\% Pd/SnO_2$

Catalyst	Surface area	Catalytic Activity /°C				
	$m^2 g^{-1}$	T10 ^{b)}	T30 ^{b)}	T70 ^{b)}	T90 ^{b)}	
Pd/Al ₂ O ₃	109	365	400	445	495	
Pd/ SnO ₂	6.4	305	345	390	440	

a) Calcined at 800°C for 5 h.

b) Temperature at which methane conversion levels are 10%, 30%, 70%, and 90%, respectively.

Reaction condition: CH₄, 1 vol%; air, 99 vol%; space velocity, 48000 h^{-1} .



Fig. 1 XRD profiles of PdO-SnO₂ mixed oxides with various PdO contents

chemisorption behavior was contrasting between the Pd/Al_2O_3 and Pd/SnO_2 catalysts because of the strong chemical interaction for the Pd/SnO_2 catalysts.

3.2 Partial oxidation hydrocarbons to produce hydrogen over hexaaluminate based catalysts

Partial oxidation of methane has been studied as a production process of synthetic gas, which is further converted into chemical products like liquid fuels or hydrocarbons [8-11].

Table 2. Physical property of PdO/SnO₂ and PdO-SnO₂ a) The amount of CO adsorbed was measured after reduction at 350°C; n.a. means no adsorption was observed.

Catalyst	Pd contents (mmol/g)	BET surface area (m ² /g)	The amount of CO adsorbed ^a (mmol/g)	Particle diameter of PdO(-SnO ₂) (nm)	Crystallite size of PdO-SnO ₂ (nm)
SnO ₂	0	4.0	n.a.	230	48.8
1.1 wt% PdO-SnO ₂	0.09	28	n.a.	32.8	12.0
5.7 wt% PdO-SnO ₂	0.47	62	n.a.	13.2	7.9
11 wt% PdO-SnO ₂	0.93	96	n.a.	9.2	5.7
22 wt% PdO-SnO ₂	1.82	113	n.a.	7.6	2.4

$$CH_4 + 1/2 O_2 \rightarrow CO + H_2 \tag{1}$$

The system with partial oxidation can quickly start-up without heat supplied from the surroundings. As the hydrogen production by partial oxidation, three Ni catalysts were tested for partial oxidation of methane [12,13]. The activity of conventional supported Ni/Al₂O₃ catalyst was compared with those of Ni catalysts prepared via reduction of LaAl_{5/6}Ni_{1/6}O₃ and BaNiAl₁₁O_{19- $\alpha}$ after calcination [14].}

The Ni/Al₂O₃ sample consisted of the NiO and Al₂O₃ phases. The phase transition of alumina from γ -Al₂O₃ to α -Al₂O₃ proceeded above 1200°C. The LaAl_{5/6}Ni_{1/6}O₃ catalysts crystallized in the perovskite phase. Calcination at higher temperature gained the intensity of the lines in the diffraction patterns of Ni/Al₂O₃ and

LaAl_{5/6}Ni_{1/6}O₃. As shown in Fig. 2, the phase of $BaNiAl_{11}O_{19-\alpha}$ (800°C) was amorphous and the BaNiAl11O19-a (1200°C) catalyst consisted of three phases of B-Al₂O₃, hexaaluminate, and spinel. After calcination at 1400°C, the catalyst was changed into uniform hexaaluminate phase, accompanied with the disappearance of the spinel phase. The calcination of LaAl_{5/6}Ni_{1/6}O₃ and BaNiAl₁₁O_{19- α} never led to precipitation of α -Al₂O₃. This implies that the of formation the perovskite or hexaaluminate single phase prevents the formation of the α -Al₂O₃ phase. These results indicate that the hexaaluminate-type catalysts retain comparably high BET surface area (24 m² g⁻¹ after heating at 1200°C) and stable structure at high temperatures.

Fig. 3 shows the catalytic activity for partial oxidation of methane at high space velocity (SV) of 120,000 l kg⁻¹ h⁻¹ over Ni/ Al₂O₃, BaNiAl₁₁O_{19- $\alpha}$ and LaAl_{5/6}Ni_{1/6}O₃. The line in the figure is}

the equilibrium conversion of methane for reaction (1). The activity of the LaAl_{5/6}Ni_{1/6}O₃ catalysts was the lowest among the catalysts investigated. It is suggested that the perovskite-type catalysts are to be calcined at low temperatures, since the activity of LaAl_{5/6}Ni_{1/6}O₃ was significantly lowered with an increase in temperature from 850°C to 1200°C due to sintering and decrease in surface area. The Ni/Al₂O₃ (1400°C) and BaNiAl₁₁O_{19- α} (1400°C) catalysts demonstrate the highest activity. The CH₄ conversion of Ni/Al₂O₃ (1000°C) was high at 700-800°C, whereas it steeply decreased below 600°C. The catalytic activity for partial oxidation of methane was measured in the course of decreasing reaction temperature from 800°C to 250°C after reduction. Therefore, the steep decrease in activity of Ni/Al₂O₃ (1000°C) may result from coke deposition, which becomes thermodynamically favorable with



Fig. 2 XRD patterns of BaNiAl₁₁O_{19- α} calcined at 800°C, 1200°C, and 1400°C.

decreasing temperature. The high activity of BaNiAl₁₁O_{19- $\alpha}$ (1400°C) catalyst could result from high dispersion of Ni, since the fine metallic particles was deposited from the homogeneous hexaaluminate phase under reducing atmosphere.}

3.3. Shift reaction with Cu based spinel

Water gas shift reaction (WGSR) has been investigated and used in industry [15-18]:

$$H_2O + CO \rightarrow H_2 + CO_2. \tag{2}$$

Hence, the WGSR is desirable for CO removal from reformed fuels containing high concentrations of CO. The copper based catalysts, e.g., Cu/ZnO/Al₂O₃ have been used for WGSR, but the catalysts were deactivated by H_2O at low temperatures. We have found out that the Cu-Mn spinel oxide showed excellent WGSR activity comparable to that of conventional Cu/ZnO/Al₂O₃ despite its low surface area [19-21]. The Cu-Mn spinel oxide with low surface area was investigated as promising catalyst for the WGSR.

The Cu-Mn oxide with [Cu]/[Mn]=1/2 were calcined at different temperatures $X^{\circ}C$, which is denoted as CuMnX. The sample consisted of major Cu₁₅Mn₁₅O₄ and small amount of Mn₃O₄ phase. Fig. 4 illustrates the WGSR activity of CuMnX as a function of reaction CuMn900 temperature. exhibited maximum activity in the temperature range studied. WGSR activity increased with an increase in calcination temperature up to 900°C. CuMn1100 showed catalytic activity comparable to that of CuMn900 above 250°C. It is clear from this result that the WGSR activity of Cu-Mn spinel oxide depended on calcination temperature, and a higher temperature was favorable. After the WGSR, the crystalline phase of CuMnX was composed mainly of Cu and MnO. Small amounts of Cu₂O or CuO were also detected, which were probably formed by oxidation in air during the XRD measurements in air. In every sample, no peak ascribed to spinel oxide was detected after the WGSR. Cu particle size of CuMnX after the WGSR estimated by N₂O titration. was Reduction of CuMnX calcined at lower temperatures tended to cause aggregation of Cu particles, leading to low WGSR activity. Thus, it is



Fig. 3 Partial oxidation of CH₄ over Ni/Al₂O₃ calcined at 1400°C (\Box) and 1000°C (\blacksquare), BaNiAl₁₁O_{19- $\alpha}$ calcined at 1400°C (\bigcirc) and 1200°C (\bigcirc), and LaAl_{5/6}Ni_{1/6}O₃; calcined at 850°C (\blacktriangle) and 1200°C (\bigtriangleup) at 120000 l kg⁻¹ h⁻¹. The line is thermodynamic equilibrium. Reaction conditions: CH₄ 10%; O₂ 5%; N₂ balance.}



Fig. 4. Catalytic activity of Cu-Mn spinel oxides for WSGR calcined at various temperatures: (\bigcirc) CuMn500, (\blacksquare) CuMn700, (\bigcirc) CuMn900, (\bigtriangledown) CuMn1100, (----) equilibrium conversion. Reaction conditions: H₂ 37.5%; CO 1.25%; H₂O 25.0%; CO₂ 12.5%; space velocity, 6400 h⁻¹.

considered that the fine particles of Cu can be formed from homogeneous phase upon reduction. High temperature calcination is effective in accommodating Cu ions at the regular site in the spinel lattice, though the surface area is lowered by this treatment.

4. Conclusion

The three examples of catalytic reaction suggest that the catalytic activity of metallic component is significantly affected by the interaction with host oxides. The metal deposits were produced from homogeneous phases with shifts of atmosphere or temperature. The fine deposits thus produced retain strong chemical interaction with host matrix. The interaction promoted the catalytic reactions in the demonstrated examples. The formation process of metal fine particles and their mechanism of interaction should be important in designing of active catalysts.

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