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# Liquid Phase Formation of Spinel Surface Layers on Hexaaluminate Microcrystals

Masato MACHIDA,* Manabu MURAKAMI, Akihiro SATO, Tsuyoshi KIJIMA,
and Hiromichi ARAI$^+$
Department of Materials Science, Faculty of Engineering, Miyazaki University,
Gakuen Kibanadai, Miyazaki 889-21
$^+$Department of Materials Science, Graduate School of Engineering Sciences, Kyushu
University, Kasuga, Fukuoka 816

Spinel oxide ($Mn_3O_4$) surface layers were produced on hexaaluminate microcrystals by means of the air-oxidation process. The surface layer completely covered the basal plane of hexagonal facets as evident from HREM observation and $CO_2$ chemisorption measurement. The catalytic activity for methane oxidation was strongly enhanced by this modification.

Hexaaluminate-related compounds possess excellent thermal stability, so that large surface area (>20 $m^2/g$) can be retained even at high temperatures (>1200 °C).[1-3] Their thermal stability is closely related to the layer structure comprised of the alternative stacking of a spinel block and a monatomic layer including large cations such as Ba or La. This structure leads to the characteristic microcrystals shaped into planar morphology, of which basal planes normal to the [001] axis possess well-defined surface with a lattice-level flatness.[4-6] Such microcrystals must be suitable for a substrate for the crystal growth of other oxide layers and resultant composite microcrystals are expected to produce interesting surface activity. In this aspect, the combination with spinel oxides ($Mn_3O_4$, $Co_3O_4$, $Fe_3O_4$, etc.) is quite promising, because their structural similarity to hexaaluminates might bring about strong interactions at the interface. In this communication, we report the liquid-phase formation of spinel surface layers on hexaaluminate microcrystals, which is an excellent surface modification technique for catalytic applications.

Barium hexaaluminates ($Ba_{0.75}MAl_{10}O_{17.25}$, M=Al or Mn) were prepared by hydrolysis of alkoxides and subsequent calcination at 1100 °C as described previously.[2,3] The air oxidation process[7-9] was adopted for the preparation of the composite between spinel $Mn_3O_4$ and hexaaluminates. Hexaaluminate powders and manganese nitrate were added to ion-exchanged water which was deoxidized by $N_2$ bubbling for overnight. The resultant suspension was vigorously stirred under $N_2$ atmosphere and was followed by air oxidation, which was performed by passing air bubbles through the solution at 70 °C and pH=ca.7. The sample as prepared was characterized by XRD, TG/DTA, XPS, and $CO_2$ chemisorption measurements.

When the present air oxidation process was performed in the absence of hexaaluminate powders, the product was a single phase of spinel $Mn_3O_4$ with the BET surface area of 24 $m^2/g$.

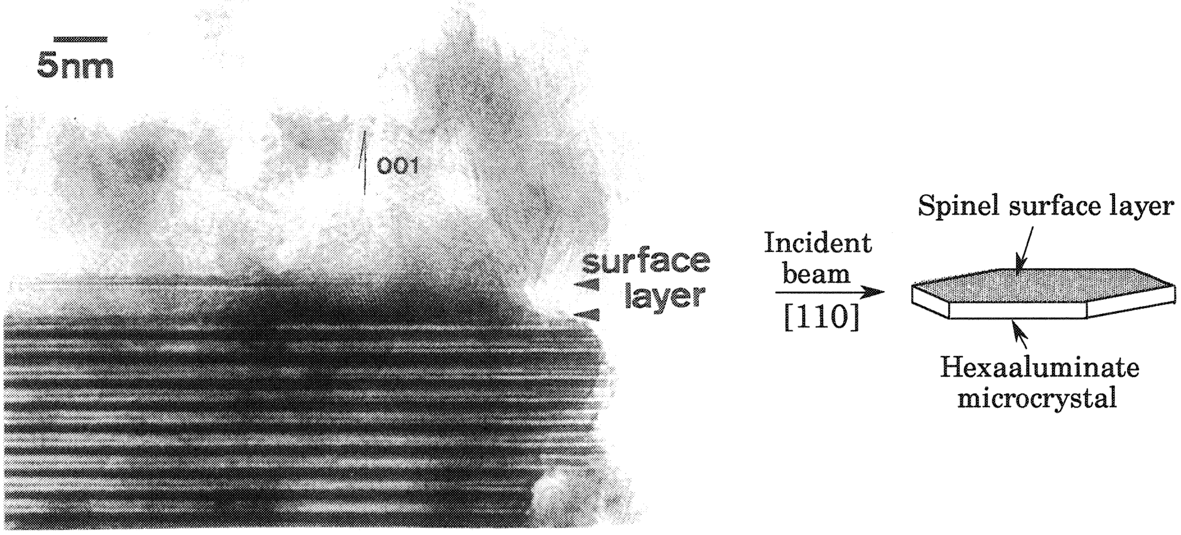


Fig. 1. TEM image of $Mn_3O_4$/hexaaluminate taken with an incident beam normal to (110) plane of hexaaluminate. Parallel contours represent layer structure of hexaaluminate along c axis.

According to the previous study by Abe and Tamaura,[8)] the spinel formation in the air oxidation process results from the following reaction;

$$2MnOH^{2+} + MnOH^{+} + OH^{-} \rightarrow Mn^{2+}Mn^{3+}{}_{2}O_{4} + 4H^{+}$$

Thus, the crystal phase of spinel $Mn_3O_4$ can be deposited without heating processes. The contamination by unreacted nitrates or hydroxides was negligible from TG/DTA analysis.

As-prepared 15 wt%$Mn_3O_4$/hexaaluminate sample showed no XRD pattern due to the spinel phase. Diffraction peaks of $Mn_3O_4$ appeared above 30 wt% of loading. Microstructural analysis was performed on 10 wt%$Mn_3O_4$/$Ba_{0.75}MnAl_{10}O_{17.25}$ by a transmission electron microscope (JEOL 2000FX, HVEM Laboratory at Kyushu University). Electron diffraction showed no significant deviation of the crystal structure but the presence of isolated $Mn_3O_4$ particles. However, structural image (Fig. 1) in the vicinity of the basal plane surface of hexaaluminate facets (incident beam normal to (110)) apparently showed the appearance of surface layers after the air oxidation process. The thickness of this surface layer is about 4 nm. While the image of hexaaluminate is characterized by an array of 1 nm-thick layers along [001], the surface layer contains no contours corresponding to the layer structure. Since the same structural image can be retained after calcination, this surface layer is believed to consist of $Mn_3O_4$ with spinel structure. This was confirmed by XPS measurement, which showed the Mn $2p_{3/2}$ peak with the binding energy corresponding to $Mn_3O_4$.

The structure of the $Mn_3O_4$ surface layer was studied by $CO_2$ chemisorption measurement, which was carried out in a conventional volumetric vacuum system at room temperature. After evacuating the sample at 500 °C, incremental $CO_2$ uptake at increasing pressures was measured with a pressure sensor (Baratron, MKS Inc.). After evacuation for 1 h, the $CO_2$ adsorption measurement was repeated. The irreversible $CO_2$ chemisorption is determined from the difference of a pair of adsorption isotherms and plotted as a function of loading amount of $Mn_3O_4$ in Fig. 2.

The amount of $CO_2$ chemisorption steeply decreased with increasing the loading, being negligible above 3 wt%. The $CO_2$ chemisorption appears to take place predominantly onto Ba species on the surface of hexaaluminate microcrystals but negligibly on $Mn_3O_4$. Thus, the amount of $CO_2$ chemisorption reflects the surface coverage by the $Mn_3O_4$ layer. Although the surface distribution of Ba ions on hexaaluminates are not clear, we assume that they should be exposed mainly on the basal plane of the facet which is just parallel to the monolayer including Ba. The result explains that the $Mn_3O_4$ layer completely covered, at least, the basal plane of hexaaluminate facets. The $CO_2$ adsorption remained almost zero even after heating at 700 °C.

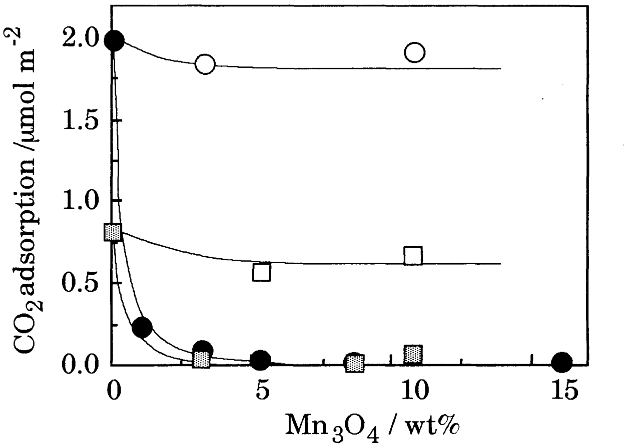
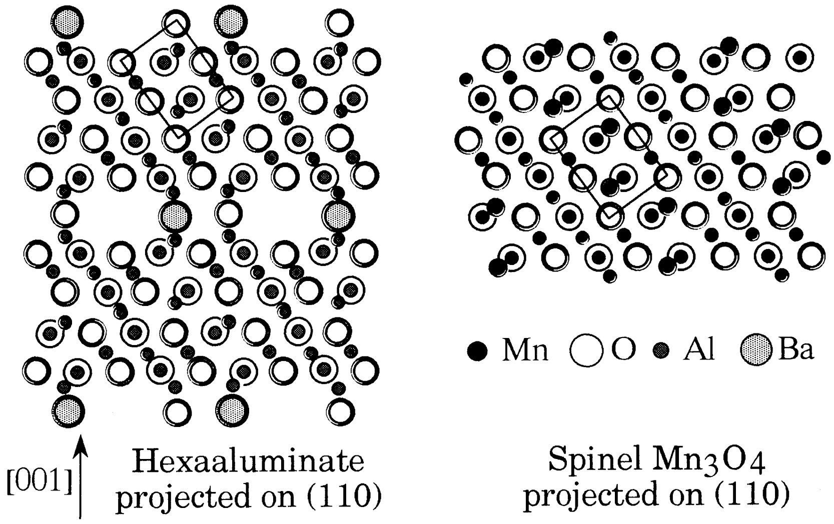


Fig. 2. Amount of irreversible $CO_2$ adsorption on $Mn_3O_4$/hexaaluminate at room temperature.
● $Mn_3O_4/Ba_{0.75}Al_{11}O_{17.25}$ (air oxidation)
▨ $Mn_3O_4/Ba_{0.75}MnAl_{10}O_{17.25}$ (air oxidation)
○ $Mn_3O_4/Ba_{0.75}Al_{11}O_{17.25}$ (evaporation to dryness)
□ $Mn_3O_4/Ba_{0.75}MnAl_{10}O_{17.25}$ (evaporation to dryness)

We believe that one of the reasons why such surface spinel layers form is the structural coherence between $Mn_3O_4$ and hexaaluminate. The projection of crystal structures (Fig. 3) shows that the ionic configuration in the spinel structure is analogous to that in the spinel blocks of hexaaluminate; they are composed of cubic close-packing of oxygen ions, of which tetrahedral and octahedral sites are partially occupied by small cations (Al and/or Mn). Therefore, the basal plane surface of hexaaluminate, being exactly parallel to the $O^{2-}$ close-packing layer, can provide coherent interface with little stress. The air oxidation process seems effective in promoting the formation of this type of interface structure because it allows continuous growth of



Hexaaluminate projected on (110)

Spinel $Mn_3O_4$ projected on (110)

Fig. 3. Projection of crystal structures of β-alumina type hexaaluminate and spinel oxide.

spinel lattices from a liquid phase. In constant, a substantial amount of $CO_2$ chemisorption was observed for $Mn_3O_4$/hexaaluminate prepared from a conven-tional evaporation-to-dryness process and subsequent calcination at 500 °C (Fig.2). This impre-gnated sample seems to contain insular $Mn_3O_4$ particles on the surface of hexa-aluminate microcrystals.

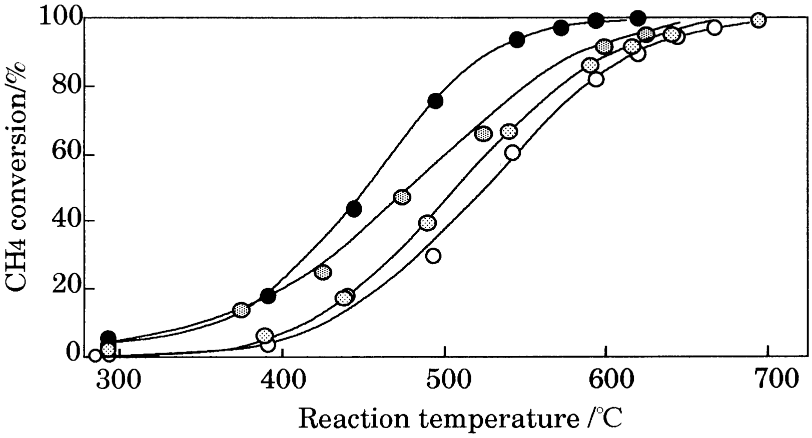


Fig. 4. Temperature dependence of methane oxidation reaction over $Mn_3O_4$/hexaaluminate. (Calcination at 500 °C)

● $Mn_3O_4$ ○ $Ba_{0.75}MnAl_{10}O_{17.25}$

◍ 5 wt%$Mn_3O_4$/$Ba_{0.75}MnAl_{10}O_{17.25}$ (air oxidation)

◍ 5 wt%$Mn_3O_4$/$Ba_{0.75}MnAl_{10}O_{17.25}$ (evaporation to dryness)

$CH_4$ 2 vol%, air 98 vol%, W/F=0.01 g min$^{-1}$ cm$^{-3}$

Catalytic activity of the $Mn_3O_4$/hexaaluminate composite for methane oxidation was evaluated in a conventional fixed bed reactor ($CH_4$ 2 vol%, air 98 vol%, W/F=0.01 g min cm$^{-3}$). Figure 4 shows the temperature dependence of $CH_4$ conversion over typical samples. The catalytic activity of $Mn_3O_4$/$BaMnAl_{10}O_{17.25}$ prepared by air oxidation is comparable to that of unsupported $Mn_3O_4$ (400 °C) , exceeding that of the sample prepared by the evaporation-to-dryness process. The $Mn_3O_4$ surface layer combined with unsubstituted hexaaluminates seemed to lack thermal stability due to solid state reactions. However, the reactivity at the $Mn_3O_4$/hexaaluminate interface can be reduced by the use of Mn-substituted hexaaluminate. These results suggests that the air oxidation process is to be expected for an excellent structural modification of hexaaluminate catalysts.

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