

# Articles

## Oxidative Dimerization of Methane over Lead Aluminate Spinel Catalysts

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*Received May 23, 1995*

Oxidative dimerization of methane to  $C_2$ -hydrocarbons was performed over lead aluminate spinel catalysts. These spinel catalysts were prepared by co-precipitation, aerogel, and sol-gel methods. The active phase of lead aluminate oxides was found to be  $PbAl_2O_4$  spinel. The activities of the catalysts were strongly dependent on the preparation method as well as the composition of  $PbAl_2O_4$  phase. The proper oxygen mobility of  $PbAl_2O_4$  spinel oxides appeared to be important to get high catalytic activity and selectivity for  $C_2$ -hydrocarbon formation.

### Introduction

Since early eighties, there has been an extensive effort throughout the world to develop an economically feasible catalytic process that would enable one to convert methane into  $C_2$  hydrocarbons, especially ethylene,<sup>1</sup> which could be so-called the oxidative dimerization of methane with oxygen. This direct activation of methane has been considered as a prominent way for the utilization of natural gas into the transportable liquid.<sup>2</sup> The attempts in the oxidative dimerization of methane have been tried over various kinds of metal oxides in the periodic regime.<sup>3</sup> Among these catalysts, supported PbO catalysts have been reported to be active for this reaction.<sup>6-15</sup> Before their discoveries, supported lead oxides were known to be active as oxidation catalysts such as the oxidative coupling of toluene into stilbene<sup>15</sup> and in the nitrooxidation of toluene into benzonitrile with nitric oxide.<sup>16</sup> It was suggested the redox behavior of these lead oxide-based catalyst systems was related to the catalytic activity in these reactions.

Also, Hinsen and Baerns<sup>6</sup> reported that PbO catalysts were active for the oxidative dimerization of methane, supplied with gas phase oxygen. They found that surface acidity of supports negatively influenced on the  $C_2$ -selectivity. So, Asami *et al.*<sup>7</sup> confirmed the improvement in methane conversion and  $C_2$ -selectivity by using basic oxides supported PbO catalysts. Besides the effect of surface acidity, they postulated that the selectivity might be depending on the ability of the catalyst to transfer lattice oxygen, which occurred by an interaction of support with the lattice oxygen of PbO. Wendt *et al.*<sup>8</sup> ascertained that there would be a key role of the reducibility of lead oxides on  $\gamma$ -alumina, which has amorphous  $PbAl_2O_4$  phase, magnetoplumbite-like structure, as an active site. However, Agarwal *et al.*<sup>9</sup> proposed an isolated site type mechanism which means that the isolation of strong oxidizing sites (PbO) on MgO could enable high selectivity. Recently, Moffat's group<sup>13</sup> reported that the oxidative dimerization of methane to ethane and ethylene could be effectively catalyzed over hydroxyapatite ion-exchanged with

lead at reaction temperatures as low as 700 °C, while hydroxyapatite itself catalyzed methane oxidation to carbon oxides. And they suggested that the lead cations on the surface of apatite played an important role on both the activation of methane and stabilization of methyl radicals on the surface.

Previously, we found the volcano-type patterns not only in the methane conversion but also in selectivity of  $C_2+$  hydrocarbons over 60 wt.% of PbO loaded  $\gamma$ -alumina catalyst which contained lead aluminate as a major phase.<sup>14</sup> On the other hand, the catalytic activity decreased with an increase in content of  $PbO_{th}$  phase in  $PbO-Al_2O_3$  catalysts. The species responsible for the selective oxidative dimerization of methane considered to be a lead aluminate or dispersed lead oxide on lead aluminate perturbed by a strong support interaction in the case of  $PbO-Al_2O_3$  system.

It is effective for catalyst design of the  $PbO-Al_2O_3$  systems to examine in detail the behavior of  $PbAl_2O_4$  spinel oxide in the oxidative dimerization of methane. In this study, we tried to prepare lead aluminates directly and investigate the effect of preparation methods and calcination temperatures on the catalytic and physical properties of lead aluminates in the oxidative dimerization of methane.

### Experimental

**Catalyst preparation.**  $Pb(NO_3)_2$  (99.999%),  $Al(NO_3)_3 \cdot 9H_2O$  (99.997%),  $Al(OPr-i)_3$  (99.99%), iso-propyl alcohol, and citric acid for preparation were purchased from Aldrich Chemical Co., Inc. Lead aluminate spinel catalysts were prepared by co-precipitation, aerogel and sol-gel methods to have the composition of 68 wt.% PbO and 32 wt.%  $Al_2O_3$ . Samples were dried at 120 °C for 12 h and calcined at different temperatures ranging from 750 °C to 950 °C in air for 4 h. The coprecipitated lead aluminates were synthesized by two ways using sodium carbonate and ammonium carbonate, respectively, as a precipitation agent. Coprecipitation was performed from the corresponding solutions of lead and aluminum salts at 60 °C and pH=10, followed by filtering with deionized

**Table 1.** Properties and Catalytic Activities of Lead Aluminate Spinel Catalysts<sup>a</sup>

Catalyst	Calcined Temp. (°C)	S <sub>BET</sub> (m <sup>2</sup> /g)	Crystalline phases <sup>b</sup>	Unit Cell Parameters of PbAl <sub>2</sub> O <sub>4</sub>				X(CH <sub>4</sub> ) (%)	S(C <sub>2</sub> ) (%)	C <sub>2</sub> -STY <sup>c</sup> (mmol/g·h)
				a <sub>0</sub> (Å)	b <sub>0</sub> (Å)	c <sub>0</sub> (Å)	V <sub>cell</sub> (Å <sup>3</sup> )			
PbAl <sub>2</sub> O <sub>4</sub> (C)	750	7.1	PbAl <sub>2</sub> O <sub>4</sub>	5.306	8.536	5.111	203.2	11.6	47.6	5.6
PbAl <sub>2</sub> O <sub>4</sub> (C)	850	2.6	PbAl <sub>2</sub> O <sub>4</sub>	5.280	8.492	5.088	200.3	12.2	50.3	6.2
PbAl <sub>2</sub> O <sub>4</sub> (C)	950	1.0	PbAl <sub>2</sub> O <sub>4</sub> , PbO <sub>rh</sub> (trace)	5.340	8.572	5.138	206.5	10.9	44.9	5.0
PbAl <sub>2</sub> O <sub>4</sub> (A)	750	36	PbAl <sub>2</sub> O <sub>4</sub>	5.273	8.466	5.076	199.0	13.3	49.6	6.6
PbAl <sub>2</sub> O <sub>4</sub> (S)	750	9.9	PbAl <sub>2</sub> O <sub>4</sub> + PbO <sub>rh</sub> (minor)	5.278	8.481	5.081	199.7	9.7*	81.0*	6.9*

C: Coprecipitation, A: Aerogel method, S: Sol-gel method. <sup>a</sup>Reaction condition; Temp.=720 °C, W/F=0.75 g·sec/mL, P(CH<sub>4</sub>)=47.7 kPa, P(CH<sub>4</sub>)/P(O<sub>2</sub>)=7.2 \*W/F=0.65 g·sec/mL, P(CH<sub>4</sub>)=35.6 kPa. <sup>b</sup>observed by XRD. <sup>c</sup>C<sub>2</sub>-Space Time Yield: mmol of produced C<sub>2</sub> hydrocarbons per unit cat. weight (g) and reaction time (h).

water and drying in air at 150 °C for 12 h. The aerogel sample of lead aluminate was prepared by cogelling lead nitrate and aluminum iso-propoxide, and then dried under supercritical condition. Cogelled gel was prepared from the metal-organic precursor dissolved in iso-propyl alcohol and hydrolyzed in stoichiometric amounts of water. The wet gel was all dried under supercritical condition with respect to iso-propyl alcohol at 250 °C (T<sub>c</sub>=235 °C). And lead aluminate *via* the sol-gel method was prepared by gelling aqueous solution of lead nitrate and aluminum nitrate with citric acid. This preparation is similar to Pechini method.<sup>16</sup>

**Catalytic measurements.** The activity of the catalysts was determined by co-feed method using a quartz flow reactor (I.D. 10 mm, length 20 cm) mounted vertically and heated by an electric furnace, equipped with a PID temperature controller. All the catalysts testing were carried out at 720 °C in atmospheric pressure. The reactant gas mixture consisted of methane and oxygen diluted with nitrogen. Their flow rates and ratios were controlled by Datametrics' mass flow controllers (model 1605). The reactants and products were analyzed by an on-lined gas chromatograph (GC) having a thermal conductivity detector unit equipped with Porapak N and MS 5A columns.

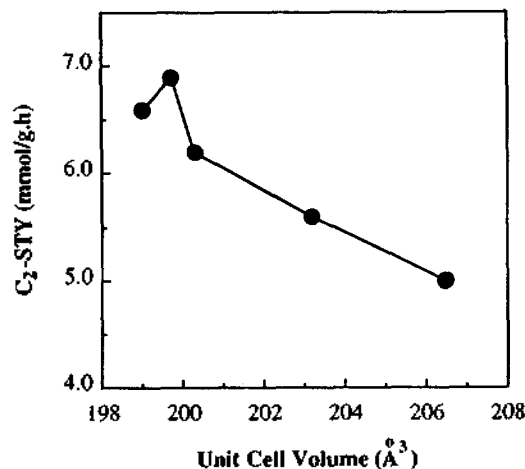
**Instrumental.** The specific surface areas of the prepared catalysts were measured on a Micromeritics' sorption analyzer (model ASAP 2400). Thermogravimetric analysis (TGA) was performed up to 800 °C on a Du Pont 9900 instrument with air flow of 50 mL/min and heating rate of 10 °C/min. Powder X-ray diffraction (XRD) measurements were taken with a Rigaku 2155D6 diffractometer using an Cu-K $\alpha$  radiation. Based on the powder XRD data, the accurate lattice (or unit cell) parameters for lead aluminate spinels were determined in the same manner as described in elsewhere.<sup>17</sup> The Raman spectra were obtained with a Jobin Yvon U1000 spectrometer using a Coherent's Innova 70 Argon ion laser, where the exciting line was typically 514.5 nm.

## Results and Discussion

In order to confirm PbAl<sub>2</sub>O<sub>4</sub> spinel oxide as an active phase among the PbO-Al<sub>2</sub>O<sub>3</sub> systems in the oxidative dimerization of methane, the catalytic activities and structural pro-

perties of lead aluminate spinel oxides prepared by different methods were examined. Properties of lead aluminates depending on the preparation methods and calcination temperature are summarized in Table 1. Although the data were not shown in this text, XRD pattern and FT-IR spectrum of the precursor of lead aluminate prepared by co-precipitation using sodium carbonate as a precipitation agent before calcination showed PbCO<sub>3</sub> phase only. Phases related to aluminum seemed to be existing in amorphous state that could not be detected by XRD. The coprecipitated lead-aluminates [PbAl<sub>2</sub>O<sub>4</sub>(C)] were prepared by calcining at from 750 °C to 950 °C, which were mainly consisted of PbAl<sub>2</sub>O<sub>4</sub> spinel phase having monoclinic crystal structure. The coprecipitated lead aluminates calcined at lower than 850 °C had a single PbAl<sub>2</sub>O<sub>4</sub> spinel phase. But in the coprecipitated lead-aluminates calcined at 950 °C, orthorhombic PbO phase was appeared together with PbAl<sub>2</sub>O<sub>4</sub> phase and the intensity of XRD lines related to the orthorhombic PbO phase was increased as the calcination temperature increased. For the lead aluminate prepared by aerogel method [PbAl<sub>2</sub>O<sub>4</sub>(A)], only a PbAl<sub>2</sub>O<sub>4</sub> spinel was also observed without any crystalline phases of precursors. Finally in lead aluminate prepared by the sol-gel method [PbAl<sub>2</sub>O<sub>4</sub>(S)], calcined at 750 °C, orthorhombic PbO phase was appeared as a minor component with PbAl<sub>2</sub>O<sub>4</sub> phase.

The catalytic activities of these lead aluminate spinel catalysts was measured at 720 °C after a reaction time of 2 h and also presented in Table 1. The reaction products were mainly ethane, ethylene, carbon dioxide and water. Over all the lead aluminate catalysts except sol-gel one, the high catalytic activities with more than 10% of methane conversions and C<sub>2</sub>-selectivities of from 40% to 50% were obtained under the given reaction conditions. The PbAl<sub>2</sub>O<sub>4</sub>(S) catalyst prepared by sol-gel method showed high C<sub>2</sub>-selectivity over 80% at slightly different reaction conditions. Oxygen conversions over all the catalysts were higher than 90%. C<sub>2</sub>-space time yields (C<sub>2</sub>-STY) of the catalysts, which were defined as a number of mmol of produced C<sub>2</sub> hydrocarbons per unit catalyst weight (g) and reaction time (h), as a measure of catalytic activity were shown to be directly relevant to their lattice parameters of unit cell and unit cell volumes calculated from the crystallographic data (Table 1 and Figure 1). A maximum C<sub>2</sub>-STY was observed over the catalyst having small unit

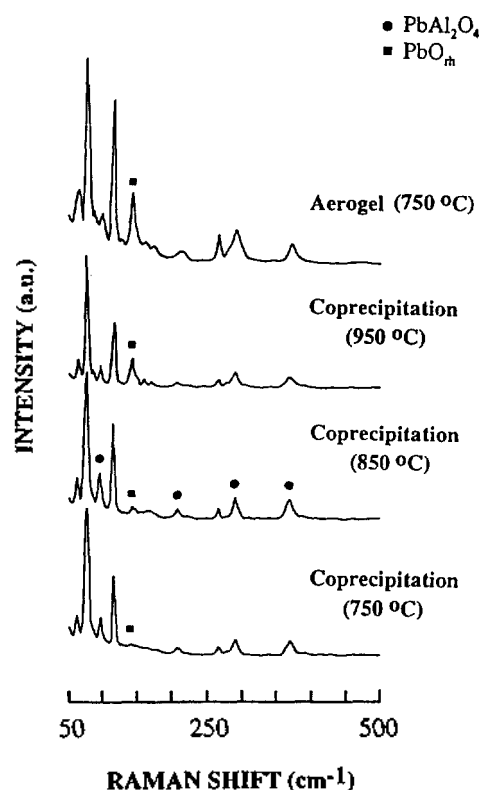


**Figure 1.** Correlation of catalytic activities  $\text{PbAl}_2\text{O}_4$  spinel oxides with unit cell volumes.

cell volume. The reduction of unit cell volume of  $\text{PbAl}_2\text{O}_4$  phases appeared to be ascribed to the reduction of distance or strength of Pb-O or Al-O bond within their lattice. It was also related to the reduction of oxygen mobility of  $\text{PbAl}_2\text{O}_4$  phase. Yang *et al.*<sup>18</sup> reported that an increase of unit cell volume of Ca-doped  $\text{La}_2\text{O}_3$  led to increasing methane conversion and selectivity for  $\text{C}_2$ -hydrocarbon formation. They pointed out that the cell volume of Ca-doped  $\text{La}_2\text{O}_3$  crystal increased because the charge of these two ions did not match each other. However, in the case of PbO- $\text{Al}_2\text{O}_3$  catalysts,  $\text{C}_2$ -selectivity was improved by the suppression of oxygen mobility since lead cations of PbO and aluminum cations of  $\gamma$ - $\text{Al}_2\text{O}_3$  were very mobile. It was clear that the proper oxygen mobility of lead aluminate spinel catalysts was an important factor to affect on the catalytic activity as indicated in previous work.<sup>14</sup>

Specific surface areas ( $S_{\text{BET}}$ ) of the  $\text{PbAl}_2\text{O}_4(\text{C})$  catalysts decreased as increasing the calcination temperatures. Comparing with the  $\text{PbAl}_2\text{O}_4(\text{C})$  catalyst,  $\text{PbAl}_2\text{O}_4(\text{S})$  catalyst prepared by sol-gel method had higher surface area. Despite of such a high calcination temperature, relatively high surface area of 36  $\text{m}^2/\text{g}$  was obtained for  $\text{PbAl}_2\text{O}_4(\text{A})$  prepared by aerogel method. Surface area of lead aluminates was strongly dependent on the preparation methods and calcination temperature, but its effect on catalytic activities did not appear to be critical. It is well known that a number of reactions, primarily ethane and ethylene combustion, do occur homogeneously in the gas phase.<sup>19</sup> Methane activation such as hydrogen abstraction of methane, however, does not occur in the gas phase. Seimanides *et al.*<sup>19</sup> claimed that the change of the catalytic activity should be attributed to the variation of catalyst surface area. In this study, however, it seemed that the catalytic activities of lead aluminate spinel catalysts were appreciably affected by the structural properties and composition of lead aluminate spinel phases formed by different preparation methods rather than catalyst surface area.

Raman spectra of lead aluminum oxides are compared in Figure 2. Raman spectra of lead aluminates showed the characteristic bands of  $\text{PbAl}_2\text{O}_4$  spinel phase at 99, 209, 291 and 372  $\text{cm}^{-1}$  and orthorhombic PbO phase at 143, 289, and 385



**Figure 2.** Raman spectra of lead aluminate spinel catalysts.

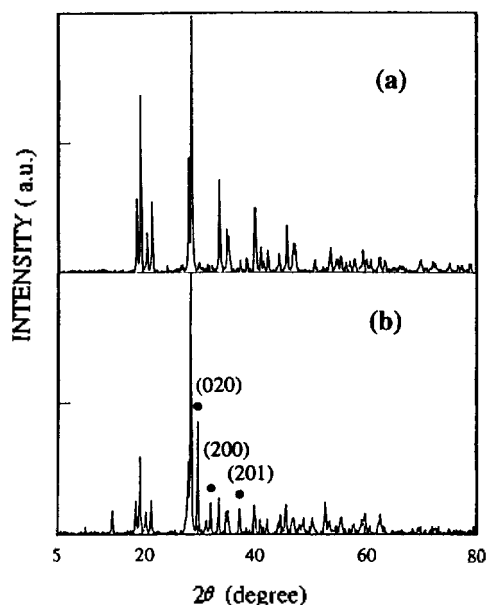
**Table 2.** Effect of Precipitation Reagent on the Preparation of  $\text{PbAl}_2\text{O}_4(\text{C})$  Catalysts\*

Precipitation Reagent	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	X( $\text{CH}_4$ ) (%)	X( $\text{O}_2$ ) (%)	S( $\text{C}_2$ ) (%)	$\text{C}_2$ -STY (mmol/g·h)
$\text{Na}_2\text{CO}_3$	7.1	11.6	98.6	47.6	5.6
$(\text{NH}_4)_2\text{CO}_3$	2.1	4.9	56.0	38.9	1.9

\*Reaction conditions: See Table 1.

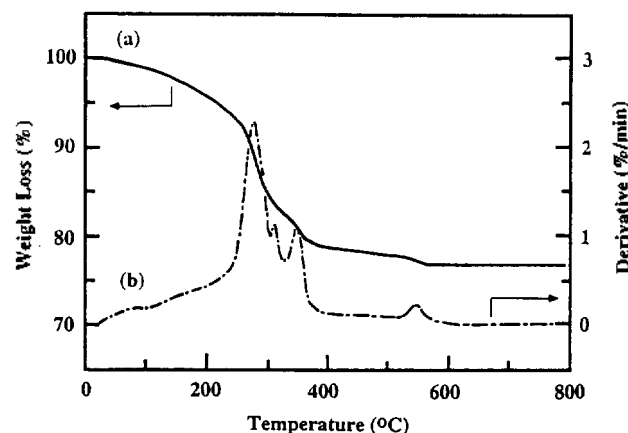
$\text{cm}^{-1}$ . In the  $\text{PbAl}_2\text{O}_4(\text{C})$  catalysts, the intensity of band at 143  $\text{cm}^{-1}$ , which is assigned to vibrational  $A_g$  and  $B_{2g}$  modes of orthorhombic PbO (massicot) phase consisting of zig-zag chains with a 2[PbO] repeat unit,<sup>20</sup> was gradually built-up as an increase of the calcination temperature, coincided with XRD results. On the other hand, a diffraction line at (020) plane, which is representative one, of orthorhombic PbO phase in the aerogel lead aluminate was absent in XRD spectra, while the intensity of Raman band at 143  $\text{cm}^{-1}$  was remarkably increased. This means that the vibrational data on phases related to lead oxides obtained from Raman spectra can give us the information of amorphous as well as crystalline phases, different from XRD spectra.

In this work, the composition of  $\text{PbAl}_2\text{O}_4$  formed in the lead aluminate spinel catalysts was strongly affected on their activities and selectivities. Considering the effect of a type of precipitation reagent in lead aluminate prepared by coprecipitation, its effect on the catalytic activities and the formation of phases was remarkable (Table 2 and Figure 3). Lead aluminate prepared by using sodium carbonate as a



**Figure 3.** XRD spectra of  $\text{PbAl}_2\text{O}_4$  spinels prepared by the co-precipitation method with different precipitation reagents; (a)  $\text{Na}_2\text{CO}_3$  and (b)  $(\text{NH}_4)_2\text{CO}_3$  (● denotes diffraction lines of  $\text{PbO}$  phase and others without symbol diffraction lines of  $\text{PbAl}_2\text{O}_4$  phase).

precipitation reagent and calcined at  $750^\circ\text{C}$  displayed a single  $\text{PbAl}_2\text{O}_4$  phase in XRD spectrum (Figure 3a). On the other hand, in the case of using ammonium carbonate XRD spectrum of the catalyst presented (020), (200) and (201) planes of orthorhombic  $\text{PbO}$  phase together with characteristic index planes of  $\text{PbAl}_2\text{O}_4$  phase, mixed with the similar composition of both ones (Figure 3b). Three times higher of surface area in the use of sodium carbonate was obtained with comparing to that of ammonium carbonate due to the contribution of  $\text{PbAl}_2\text{O}_4$  spinel phase having higher surface area than orthorhombic  $\text{PbO}$  phase. This suggests the use of proper precipitation reagent is important in the efficient mixing of the co-

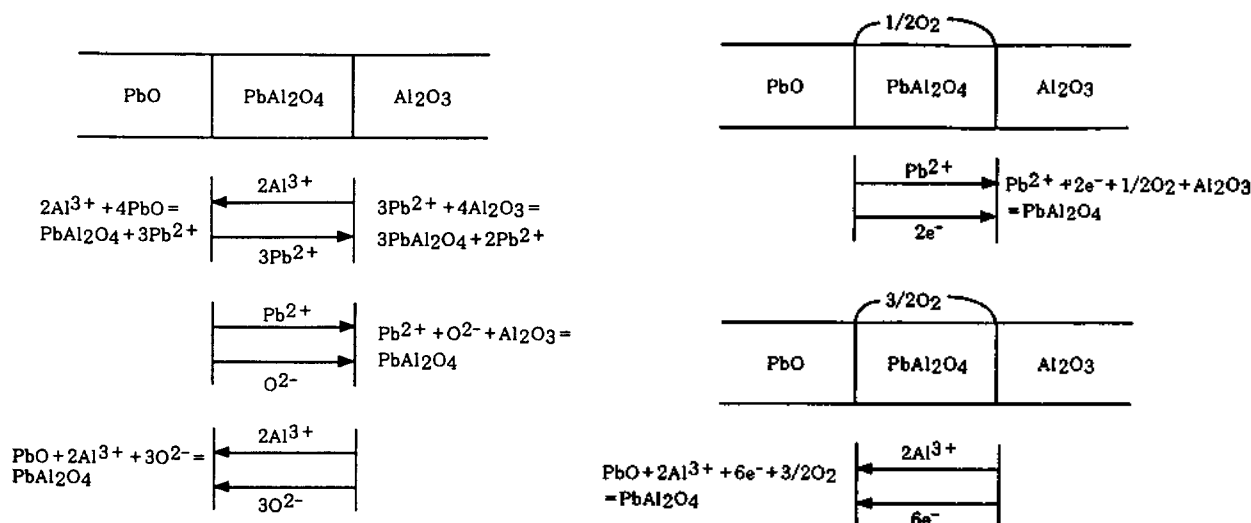


**Figure 4.** (a) TGA and (b) differential thermogravimetric (DTG) curves of  $\text{PbAl}_2\text{O}_4$  spinel precursor prepared by the co-precipitation method (carrier gas, air 50 mL/min; heating rate,  $15^\circ\text{C}/\text{min}$ ).

ponents of Pb and Al, and therefore the formation of  $\text{PbAl}_2\text{O}_4$  spinel phase. Comparing to their catalytic activities, lead aluminate prepared by sodium carbonate gave much higher activity and  $\text{C}_2$  selectivity than one prepared by ammonium carbonate (Table 2). This demonstrates that  $\text{PbAl}_2\text{O}_4$  spinel phase in the catalysts is active one and its concentration is closely related with the catalytic activity for the oxidative dimerization of methane.

TGA/DTG curves for  $\text{PbAl}_2\text{O}_4$  spinel precursor prepared by co-precipitation method are shown in Figure 4. Metastable  $\text{PbO}$  phase with pseudo-alumina phase was firstly formed with showing large endothermic peaks at lower temperature of  $200^\circ\text{C}$  to  $400^\circ\text{C}$ , which was resulted from the decomposition of the carbonate precursors.  $\text{PbAl}_2\text{O}_4$  spinel phase was formed above  $500^\circ\text{C}$  by solid-state reaction of these  $\text{PbO}$  and alumina phases without weight loss of sample. Small weight loss peak at  $550^\circ\text{C}$  from DTG curve was due to removal of carbon dioxide by the combustion of residual organic carbons in the sample.

In Scheme 1 are shown a number of possible mechanisms



**Scheme 1.** Possible formation of  $\text{PbAl}_2\text{O}_4$  spinel by solid-solid reaction in  $\text{PbO}-\text{Al}_2\text{O}_3$  system.

for the  $\text{PbAl}_2\text{O}_4$  spinel formation in  $\text{PbO-Al}_2\text{O}_3$  catalyst system. These mechanisms are based on the one proposed by Schmalzried.<sup>21</sup> There included mechanisms which the oxygen is transported through the gas phase and local electrical neutrality is maintained by means of electronic semiconduction in  $\text{PbAl}_2\text{O}_4$  spinel oxide. A part of the suggested mechanisms can be eliminated because it is generally known that in oxide spinels the diffusion of oxygen is rather slow compared to the cationic diffusion.<sup>20</sup> Furthermore, if ideal contact is maintained at the phase boundaries so that gas phase oxygen cannot enter, then mechanisms related to the counter-diffusion of cations, *i.e.*  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$ , and the diffusion of lattice oxygen may be probable only. And the spinel formation reaction,  $\text{PbO} + \text{Al}_2\text{O}_3 = \text{PbAl}_2\text{O}_4$ , is a heterogeneous reaction. Therefore, two cation fluxes must be transported across the phase boundaries and through the spinel oxide lattice.

The formation of spinel phase such as lead aluminate seemed to be the evidence of occurring the diffusion of both cations and lattice oxygens during not only calcination but also methane dimerization reaction at such a high temperature. Thus, it means lead species on the surface interact with support materials during the calcination of catalysts and the reaction. In other words, the movement of lead cations and lattice oxygens of the support are possible on the surface and lead aluminate is an active phase for the oxidative dimerization of methane.

In previous study, we found that lattice oxygen of lead aluminate spinel was responsible for the selective conversion of methane into  $\text{C}_2$ -hydrocarbons, by observing the participation of its lattice oxygen into methane dimerization without oxygen supply and regeneration of reduced lead aluminate spinel into oxidized one by oxidation.<sup>14</sup> Bytyn and Baerns<sup>6</sup> ascertained that the ability to transfer lattice oxygen was important in  $\gamma$ -alumina-supported  $\text{PbO}$  catalysts. Asami *et al.*<sup>7</sup> claimed that the abstraction site of hydrogen by lattice oxygen was  $\text{PbO}$  site. However, Wendt *et al.*<sup>8</sup> and Agarwal *et al.*<sup>9</sup> proposed that the catalytically active sites were magnetoplumbite phase and isolated  $\text{PbO}$  site as the strong oxidizing one, respectively. It is known that the bulk diffusion of oxygen which is a key factor for the selective oxidation, *i.e.* oxygen transfer from the bulk to the surface, is a function of the oxygen mobility in the oxide which depends on the chemical structure of the oxide and the temperature.<sup>15</sup> In this study,  $\text{PbAl}_2\text{O}_4$  spinel oxides in the  $\text{PbO-Al}_2\text{O}_3$  catalyst systems seemed to be adequate for the diffusion of lattice oxygen into surface oxide for the selective reaction.

In summary,  $\text{PbAl}_2\text{O}_4$  phase in the lead aluminate spinel catalysts which is formed by the interaction of  $\text{PbO}$  with alumina is an active species in the oxidative dimerization of methane. The structural properties of phases formed by different preparation methods are strongly influenced in their catalytic activities.  $\text{PbAl}_2\text{O}_4$  spinel oxides appear to have the proper oxygen mobility of their own lattice oxygen to

get high catalytic activity and selectivity for  $\text{C}_2$ -hydrocarbon formation.

**Acknowledgment.** The authors thank Ms. S. Y. Lee and Mr. M. S. Park for technical assistance in the experimental work.

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