Performance Comparison of Spray-dried Mn-based Oxygen Carriers Prepared with γ-Al₂O₃, α-Al₂O₃, and MgAl₂O₄ as Raw Support Materials

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Abstract

In chemical-looping combustion, pure oxygen is transferred to fuel by solid particles called as oxygen carrier. Chemical-looping combustion process usually utilizes a circulating fluidized-bed process for fuel combustion and regeneration of the reduced oxygen carrier. The performance of an oxygen carrier varies with the active metal oxide and the raw support materials used. In this work, spray-dried Mn-based oxygen carriers were prepared with different raw support materials and their physical properties and oxygen transfer performance were investigated to determine that the raw support materials used are suitable for spray-dried manganese oxide oxygen carrier. Oxygen carriers composed of 70 wt% Mn₃O₄ and 30 wt% support were produced using spray dryer. Two different types of Al₂O₃, γ-Al₂O₃ and α-Al₂O₃, and MgAl₂O₄ were applied as starting raw support materials. The oxygen carrier prepared from γ-Al₂O₃ showed high mechanical strength stronger than commercial fluidization catalytic cracking catalyst at calcination temperatures below 1100 °C, while the ones prepared from α-Al₂O₃ and MgAl₂O₄ required higher calcination temperatures. Oxygen transfer capacity of the oxygen carrier prepared from γ-Al₂O₃ was less than 3 wt%. In comparison, oxygen carriers prepared from α-Al₂O₃ and MgAl₂O₄ showed higher oxygen transfer capacity, around 3.4 and 4.4 wt%, respectively. Among the prepared Mn-based oxygen carriers, the one made from MgAl₂O₄ showed superior oxygen transfer performance in the chemical-looping combustion of CH₄, H₂, and CO. However, it required a high calcination temperature of 1400 °C to obtain strong mechnical strength. Therefore, further study to develop new support compositions is required to lower the calcination temperature without decline in the oxygen transfer performance.

Keywords: Carbon dioxide, chemical looping combustion, oxygen carrier, manganese oxide

I. INTRODUCTION

Post-2020 Climate Agreement adopted at Confernce of Parties (COP21) decided to cap the increase in the global average temperature to well below 2 °C above pre-industrial levels. Carbon capture and storage (CCS) is recognized as one of the major options to mitigate CO_2 emission. Among the carbon capture technologies, post-combustion and pre-combustion technologies require a CO_2 capture facility to separate CO_2 from a gas stream. The installation and operation of the CO_2 capture facility result in considerable a efficiency loss and increase in energy cost. Oxyfuel combustion has been studied as an alternative carbon capture technology which does not need a CO_2 capture facility because CO_2 is inherently separated during fuel combustion. However, the cost to produce pure oxygen from air is still too high to apply oxyfuel combustion to a commercial scale. Chemical-looping combustion (CLC) has been noticed as another promising technology with the feature of inherent separation of CO_2 without a capture facility. CLC also uses pure oxygen for fuel combustion. However, the oxygen required for fuel combustion is supplied by a solid particle containing oxygen, or an oxygen carrier (OC). It is expected that the cost penalty and the system efficiency loss accompanied by CO_2 capture will be less in CLC than other CO_2 capture technologies [1]–[3].

A circulaing fluidized-bed process which is consisted of two interconnected fluidized-bed reactors, a fuel reactor and an air reactor, is usually used in a CLC process as shown in Fig. 1. An OC transfers oxygen from air to fuel while circulating between the two reactors. In the fuel reactor, the OC gives its oxygen to the fuel for fuel combustion. The fuel is oxidized and emits CO_2 and H_2O. In the air reactor, the reduced OC is regenerated to oxidized state by receiving oxygen in the air supplied into the air reactor. The flue gas from the fuel reactor theoretically contains only CO_2 and H_2O. Pure CO_2 can be obtained after condensation of H_2O. Therefore, the OC requires excellent physical properties suitable for the fluidized-bed process applications and high oxygen transfer performance for complete combustion of fuel. Long term durability to endure cyclic redox reaction at high temperatures is also important to be a quality OC.

An OC is composed of acive metal and support. The active metal transfers oxygen and the support enhances physical and chemical properties of OC such as porosity, surface area, dispersion of metal oxide, and mechanical strength. Oxidized- and reduced-forms of primary transition metal, NiO-Ni, Mn_3O_4-MnO, Fe_2O_3-Fe_3O_4, and CuO-Cu, are commonly studied forms of active metal for CLC of gaseous fuels in a temperature range of 800 to 1200 °C . The oxygen ratios of each pair are 21.4, 7.0, 3.3, and 20.1, respectively. NiO has been the most extensively studied metal oxide for CLC because it has high oxygen ratio and NiO-based OCs have high oxygen transfer capacity, good reactivity, and superior physical properties [4][5]. However, NiO
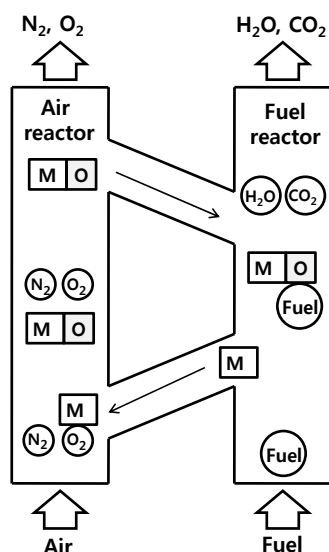
Fig. 1. Schematic of chemical looping combustion process (M: metal, O: oxygen).

is expensive and a small amount of CO and H_2 is emitted in the outlet gas of the fuel reactor due to the thermodynamic restrictions [6][7]. Although CuO has high oxygen ratio and the capability of complete fuel conversion to CO_2 and H_2O, low melting temperature of Cu, 1085 °C, inhibits its use. Fe_2O_3 is cheap and environmentally safe, but the amount of transferable oxygen is small and its reactivity with CH_4 is poor. Mn_3O_4 has relatively high oxygen ratio. It can fully convert CH_4 to CO_2 and H_2O and has good reactivity [7][8]. Morevoer, it is inexpensive and non-toxic.

Several inorganic materials such as Al_2O_3, SiO_2, TiO_2, or ZrO_2, etc. were tested as suppot matrials for above metal oxides. The test results were well summarized in the literature [9][10]. The use of Al_2O_3 resulted in high reactivity with fuel gases and good physical properties on the NiO-, CuO-, Fe_2O_3-based OCs. SiO_2 was suitable for CuO-based OCs and TiO_2 was recommendable for CuO-, Fe_2O_3-based OCs. Most metal oxides supported on ZrO_2 showed good reactivity, but poor mechanical stability. In Mn-based OC, particles derived from ZrO_2 stabilized with MgO showed good reactivity and physical stability. On the whole, alumina was well machted with most metal oxides as a support material. Structurally less-stable alumina like $γ-Al_2O_3$ forms metal compounds such as $NiAl_2O_4$, $CuAl_2O_4$, $FeAl_2O_4$, and $MnAl_2O_4$, after calcination due to the strong metal-support interaction [11][12]. The reactivity of $NiAl_2O_4$ and $MnAl_2O_4$ is poor [13][14] while $CuAl_2O_4$ has similar reduction reaction rate to that of CuO [12]. $FeAl_2O_4$ had positive effect on the oxygen transfer capacity of Fe-based OCs. Structurally more stable materials such as $α-Al_2O_3$ and $MgAl_2O_4$ have been tested to lessen the metal-support interaction.

An OC can be prepared by physical mixing, impregnation, and spray drying method. Among them, spray drying is the most suitable method to produce a large amount of OC with spherical shape for the devlopment of MW or larger scale CLC processes. The result of the tests on the OCs prepared by laboratorial preparation method such as physical mixing and impregnation is not always consistent with that by spray drying method as shown in our previous works [15][16]. This is due to that a high proportion of metal oxide is preferred in the spray drying method. Therfore, support materials for spray-drying method should be searched for or tested separately, along with the study by the laboratorial preparation methods.

In this paper, Mn-based OCs were designed using sructurally less-stable and stable raw support materials to develop low-cost OCs. The designed OCs were prepared by spray drying method and their performances were investigated in terms of the physical properties and reactivity to determine whether the support materials used are suitable for spray-dried Mn-based OC. Different calcination temperatures by the type of raw support materials were applied to obtain sufficient mechanical strength and the resultant physical characteristics were analyzed. The combustion performance was measured using CH_4, CO, and H_2 as fuel gases. The best support material among the tested ones and future works were suggested based on the results of this work.

II. EXPERIMENTAL

A. Preparation of oxygen carriers

Commercially available powder-type Mn_3O_4 was well-mixed with support materials in pure water. $γ-Al_2O_3$ was used as structurally less-stable raw support material and $α-Al_2O_3$ and $MgAl_2O_4$ were used as structurally stable ones. $γ-Al_2O_3$ turns to $α-Al_2O_3$ by structure change when it was calcined above 1100 °C. The ratio of Mn_3O_4 to support was 7 : 3 on the dry weight basis. During the mixing of solid powder, an organic dispersant was added to prevent the agglomeration of the solid powder. The suspension was comminuted with a ball mill to make a homogeneous colloidal slurry. The homogenized slurry was sprayed throuhg a nozzle positiond in the center of hot chamber to form spherical particles, i.e., green body. The green body was calcined at targetted temperatures in a muffle oven for 5 h after pre-drying at 120 °C overnight. The prepared OCs were designated by abbreviation implying information on the proportion of Mn_3O_4, the raw support material and the calcination temperature. GA, AA, and MA in the names of the OCs mean $γ-Al_2O_3$, $α-Al_2O_3$, and $MgAl_2O_4$, respectively. For example, "Mn70GA-900" indicates that the OC was prepared using 70 wt% Mn_3O_4 and 30 wt% $γ-Al_2O_3$, and was calcined at 900 °C for 5 hours.

B. Characterization of oxygen carriers

The spray-dried OCs were characterized by the physical properties related to fluidization and reactivity. After calcination, the mechanical strength, or attrition resistance, was measured first to decide whether the prepared OC can be used in an actual CLC process. A three-hole air-jet attrition test apparatus based on American Society for Testing and Materials (ASTM) D 5757-95, which is the standard fluidized-bed test method for determination of attrition and abrasion of powdered catalysts, was used to measure the attrition resistance of the prepared OCs. The attrition resistance was determined at 10 slpm over 5 hours, as described in the ASTM method. The attrition index (AI), or attrition loss is the percentage of fines generated over 5 hours. The fines are particles collected at the thimble, which was attached to the gas outlet.

AI = [amount of total fine collected for 5 hours/amount of initial sample (50 g)] × 100% (1)

Lower AI values indicate better attrition resistance of the

Table 1. Physical properties of the spray-dried Mn_3O_4 oxygen carriers

Oxygen carrier	Composition of raw materials (wt%)	Calcination temperature (°C)	Average particle size (μm)	Tapped density (g/mL)	BET surface area (m²/g)	Specific pore volume[1] (mL/g)			Hg porosity (%)	Attrition Index (%)
						Total	Mesopore	Macropore		
Mn70GA	Mn_3O_4 (70),	900	123	1.5	9.2	0.18	0.01	0.17	21.0	11.1
	γ-Al_2O_3 (30),	1100	111	2.5	0.3	0.00	0.00	0.001	0.3	0.2
Mn70AA	Mn_3O_4 (70),	1100	-	-	-	-	-	-	-	86.3
	α-Al_2O_3 (30)	1200	133	2.1	0.3	0.04	0.00	0.04	6.5	7.5
Mn70MA	Mn_3O_4 (70),	1300	-	-	-	-	-	-	-	27.2
	$MgAl_2O_4$ (30)	1400	113	1.7	0.2	0.03	0.00	0.03	4.8	9.4

[1] Calculated from Hg intrusion data

bulk particles. The AI of the commercial fluid-catalytic-cracking (FCC) catalyst, Akzo, was 22.5% and it was used as a comparison standard.

The shape and surface image of the OCs were obtained by a field emission scanning electron microscope (FE-SEM; JOEL JSM 6400). The particle size distribution and average particle size of the sample were measured following ASTM E-11. Autotap instrument (Quantachrome) described in ASTM D 4164-88 was used to measure the packing density of the sample. Brunauer-Emmett-Teller (BET) surface area of the sample was determined by N_2 physisorption using an ASAP 2420 (Micro meritics Inc.) automated system. Porosity and the distribution of pore volume by pore size were calculated from Hg intrusion data collected with an AutoPore IV 9500 (Micromeritics Inc.).

C. Reactivity investigation in TGA

The OCs with sufficient mechanical strength were selected for the oxygen transfer reactivity test. The cyclic reaction data on reduction and oxidation of OCs were obtained using thermogravimetric analyzer (TGA; Thermo Cahn, TherMax500) under ambient pressure. Approximately 30 mg of sample was placed on the alumina crucible and heated up to 950 °C in a nitrogen atmosphere. 10 vol% CH_4 balanced with CO_2, 40 vol% CO balanced with CO_2, or 40 vol% H_2 balanced with CO_2 were used for a fuel gas and air was used to oxidation of the reduced OC. After each reduction and oxidation reaction, N_2 was introduced to prevent direct contact of gaseous fuels and air. The total flow rate of gases was kept at 0.3 slpm. For the OCs with very slow reaction rate, the fuel or air was switched to N_2 after 30 minutes from the beginning of the reaction.

The oxygen transfer reactivity was analyzed in terms of oxygen transfer capacity and oxygen transfer rate. Oxygen transfer capacity is the maximum percentage of oxygen mass transferable to a fuel under a given experimental condition. It is calculated on the basis of the mass of the fresh OC in its fully-oxidized state. For example, if 5 g of oxygen is transferred to a fuel at the end of reduction from 100 g of a fully oxidized fresh OC under a given experimental condition, the oxygen transfer capacity of the OC is 5 wt%. The degree of conversion, X, of an OC is defined as:

$$x = \frac{m_0 - m}{m_0 - m_{red}} \tag{2}$$

where m is the instantaneous mass of an OC measured by the TGA. m_0 and m_{red} are the theoretical masses of the OC in its fully-oxidized and fully-reduced state, respectively. The denominator of Eq. 2, the weight difference between m_0 and m_{red}, is the theoretical maximum amount of oxygen that can be transferred to a fuel. Oxygen utilization is percentage of the mass of oxygen

actually transferred to a fuel among the total mass of oxygen transferable to a fuel. A mass-based conversion, ω, was used to compare the mass change as a function of time. It is defined as:

$$\omega = \frac{m}{m_0} \tag{3}$$

The oxygen transfer rate is expressed as the mol of transferred oxygen per unit kilogram of OC per unit time (mol O/kg/s).

III. RESULTS AND DISCUSSION

A. Physical properties

The physical properties measured by the standard test methods were summarized in Table 1. The most important property is mechanical strength, or attrition loss. The AI values were quite different even at the same calcination temperature, depending on the raw support materials used. The OC prepared from γ-Al_2O_3 showed the highest mechanical strength at the same calcination temperature. Even at the calcination temperature of 900 °C, it showed much higher mechanical strength than the commercial FCC catalyst, Akzo. In comparison, The OCs prepared from α-Al_2O_3 and $MgAl_2O_4$ required 1200 and 1400 °C, respectively, to obtain high mechanical strength less than 10% in AI value. This resulted from the fact that the structurally less-stable material, γ-Al_2O_3, strongly interact with active metal oxide, Mn_3O_4, even at a lower calcination temperature while structurally stable materials, α-Al_2O_3 and $MgAl_2O_4$, have loose interaction with Mn_3O_4. Therefore, they required a much higher calcination temperature to obtain sufficent mechanical strength by the binding of raw materials.

The average particle size of the OCs was 120±15 μm and tapped density was 2.0±0.5 g/mL, which are suitable range for fluidization of particles. All OCs with high mechanical strength, or AI values less than 10%, had very low BET surface area below 0.5 m²/g. Their porosity were also not high. Mn70GA-900 only had a little high surface area and porosity. The majority of the pore volume of all OCs was contributed by macropore as given in Table 2. Well developed macropore and mesopore will enhance the transport of the reactant gases.

All OCs had sphere-like shape as shown in Fig. 2(a) as an example. Spherical or sphere-like shape is preferred in fluidization process to reduce attrition loss. The surface image of Mn70GA calcined at 900 °C, Fig. 2(b), revealed that the grains of raw materials still maintained their body shapes although they combined each other. However, in Mn70GA calcined at 1100 °C the grains grew to form bigger crytalloid structures as shown in Fig. 2(c). Mn70AA and Mn70MA calcined at 1200 and 1400 °C,
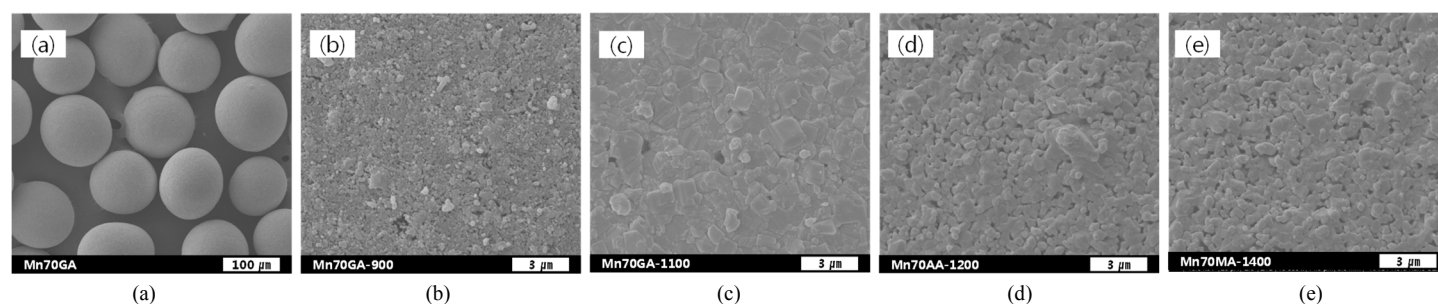
Fig. 2. SEM images of the spray-dried Mn_3O_4 Oxygen carriers. (a) Mn70GA, (b) Mn70GA-900, (c) Mn70GA-1100, (d) Mn70AA-1200, (e) Mn70MA-1400.

Table 2. Oxygen transfer capacity and the highest oxygen transfer rate in reduction at 950 °C

Oxygen carrier	Oxygen transfer capacity (wt%)						The highest oxygen transfer rate (mol O/kg$_{oc}$/s)		
	CH_4 10%, CO_2 90%		CO 40%, CO_2 60%		H_2 40%, CO_2 60%		CH_4 10%, CO_2 90%	CO 40%, CO_2 60%	H_2 40%, CO_2 60%
	30 s	300 s	30 s	300 s	30 s	300 s			
Mn70GA-900	0.9	1.4	0.7	1.3	0.4	1.5	0.059	0.043	0.022
Mn70AA-1200	1.1	2.6	1.2	2.7	1.2	2.9	0.042	0.047	0.037
Mn70MA-1400	1.3	4.1	1.9	4.1	1.4	4.2	0.039	0.061	0.049

Table 3. Oxygen transfer capacity and the highest oxygen transfer rate in oxidation at 950 °C

Oxygen carrier	Oxygen transfer capacity (wt%)		The highest oxygen transfer rate (mol O/kg$_{oc}$/s)
	Air		Air
	30 s	300 s	
Mn70GA-900	2.2	2.2	0.137
Mn70AA-1200	1.5	2.6	0.087
Mn70MA-1400	2.5	4.3	0.115

respectively, also showed grain growth through the combining of the raw grains as shown in Fig. 2(d)(e). As expected from the attrition loss test results, grain growth was observed in OCs with high mechanical strengh.

B. TGA reactivity

The TGA reactivity tests were performed for the OCs with sufficient mecahnical strength, Mn70GA-900, Mn70AA-1200, and Mn70MA-1400. The mass-based conversion as a function of reaction time and oxygen transfer rate as a function of degree of conversion (X) are presented in Fig. 3 and Fig. 4, respectively. The oxygen transfer capacities of Mn70GA-900, Mn70AA-1200, and Mn70MA-1400 for 30 minutes were 2.3, 3.4, and 4.4 wt%, respectively, by H_2. The theoretical maximum oxygen transfer capacity of an OC containing 70 wt% Mn_3O_4 is 4.9 wt% at 950 °C in the Mn_3O_4–MnO system. Therefore, Mn70GA-900 and Mn70AA-1200 transferred only 46.9% and 69.4%, respectively, among their transferrable oxygen.

The oxygen transfer capacities of Mn70GA-900 for 30 minutes were 1.9, 2.1 and 2.3 wt% for CH_4, CO, and H_2, respectively. For all fuel gases, they were the lowest capacities among the three OCs in spite of its higher porosity and BET surface area. Mn70GA-900 reacted with CH_4 most rapidly even though the driving force of gas diffusion by fuel concentration is lower in 10% CH_4 than that in 40% CO or 40% H_2. From the graphs of Mn70GA-900 in Fig. 4(a)-(c), it was observed that the highest oxygen transfer rate appeared at the degree of conversion

(X) below 0.1. The oxidation reaction completed within 30 seconds. This means that oxygen exposed on the surface of the OC reacted fast with fuel, and then the oxygen hardly transported from inside of the grain to the surface.

The oxygen transfer capacities of Mn70AA-1200 for 30 minutes were 3.3, 3.2 and 3.4 wt% for CH_4, CO, and H_2, respectively. Mn70AA-1200 showed higher oxygen transport capacity than Mn70GA-900. Oxygen was transferred to fuel steadily at the degree of conversion below 0.6 and the highest oxygen transfer rate appeared at the degree of conversion around 0.1, as shown in Fig. 4(a)-(c). Oxygen transfer rate sharply decreased at the degree of conversion around 0.2. After 30 or 40 % of the transferable oxygen reacted fast, oxygen transport proceeded slowly in both reduction and oxidation.

The oxygen transfer capacities of Mn70MA-1400 for 30 minutes were 4.4 wt% for all fuel gases. Mn70MA-1400 showed the highest oxygen transfer capacity among the three OCs. Most of the transferable oxygen reacted with fuel within 2 minutes. In the reaction with CH_4 and H_2, high oxygen trasfer rate was still maintained even at the degree of conversion around 0.5. This indicates that the oxygen inside of the grain moves easily to the surface even after more than half of the transferable oxygen was exhausted. These characteristics should be considered when a CLC process is designed using Mn70MA-1400.

The oxidation of the reduced OCs proceeded more rapidly compared to the reductuion. Most of the transferable oxygen was absorbed into the OCs within one minute. Although oxygen transfer capacity of Mn70GA-900 is lower than those of Mn70AA-1200, and Mn70MA-1400, Mn70GA-900 showed the highest oxygen trnasfer rate in oxidation. The higher oxygen transfer rate appeared in the latter half of the oxidation reaction for Mn70GA-900, while it was observed in the first half for Mn70AA-1200, and Mn70MA-1400, as shown in Fig. 4(d). The highest oxygen transfer rates in oxidation were almost two times higher than those in reduction, as given in Table 2 and 3. Although the exact reason for this is unclear right now, it is estimated that the dissimilar reaction patterns between OCs resulted from the differences in the chemical state of the active metal and physical structure of the OCs. It should be clarified through further study. The reaction chateristics obtained in this work on the spray-dried Mn-based OCs can be usefully utilized in the design of CLC processes.

IV. CONCLUSIONS

To develop a low-cost OC, Mn-based spray-dried OCs were prepared with different raw support materials, γ-Al_2O_3 and α-Al_2O_3, and $MgAl_2O_4$. The OC prepared from the structurally less-
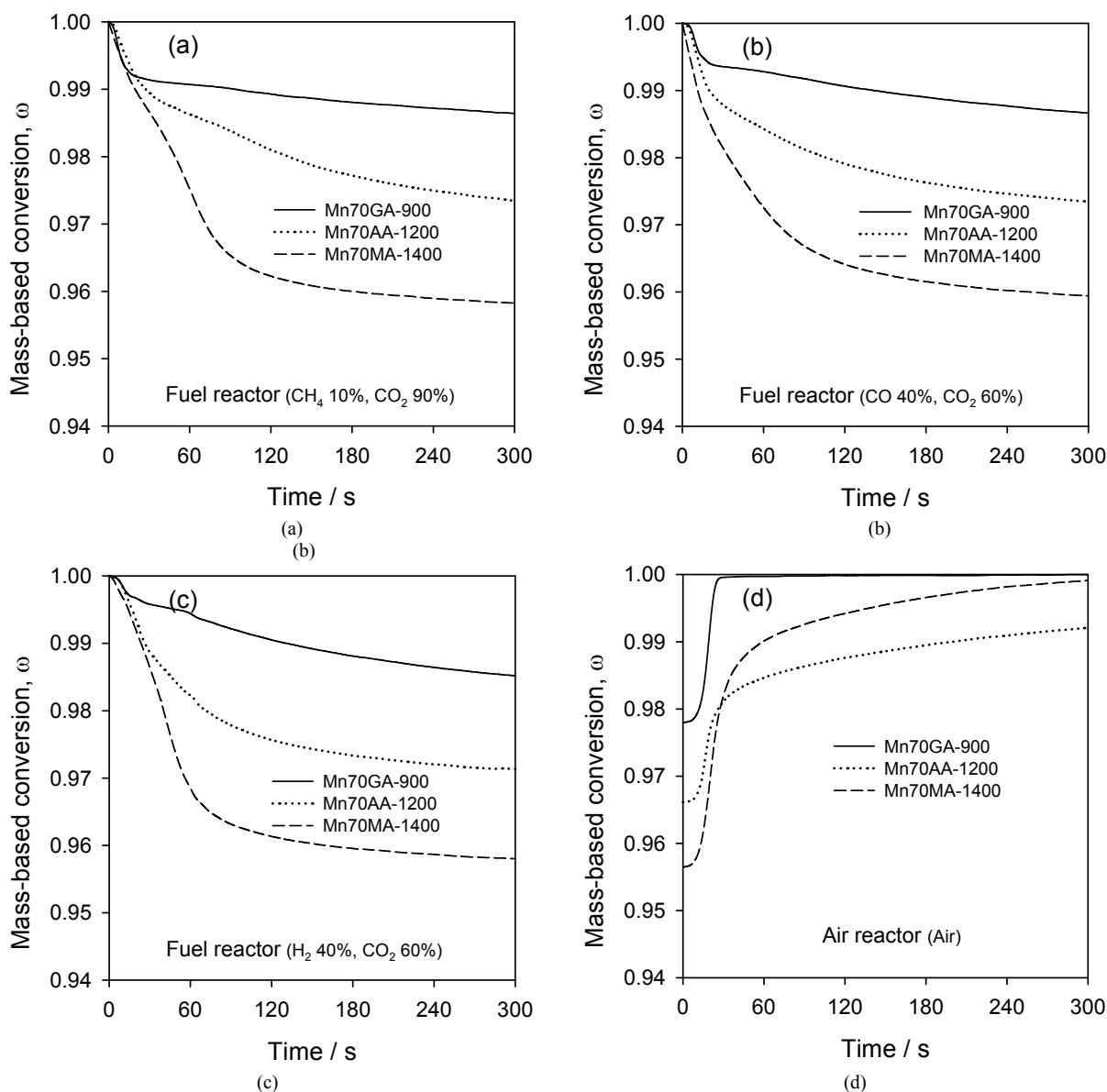
(a)

(b)

(c)

(d)

Fig. 3. Mass-based conversion of the spray-dried Mn_3O_4 oxygen carriers as a function of reaction time at 950 °C using (a) CH_4 10% and CO_2 90%, (b) CO 40% and CO_2 60%, (c) H_2 40% and CO_2 60% in the fuel reactor, (d) air in the air reactor.

stable raw support material, γ-Al_2O_3, exhibited sufficient mechanical strength at lower calcination temperatures compared to the OCs prepared from structurally stable raw support materials, α-Al_2O_3, and $MgAl_2O_4$. The OC prepared from γ-Al_2O_3 showed the worst oxygen transfer performance although it has higher porosity and surface area. Among the three OCs, the OC prepared from $MgAl_2O_4$ had the best oxygen transfer reactivity for all fuel gases, CH_4, CO, and H_2. It had high oxygen transfer capacity of 4.4 wt%, utilizing around 90% of theoretically tranferable oxygen, and higher reaction rate. For all OCs, oxidation proceeded more rapidly than reduction. The experimental results of this work suggest that $MgAl_2O_4$ can be a recommendable support material for Mn-based OCs prepared by spray drying method. However, the OC prepared from $MgAl_2O_4$ required a high calcination temperature of 1400 °C to obtain strong mechnical strength. Therefore, further studies are needed to find out new support compositions which can reduce the calcination temperature with maintaining or improving the

oxygen transfer performance.

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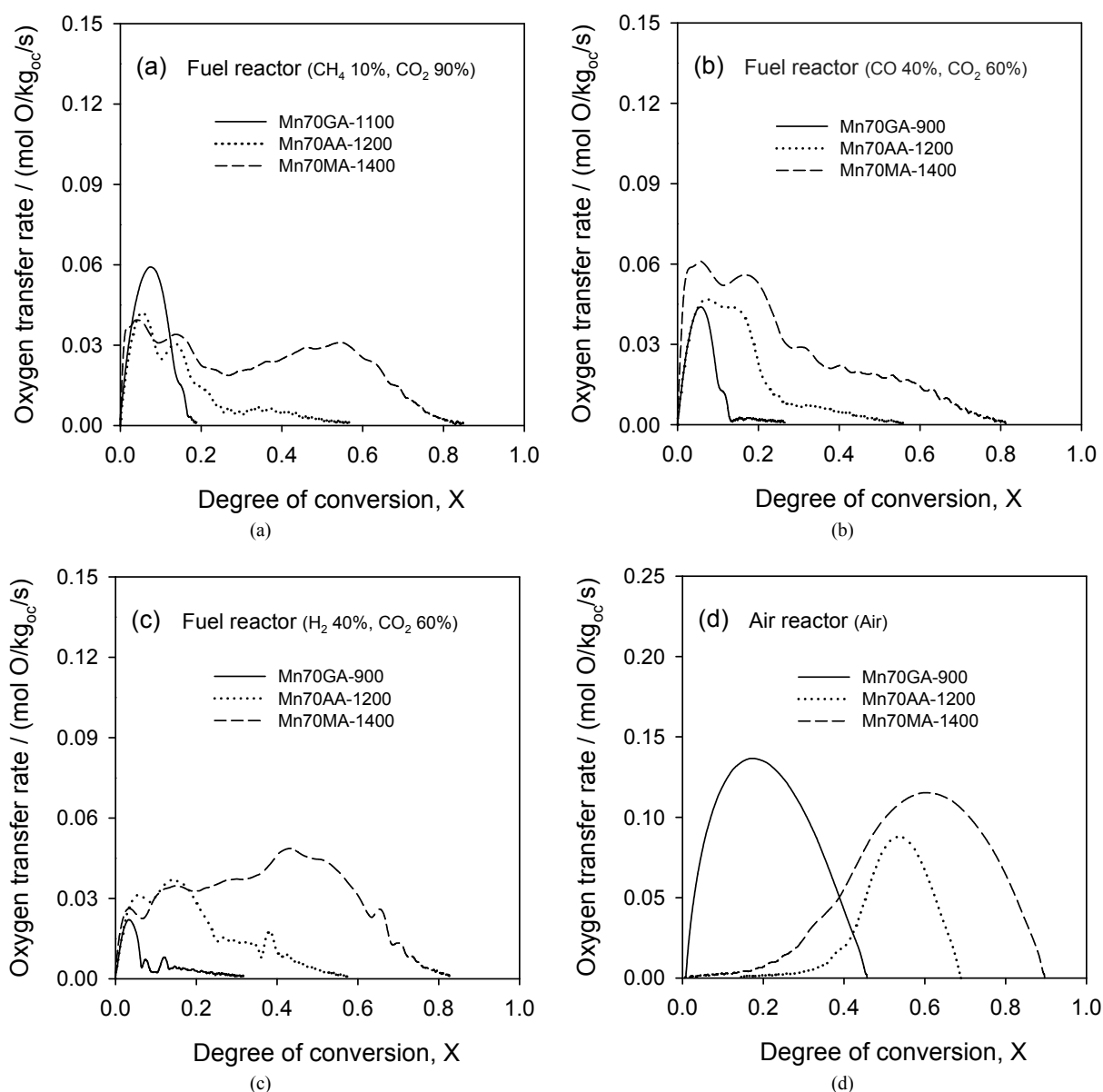[2] Lyngfelt, A., Leckner B., and Mattisson, T., "A Fluidized-bed

Fig. 4. Oxygen transfer rate of the Mn-based spray-dried oxygen carriers as a function of degree of conversion at 950 °C using (a) CH_4 10% and CO_2 90%, (b) CO 40% and CO_2 60%, (c) H_2 40% and CO_2 60% in the fuel reactor, (d) air in the air reactor.

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