Synthesis of aluminum based core−shell metal−ceramic microstructures for catalyst materials and selective CO oxidation

Jieun Kim[a,b], **Tae Wook Kim**[a,b], **Doohwan Lee**[c], **Eun Duck Park**[a,b,*]

[a]*Department of Chemical Engineering, Ajou University, Suwon,16499, Republic of Korea*
[b]*Department of Energy Systems Research, Ajou University, Suwon,16499, Republic of Korea*
[c]*Catalysis and Nanomaterials Laboratory, Department of Chemical Engineering, University of Seoul, Seoul,02504, Republic of Korea*
**Corresponding author: +82-31-219-1612, edpark@ajou.ac.kr*

Abstract: The Al@γ-Al_2O_3 core-shell microstructure contained highly heat conductive Al metal core and high surface area γ-Al_2O_3 shell was prepared simply by hydrothermal surface oxidation of Al metal particle. The functional structure is expected to exhibit high activity and selectivity by facilitating heat transfer when used as a catalyst structure for catalytic reactions requiring high heat transfer. Herein, core-shell microstructure with Al metal core encapsulated by aluminum based spinel shell ($MeAl_2O_4$, Me= Zn, Ni, Co, Mn, and Mg) were synthesized by direct synthesis method and reported on the formation mechanism. In addition, Ru supported on Al@γ-Al_2O_3 was applied to the selective CO oxidation of exothermic reaction requiring high heat flux ($\triangle H^0_{298}$ = - 283.0 kJ/mol).

Keywords: Core-shell catalyst, Metal-ceramic composite, Catalyst.

1. Introduction

The enhanced heat transfer of catalyst was very important to use the full potential of catalyst during highly endothermic and exothermic reactions and avoid the hot spot formation [1,2]. However, most supports for catalyst were used low thermal conductive ceramic materials (alumina, zirconia, zeolite, etc.). Al@γ-Al_2O_3 core-shell microstructures simply synthesized by hydrothermal surface oxidation of Al particles [3,4]. The core-shell microstructures that consist of highly thermal conductive aluminum core with high surface area crystalline aluminum oxide shell are expected to enhance thermal conductivity and high surface area for catalyst support. In this study, aluminum-aluminum based spinel core-shell structures synthesized by direct synthesis method that is hydrothermal surface oxidation in various metal nitrate solution (metal cation: K^+, Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{3+}) and analyzed physical/chemical properties and considered about mechanism and intrinsic thermal conductivity of support material. In addition, we demonstrate that these core-shell structures facilitate the heat and mass transport required for the catalytic reactions by using Al@γ-Al_2O_3 as the support for a Ru catalyst for selective CO oxidation.

2. Experimental

The core-shell Al@$MeAl_2O_4$ metal-ceramic composites were prepared by hydrothermal surface oxidation of Al metal particles in aqueous solution in Teflon-lined autoclave. The additive metal precursors used for aqueous solution were $Mg(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$. The hydrothermal synthesis was conducted at 273-473 K for 3 h under autogenous pressure. The resulting samples were washed, filtered, dried at 393 K for 12 h, and calcined at 823 K for 4 h (ramp = 10 K min^{-1}). Ruthenium catalysts supported on the Al@Al_2O_3 core-shell were prepared by incipient wetness impregnation with an aqueous solution of ruthenium nitrosyl nitrate. The activity tests of selective CO oxidation were conducted at fixed-bed reactor system. Before the CO oxidation reaction, the catalysts were reduced in flowing H_2 (30 ml min^{-1}) at 573 K for 1 h and subsequently purged in He (10 ml min^{-1}) for 0.5 h. The composition of the reactants was based on 1 vol.% CO, 1 vol.% O_2, 50 vol.% H_2, and 48 vol.% He at a flow rate of 1,000mL/min.

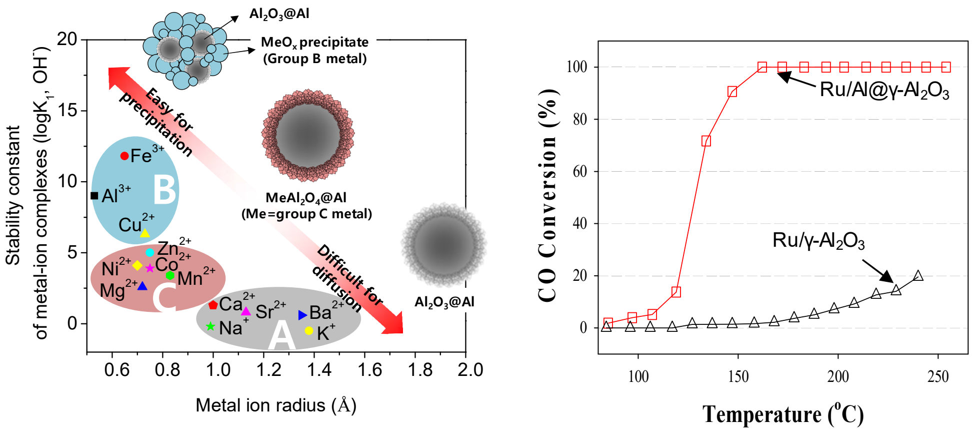

Figure 1. a) The synthesis mechanism and ion radius with respect to stability constants of metal ion complexes (metal cation: K^+, Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{3+}), b) CO conversion over Ru/Al@Al_2O_3 (□), Ru/γ-Al_2O_3 (△) catalysts during selective CO oxidation.

3. Results and discussion

The core-shell structure synthesis was performed in various metal nitrate solution (K^+, Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Fe^{3+}). As a result, the synthesis is separated by group A, B, C according to the metal cations (Figure 1.a). The group A, larger metal ion (Na^+, Ca^{2+}, Sr^2, Ba^{2+}, K^+) than 1 Å was not synthesized on aluminum based spinel core-shell structure because difficult to diffuse into oxidized aluminum. On the other hand, group B, Fe^{2+} (0.65 Å) and Cu^{2+} (0.72 Å) ion had not been synthesized aluminum based spinel shell in spite of small metal ion size. This was because the metal ions were easily homogeneous hydrolysis due to high stability constant of metal-ion for formation of hydroxide. Consequently, metal ion of group C (Ni^{2+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}) which have small metal ion size and low stability constant synthesized aluminum based spinel.

In addition, Ru catalyst supported on Al@γ-Al_2O_3 core-shell structures was prepared, and ther properties were investigated for selective CO oxidation. The results were compared with a Ru supported on commercial γ-Al_2O_3. The Figure 1b) shows CO conversion on these catalysts. The Ru/Al@γ-Al_2O_3 showed 100% CO conversion above 160 ℃, but Ru/γ-Al_2O_3 exhibited very low CO conversion. The results were related to a facilitated heat transport through the metal-ceramic composite catalyst structure, and Ru catalyst particle oxidation.

4. Conclusions

The Aluminum-aluminum based spinel core-shell structure were synthesised by direct synthesis method that is hydrothermal surface oxidation. As a result, the spinel shells were synthesised in only Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} solution, among various ion solutions. The most important factor for aluminum-aluminum based spinel core-shell structure synthesis was (i) the thermodynamic stability constant of the metal hydroxide complex and (ii) size of metal ion. In addition, Ru/Al@γ-Al_2O_3 and Ru/γ-Al_2O_3 were applied on the selective CO oxidation so that the heat transfer effects of core-shell microstructures that consist of highly thermal conductive aluminum core would confirm. The Ru/Al@γ-Al_2O_3 shows batter CO conversion than Ru/γ-Al_2O_3 due to facilitated heat transfer.

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