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Formation of catalytic $CuLaAl_{11}O_{19}/Al_2O_3$ composite powder

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The solid-state reaction and hydrocarbon-removal activities of composite powders in the system of CuO and La-modified Al_2O_3 were studied for the purpose of their application to heat-stable catalyst in exhaust-treatment. X-ray diffraction revealed the formation of catalytic nanocomposite-powder of $CuLaAl_{11}O_{19}$ and γ-Al_2O_3 at 1100 °C from the solid-state reaction between γ-Al_2O_3, CuO and La_2O_3. The La-modification of γ-Al_2O_3 was effective to maintain the large surface areas of these composite powders. The C_6H_6 removal activities were compared with practical automotive catalyst in the system of Pt–Ce and γ-Al_2O_3. The composite-powder of $CuLaAl_{11}O_{19}$ and γ-Al_2O_3 is active for complete oxidation of benzene and the microstructure is favourable as a powder for catalytic coat-layer.

1. Introduction

Alumina-based catalysts for poison-gas removal from engine exhaust have been extensively studied. Recently, novel materials with high catalytic performance meet large demands for catalytic combustion process of fuels used at temperatures over 1000 °C. [1, 2] Transition alumina, such as γ-, δ- and θ-Al_2O_3, is known as a useful support for various industrial catalytic applications including combustion catalysts and automotive catalytic converters [3]. Besides precious metal-impregnated alumina, the use of so called "base-metals", which are not expensive transition metals, have been tried as practical catalytic products. However, these metals easily sinter during operation at elevated temperatures, resulting in the deactivation of catalysts. Recent researches describe that the complex metal oxides of magnetoplumbite-type structures are heat stable and effective for oxidation catalysis of hydrocarbons [4–7]. Although the oxides are usually made by solid-state reaction using fine oxide powders or sol–gel processed precursors, monolithic powder aggregates sinter to result in dense ceramic bodies through heat treatment during both their forming and using conditions at high temperature. In this study, we demonstrate the route to fabricate composite-powders having the mixed phases of $CuLaAl_{11}O_{19}$ and γ-Al_2O_3, which has relatively large surface area as well as porous microstructure. Magnetoplumbite-structured $CuLaAl_{11}O_{19}$ is active for oxidation reactions of hydrocarbons. On the other hand, La-modification of γ-Al_2O_3 is effective to maintain surface area of alumina support, as described elsewhere [8–10]. This research is to study the synthesis condition of composite powder; γ-Al_2O_3-supported $CuLaAl_{11}O_{19}$, which should be more suitable as a coat layer of a practical catalyst converter. First, we examine the solid-state reactions of composite powders in the Cu–La–Al_2O_3 system, which are prepared by a two-step impregnation process. Here, copper was selected as a useful element for oxidation reaction of hydrocarbons as well as a promoter to control de-NO_x reactions. Then, the evolution of microstructures in these nanocomposite powders are described. Finally, we measure the activity for complete oxidation of benzene (C_6H_6) over $CuLaAl_{11}O_{19}/Al_2O_3$, which should be compared with the data of a practical Pt–Ce–Al_2O_3 automotive catalyst.

2. Experimental procedure

2.1. Preparation

Pure γ-Al_2O_3 powder (from Nikki-Universal, Japan) was with the surface area of 115 $m^2\,g^{-1}$ and the purity of 99.9%. The powder was impregnated with aqueous lanthanum nitrate, followed by agitation of the suspension, dried at 110 °C for 8 h, and heated at 600 °C for 3 h in air (1 mol % La-modified Al_2O_3 support). It was ground again, and further impregnated with aqueous copper nitrate, followed by the same process as La impregnation and heat treatment at 500 °C for 3 h in air. The powder was heat treated at various temperatures up to 1200 °C for 1–30 h in air.

2.2. Characterization

Powder X-ray diffraction (XRD) apparatus (Rigaku-Rint2000, Japan) with CuK_α source (30 kV, 20 mA) was used for the identification of phases formed in the samples. The surface areas of powders were derived by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption at 77 K. The powder samples were pelletized and pre-heated at 200 °C for 3 h in flowing nitrogen before the BET measurement procedure. Transmission electron microscopy (TEM; Jeol-2000EX, Japan) was used for the observation of microstructural evolution of the powders heated at 1100 °C.

2.3. Catalytic activity

Catalytic evaluation was performed on the complete oxidation reaction of benzene (C_6H_6). The samples were pressed into pellets of diameter of ca. 2 mm and set in a quartz tube reactor with a home-made furnace. The weight of each catalyst was 0.2 g. The reactant gas mixture composed of benzene (2 vol %) and air. The total gas flow rate was set at 350 ml min^{-1}. The analysis of C_6H_6 in exhaust was performed using gas chromatography–mass spectrometry (GCMS; Shimazu QP5000, Japan). The removal efficiencies of benzene were plotted as a function of inlet-gas temperature measured by a thermocouple.

3. Results and discussion

3.1. Solid-state reaction and sintering

The phases and sintering of the heated powders were examined by XRD and surface-area measurement. Pure γ-Al_2O_3 transformed to δ-Al_2O_3 at 800 °C, θ-Al_2O_3 at 900 °C, and then to α-Al_2O_3 at 1050 °C. The effect of La on thermal stabilization of alumina support has been known. The behaviour of sintering is seriously influenced by the additional promoter composition. Previous work suggested that La-modification of γ-Al_2O_3 stabilized the metastable phases of alumina (γ-, δ- and θ-Al_2O_3), resulting in the increase of α-transformation temperatures [8–10]. Oudet *et al.* [11] described how the coherency of thin layer of $LaAlO_3$ on γ-Al_2O_3 was important for thermal stabilization of transition alumina. However, XRD peaks of $LaAlO_3$ were not observed in present samples.

Fig. 1 shows the XRD patterns for the composite powder of Al_2O_3/La/Cu (100/1/10 as molar ratio), which was heated at temperatures up to 1200 °C for 3 h in air. The detected compounds were CuO, γ-Al_2O_3, α-Al_2O_3, $CuLaAl_{11}O_{19}$, and a small amount of $CuAl_2O_4$ [12]. Surprisingly, in these Cu–La–Al_2O_3 powders, there was observed no formation of crystalline La- and Cu-related compounds in the heat treatment below 1000 °C. Here, the phase of γ-Al_2O_3 (appeared at 800–1000 °C) is modified with CuO, forming a metastable solid solution, as discussed in previous papers [13–15]. A series of solid-state reactions (heat treatment for 3 h) in the system of present Cu–La–Al_2O_3 was summarized as

$$\begin{aligned}
&\gamma\text{-}Al_2O_3(+La_2O_3) + CuO && (600\,^\circ C)\\
&\rightarrow \gamma\text{-}Al_2O_3(+La_2O_3 + CuO) && (800-1000\,^\circ C)\\
&\rightarrow \gamma\text{-}Al_2O_3 + CuLaAl_{11}O_{19} && (\sim 1100\,^\circ C)\\
&\rightarrow \alpha\text{-}Al_2O_3 + CuLaAl_{11}O_{19} + CuO && (\sim 1200\,^\circ C)
\end{aligned} \tag{1}$$

The BET surface areas of powders were 110 $m^2\,g^{-1}$ (600 °C), 48 $m^2\,g^{-1}$ (1000 °C), 23 $m^2\,g^{-1}$ (1100 °C), and 2 $m^2\,g^{-1}$ (1200 °C), when the heat-treatment period was 3 h in air. The apparent sintering of this composite powder was accelerated by the increase of heat-treatment temperature. The XRD (Fig. 1) and microscopic observation (see Fig. 3) suggest that $CuLaAl_{11}O_{19}$ are more well-grown crystalline particles than γ-Al_2O_3. Furthermore, the formation of α-Al_2O_3 results in catastrophic growth of alumina grain and a large decrease of surface area. The decrease of surface area against temperature is considered to correspond to the increasing amount of these compounds at 1000–1200 °C. It is noted that the surface area of powder after heat treatment at 1100 °C was moderate (23 $m^2\,g^{-1}$), and that a composite powder of γ-Al_2O_3 and $CuLaAl_{11}O_{19}$ appears with no formation of α-Al_2O_3.

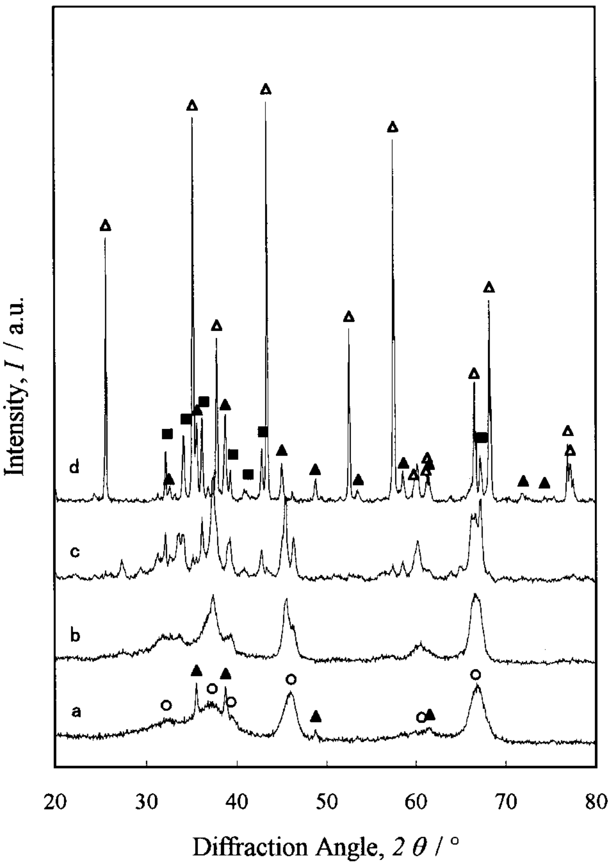

Figure 1 XRD patterns (CuK_α source) for Cu–La–Al_2O_3 (10/1/100) heated at various temperatures. (○)γ-Al_2O_3, (△)α -Al_2O_3, (▲) CuO, (■) $CuLaAl_{11}O_{19}$.

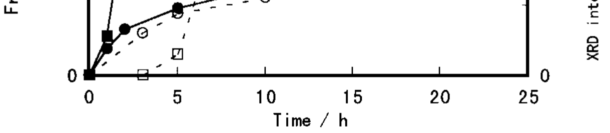

Figure 2 The fraction of α-Al_2O_3 at 1100 °C (□) and 1150 °C (■) and the amount of $CuLaAl_{11}O_{19}$ at 1100 °C (○) and 1150 °C (●) versus heat treatment period in air; obtained from XRD data.

Next, we examined the formation rate of α-Al_2O_3 and CuLa $Al_{11}O_{19}$, and the condition of synthesis of composite powder (γ-Al_2O_3 + $CuLaAl_{11}O_{19}$) by heat treatment in air. Fig. 2 illustrates the fraction of α-Al_2O_3 and

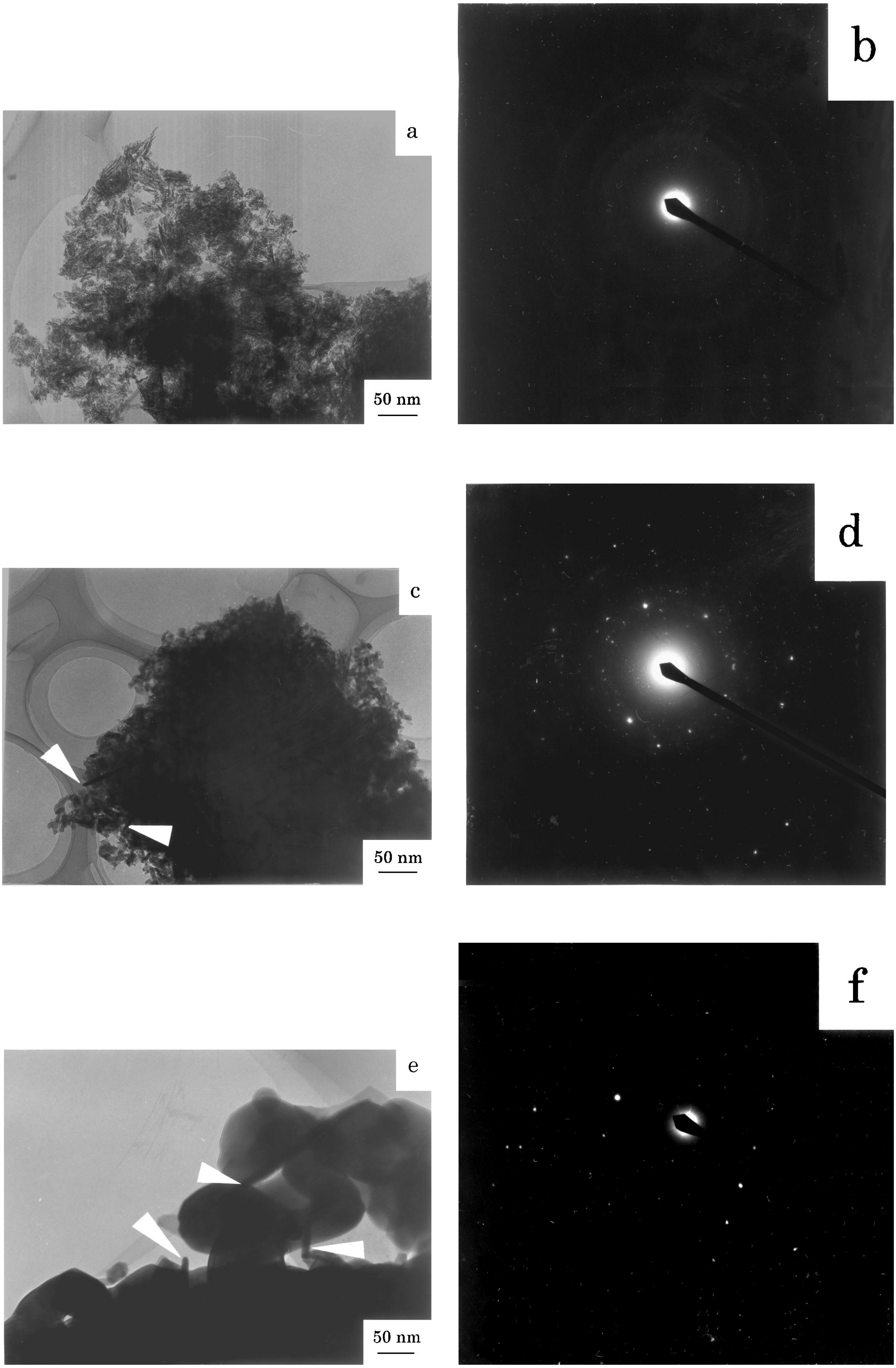

Figure 3 Transmission electron microscopic images and selected area electron diffraction patterns of Cu–La–Al_2O_3 heated in air for different periods at 1100 °C. (a) and (b) Initial state; (c) and (d) 5 h; (e) and (f) 30 h. White arrows indicate fibrous $CuLaAl_{11}O_{19}$.

the amount of $CuLaAl_{11}O_{19}$ versus the heat-treatment period at 1100 °C and 1150 °C. At 1150 °C, the formation rate of $CuLaAl_{11}O_{19}$ was apparently the same as the α-transformation rate of γ-Al_2O_3. Therefore, in this temperature, the mixed phase of γ-Al_2O_3 and $CuLaAl_{11}O_{19}$ was not able to form. On the other hand, at 1100 °C, the compound of $CuLaAl_{11}O_{19}$ formed before α-transformation. The solid-state reaction with no α-transformation is described as

$$11Al_2O_3 + 2CuO + La_2O_3 \rightarrow 2CuLaAl_{11}O_{19} \quad (2)$$

The reaction rate should depend on the diffusion of each composition. The diffusion of impregnated CuO and La_2O_3 on γ-Al_2O_3 particle may be easy to form $CuLaAl_{11}O_{19}$ at 1100 °C. Thus, by selecting the heat-treatment temperature and period, we are able to obtain the nanocomposite powder of γ-Al_2O_3 and $CuLaAl_{11}O_{19}$, which has moderate surface area and catalytic oxidation activity. This powder is expected to show good heat stability as a catalytic material used at around 1000 °C.

3.2. Morphology of powder

Fig. 3 shows a series of TEM images and electron diffractions for Cu–La–Al_2O_3 powders heated at 1100 °C for different times in air. The change of morphology for these powders corresponds to solid-state reactions; γ-Al_2O_3 (Fig. 3a) $\rightarrow$ $CuLaAl_{11}O_{19} + \gamma$-$Al_2O_3$ (Fig. 3c) $\rightarrow$ $CuLaAl_{11}O_{19} + \alpha$-$Al_2O_3$ + CuO (Fig. 3e). Fig. 3c shows the fibrous shape of $CuLaAl_{11}O_{19}$ which is grown in γ-Al_2O_3 aggregate. Here, a fibre is able to pin up the aggregate of γ-Al_2O_3 to be strongly cross-linked. This effect will be favourable for maintaining the strength of agglomeration so that the porous coat layer with γ-Al_2O_3 on a substrate is stabilized.

3.3. Benzene oxidation activity

Fig. 4 compares the complete oxidation activities for C_6H_6 over both the present composite powder ($CuLaAl_{11}O_{19} + \gamma$-$Al_2O_3$, heated at 1100 °C for 3 h in air) and practical Pt (0.5 wt %)–Ce (30 wt %)–γ-Al_2O_3 (heated at 1100 °C for 3 h in air). A Pt catalyst shows a bit better activity for this reaction than Cu–La–Al_2O_3. The initiation of combustion of benzene (30% conversion) occurred at ca.380 °C for Cu–La–Al_2O_3, whereas at ca.340 °C for Pt–Ce–Al_2O_3. With respect to the cost of the catalyst, Pt–Ce catalyst is more expensive (about one order) than Cu–La catalyst. The present inexpensive catalyst in the Cu–La–Al_2O_3 system is useful as well as heat stable for complete oxidation catalysis, if it is used in a combustion apparatus operated below 1100 °C.

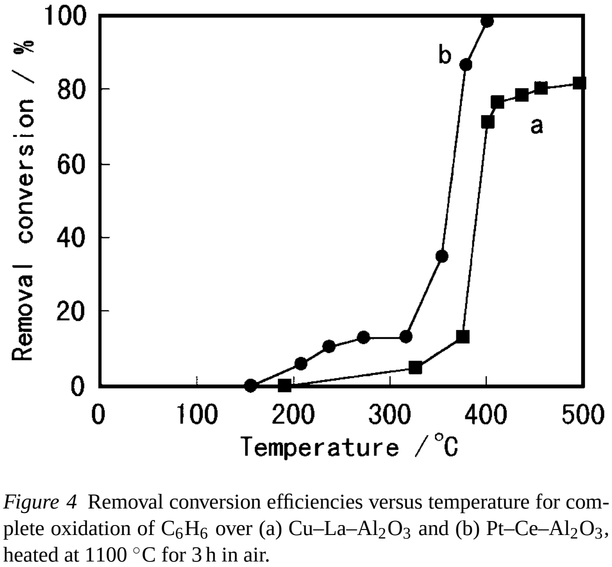

Figure 4 Removal conversion efficiencies versus temperature for complete oxidation of C_6H_6 over (a) Cu–La–Al_2O_3 and (b) Pt–Ce–Al_2O_3, heated at 1100 °C for 3 h in air.

4. Conclusion

The solid-state reaction and hydrocarbon oxidation activities of nanocomposite powders in the system of Cu–Al_2O_3 with small amount of La were studied toward their application to heat-stable exhaust catalyst. X-ray diffraction revealed the formation of catalytic composite powder of $CuLaAl_{11}O_{19} + \gamma$-$Al_2O_3$ at 1100 °C from the solid-state reaction between γ-Al_2O_3, CuO and La_2O_3. The La stabilization of starting γ-Al_2O_3 was effective to maintain the large surface areas of the composite powder. The C_6H_6 removal activities were compared with practical Pt–Ce/γ-Al_2O_3 catalyst. The present inexpensive catalyst in the Cu–La–Al_2O_3 system is useful and heat stable for a combustion apparatus operated below 1100 °C.

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