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,[1] 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.[2] The attempts in the oxidative dimerization of methane have been tried over various kinds of metal oxides in the periodic regime.[3] Among these catalysts, supported PbO catalysts have been reported to be active for this reaction.[6~15] Before their discoveries, supported lead oxides were known to be active as oxidation catalysts such as the oxidative coupling of toluene into stilbene[15] and in the nitroxidation of toluene into benzonitrile with nitric oxide.[16] 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[6] 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.*[7] 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.*[8] ascertained that there would be a key role of the reducibility of lead oxides on γ-alumina, which has amorphous $PbAl_{12}O_{19}$ phase, magnetoplumbite-like structure, as an active site. However, Agarwal *et al.*[9] 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[13] reported that the oxidative dimerization of methane to ethane and ethylene could be effectively catalyzed over hydroxyapatite ion-exchanged with lead at reaction temepratures as low as 700 ℃, 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 γ-alumina catalyst which contained lead aluminate as a major phase.[14] On the other hand, the catalytic activity decreased with an increase in content of PbO_{rh} 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%), $Al(OPr\text{-}i)_3$ (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 ℃ for 12 h and calcined at different temperatures ranging from 750 ℃ to 950 ℃ 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 ℃ and pH=10, followed by filtering with deionized

Table 1. Properties and Catalytic Activities of Lead Aluminate Spinel Catalysts[a]

Catalyst	Calcined	S_{BET}	Crystalline	Unit Cell Parameters of $PbAl_2O_4$				$X(CH_4)$	$S(C_2)$	C_2-STY[c]
	Temp. (℃)	(m^2/g)	phases[b]	a_0 (Å)	b_0 (Å)	c_0 (Å)	V_{abc} ($Å^3$)	(%)	(%)	(mmol/g·h)
$PbAl_2O_4$(C)	750	7.1	$PbAl_2O_4$	5.306	8.536	5.111	203.2	11.6	47.6	5.6
$PbAl_2O_4$(C)	850	2.6	$PbAl_2O_4$	5.280	8.492	5.088	200.3	12.2	50.3	6.2
$PbAl_2O_4$(C)	950	1.0	$PbAl_2O_4$, PbO_{rh}(trace)	5.340	8.572	5.138	206.5	10.9	44.9	5.0
$PbAl_2O_4$(A)	750	36	$PbAl_2O_4$	5.273	8.466	5.076	199.0	13.3	49.6	6.6
$PbAl_2O_4$(S)	750	9.9	$PbAl_2O_4$+ PbO_{rh}(minor)	5.278	8.481	5.081	199.7	9.7*	81.0*	6.9*

C: Coprecipitation, A: Aerogel method, S: Sol-gel method. [a]Reaction condition; Temp.=720 ℃, W/F=0.75 g·sec/mL, $P(CH_4)=47.7$ kPa, $P(CH_4)/P(O_2)=7.2$ *W/F=0.65 g·sec/mL, $P(CH_4)=35.6$ kPa. [b]observed by XRD. [c]C_2-Space Time Yield: mmol of produced C_2 hydrocarbons per unit cat. weight (g) and reaction time (h).

water and drying in air at 150 ℃ 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 ℃ (T_c=235 ℃). And lead aluminate *via* the sol-gel method was prepared by gelling aqeuous solution of lead nitrate and aluminum nitrate with citric acid. This preparation is similar to Pechini method.[16]

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 ℃ 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 equiped 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 ℃ on a Du Pont 9900 instrument with air flow of 50 mL/min and heating rate of 10 ℃/min. Powder X-ray diffraction (XRD) measurements were taken with a Rigaku 2155D6 diffractometer using an Cu-Kα 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.[17] 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 $PbAl_2O_4$ spinel oxide as an active phase among the $PbO-Al_2O_3$ systems in the oxidative dimerization of methane, the catalytic activities and structural properties 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 $PbCO_3$ phase only. Phases related to aluminum seemed to be existing in amorphous state that could not be detected by XRD. The coprecipitated lead-aluminates [PbA12O4(C)] were prepared by calcining at from 750 ℃ to 950 ℃, which were mainly consisted of $PbAl_2O_4$ spinel phase having monoclinic crystal structure. The coprecipitated lead aluminates calcined at lower than 850 ℃ had a single $PbAl_2O_4$ spinel phase. But in the coprecipitated lead-aluminates calcined at 950 ℃, orthorhombic PbO phase was appeared together with $PbAl_2O_4$ 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 [$PbAl_2O_4$(A)], only a $PbAl_2O_4$ spinel was also observed without any crystalline phases of precursors. Finally in lead aluminate prepared by the sol-gel method [$PbAl_2O_4$(S)], calcined at 750 ℃, orthorhombic PbO phase was appeared as a minor component with $PbAl_2O_4$ phase.

The catalytic activities of these lead aluminate spinel catalysts was measured at 720 ℃ 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_2-selectivities of from 40% to 50% were obtained under the given reaction conditions. The $PbAl_2O_4$(S) catalyst prepared by sol-gel method showed high C_2-selectivity over 80% at slightly different reaction conditions. Oxygen conversions over all the catalysts were higher than 90%. C_2-space time yields (C_2-STY) of the catalysts, which were defined as a number of mmol of produced C_2 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_2-STY was observed over the catalyst having small unit

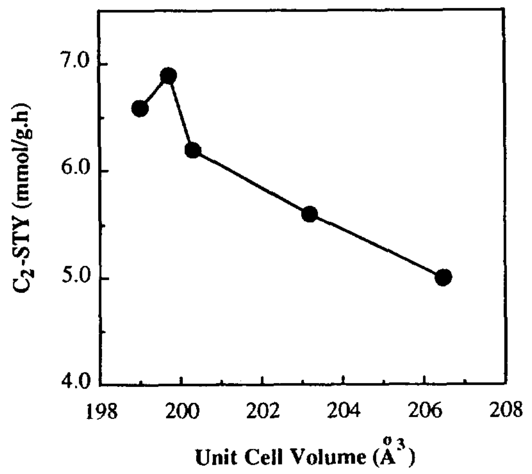


Figure 1. Correlation of catalytic activities $PbAl_2O_4$ spinel oxides with unit cell volumes.

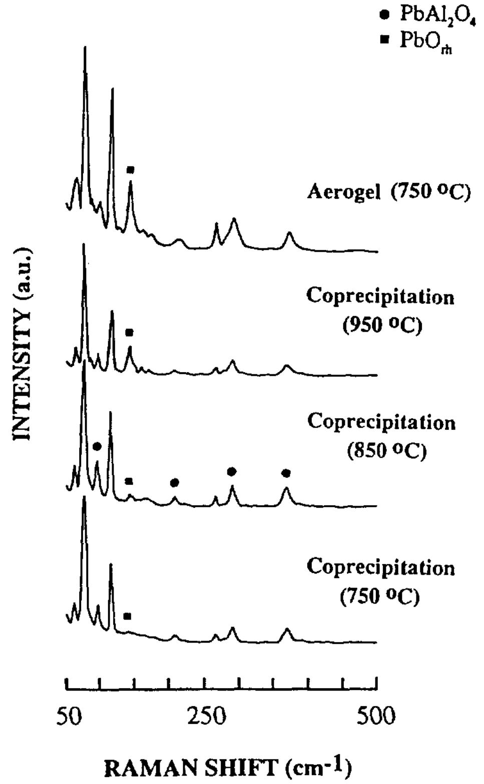


Figure 2. Raman spectra of lead aluminate spinel catalysts.

Table 2. Effect of Precipitation Reagent on the Preparation of $PbAl_2O_4$(C) Catalysts*

Precipitation Reagent	S_{BET} (m^2/g)	$X(CH_4)$ (%)	$X(O_2)$ (%)	$S(C_2)$ (%)	C_2-STY (mmol/g·h)
Na_2CO_3	7.1	11.6	98.6	47.6	5.6
$(NH_4)_2CO_3$	2.1	4.9	56.0	38.9	1.9

*Reaction conditions: See Table 1.

cell volume. The reduction of unit cell volume of $PbAl_2O_4$ 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 mobilty of $PbAl_2O_4$ phase. Yang *et al.*[18] reported that an increase of unit cell volume of Ca-doped La_2O_3 led to increasing methane conversion and selectivity for C_2-hydrocarbon formation. They pointed out that the cell volume of Ca-doped La_2O_3 crystal increased because the charge of these two ions did not match each other. However, in the case of PbO-Al_2O_3 catalysts, C_2-selectivity was improved by the suppression of oxygen mobility since lead cations of PbO and aluminum cations of γ-Al_2O_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.[14]

Specific surface areas (S_{BET}) of the $PbAl_2O_4$(C) catalysts decreased as increasing the calcination temperatures. Comparing with the $PbAl_2O_4$(C) catalyst, $PbAl_2O_4$(S) catalyst prepared by sol-gel method had higher surface area. Despite of such a high calcination temperature, relatively high surface area of 36 m^2/g was obtained for $PbAl_2O_4$(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 homogeously in the gas phase.[19] Methane activation such as hydrogen abstraction of methane, however, does not occur in the gas phase. Seimanides *et al.*[19] 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 $PbAl_2O_4$ spinel phase at 99, 209, 291 and 372 cm^{-1} and orthorhombic PbO phase at 143, 289, and 385 cm^{-1}. In the $PbAl_2O_4$(C) catalysts, the intensity of band at 143 cm^{-1}, which is assigned to vibrational A_g and B_{2u} modes of orthorhombic PbO (massicot) phase consisting of zig-zag chains with a 2[PbO] repeat unit,[20] 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 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 $PbAl_2O_4$ 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

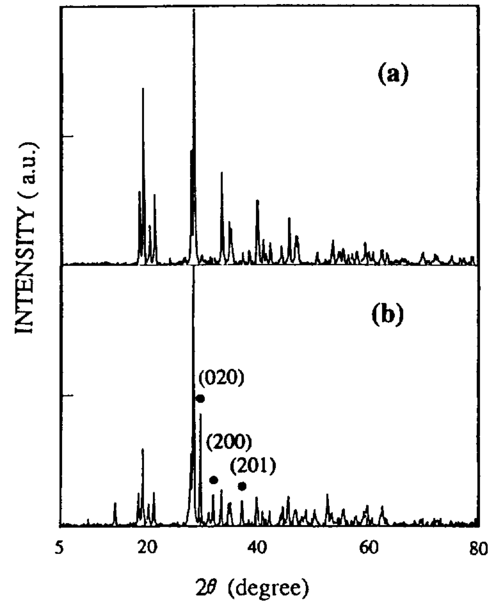


Figure 3. XRD spectra of $PbAl_2O_4$ spinels prepared by the co-precipitation method with different precipitation reagents; (a) Na_2CO_3 and (b) $(NH_4)_2CO_3$ (● denotes diffraction lines of PbO_{rh} phase and others without symbol diffraction lines of $PbAl_2O_4$ phase).

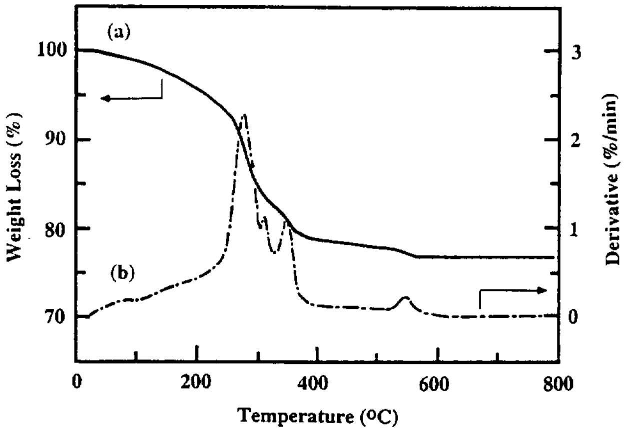
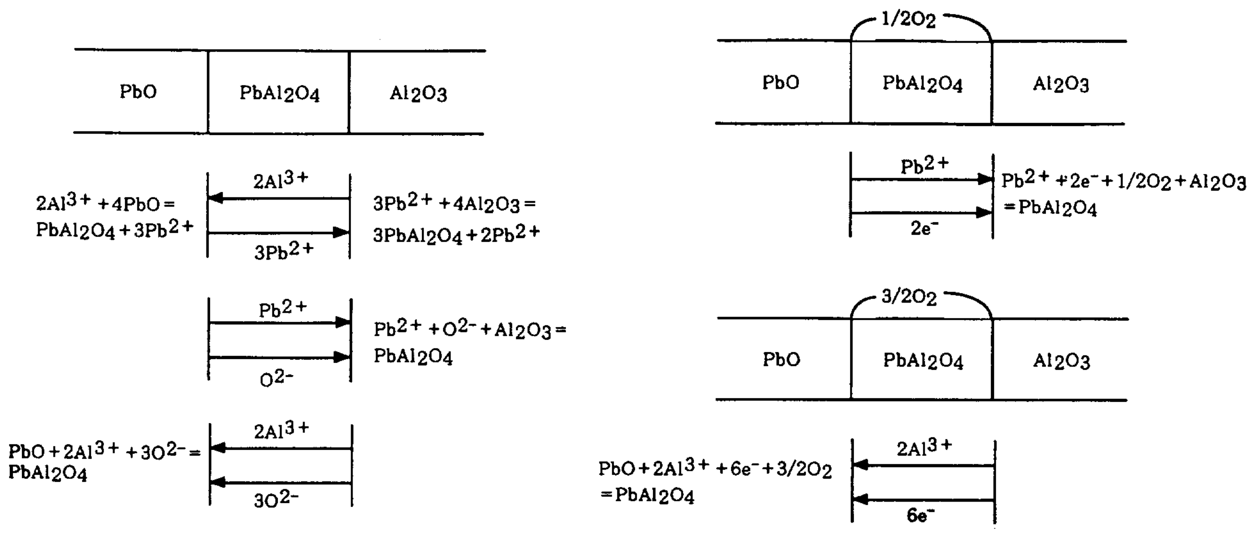


Figure 4. (a) TGA and (b) differential thermogravimetric (DTG) curves of $PbAl_2O_4$ spinel precursor prepared by the co-precipitation method (carrier gas, air 50 mL/min; heating rate, 15 ℃/min).

precipitation reagent and calcined at 750 ℃ displayed a single $PbAl_2O_4$ 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 PbO phase together with characteristic index planes of $PbAl_2O_4$ 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 $PbAl_2O_4$ spinel phase having higher surface area than orthorhombic PbO phase. This suggest the use of proper pricipitation reagent is important in the efficient mixing of the components of Pb and Al, and therefore the formation of $PbAl_2O_4$ spinel phase. Comparing to their catalytic activities, lead aluminate prepared by sodium carbonate gave much higher activity and C_2 selectivity than one prepared by ammonium carbonate (Table 2). This demonstrates that $PbAl_2O_4$ 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 $PbAl_2O_4$ spinel precursor prepared by co-ppreciption method are shown in Figure 4. Metastable PbO phase with pseudo-alumina phase was firstly formed with showing large endothermic peaks at lower temperature of 200 ℃ to 400 ℃, which was resulted from the decomposition of the carbonate precursors. $PbAl_2O_4$ spinel phase was formed above 500 ℃ by solid-state reaction of these PbO and alumina phases without weight loss of sample. Small weight loss peak at 550 ℃ 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 $PbAl_2O_4$ spinel by solid-solid reaction in $PbO\text{-}Al_2O_3$ system.

for the $PbAl_2O_4$ spinel formation in $PbO-Al_2O_3$ catalyst system. These mechanisms are based on the one proposed by Schmalzried.[21] There included mechanisms which the oxygen is transported through the gas phase and local electrical neutrality is maintained by means of electronic semiconduction in $PbAl_2O_4$ 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.[20] Furthermore, if ideal contact is maintained at the phase boundaries so that gas phase oxygen cannot enter, then mechanisms related to the couter-diffusion of cations, *i.e.* Pb^{2+} and Al^{3+}, and the diffusion of lattice oxygen may be probable only. And the spinel formation reaction, $PbO+Al_2O_3=PbAl_2O_4$, 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 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.[14] Bytyn and Baerns[6] ascertained that the ability to transfer lattice oxygen was important in γ-alumina-supported PbO catalysts. Asami *et al.*[7] claimed that the abstraction site of hydrogen by lattice oxygen was PbO site. However, Wendt *et al.*[8] and Agarwal *et al.*[9] proposed that the catalytically active sites were magnetoplumbite phase and isolated 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.[15] In this study, $PbAl_2O_4$ sinel oxides in the $PbO-Al_2O_3$ catalyst systems seemed to be adequate for the diffusion of lattice oxygen into surface oxide for the selective reaction.

In summary, $PbAl_2O_4$ phase in the lead aluminate spinel catalysts which is formed by the interaction of 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. $PbAl_2O_4$ spinel oxides appear to have the proper oxygen mobility of their own lattice oxygen to get high catalytic activity and selectivity for 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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