Oxidative Coupling of Methane over Hydroxyapatite Catalysts

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Introduction
Lead substituted hydroxyapatite (Pb-HAP) has been an active catalyst for oxidative coupling of methane (OCM) reactions[1]. Recent report on B-site substituted HAP-CO3, in which the PO43− of HAP are partially substituted by CO32−, show that its oxide ion conduction is comparable to the YSZ superionic conductor at 700°C[2]. Given the catalytic properties of Pb-HAP and oxide ion conductive properties of HAP-CO3, Pb-HAP-CO3 is a promising apatite-based ceramic material possessing CH4 activation and O2 permeation properties for efficient OCM reactions.

In this work, the effects of substitutions for both cation (Pb2+) and anion (CO32−) in HAP structure on OCM reactions were studied. The basicity and acidity of HAP catalysts were strengthened by the cation and anion substitutions, respectively, and as consequences, the OCM catalytic performances were influenced. Kinetic studies, including the reaction orders with respect to methane conversion were also done to determine a reaction mechanism for the reaction using HAP-based catalysts, including the rate-determining step and the type of oxygen adsorption onto the catalyst surface.

Materials and Methods

The cation and anion substituted HAP-based catalyst were prepared by co-precipitation method using Ca(NO3)2, 4H2O, (NH4)2HPO4, Pb(NO3)2, and NaHCO3 as the starting materials and the synthesis method was carried out according to the procedures reported elsewhere[3]. The resultant catalysts were designated as HAP, HAP-CO3, Pb-HAP, and Pb-HAP-CO3, respectively. The textural properties and acidity/basicity of the catalysts were systematically characterized, including N2-sorption isotherms to determine BET surface area, elemental analysis to quantify cation and anion substitution, NH3 temperature programmed desorption (NH3−TPD) to determine the acidities of the catalysts and CO2−TPD to determine surface basicity of the catalyst. OCM reactions were performed using U-shape tubular packed-bed quartz reactor at 973K with reactant flowrate fixed at 8 ml/min CH4 and 3 ml/min O2 (CH4/O2 ratio: 2.7) at normal temperature and pressure (NTP) condition. Kinetics studies were conducted by running the reactions at different reaction temperatures and at different partial pressures of CH4 and O2, respectively.

Results and Discussion

Figure 1(A) and (B) show the NH3−TPD and CO2−TPD of the carbonate-based HAP catalysts, indicating that cation and anion substitution can change the surface acidity and basicity of the catalysts. The activities were stable over the investigated time on stream (10 hours) for all the prepared catalyst systems except HAP-CO3 while the product selectivity varies with different types of substitution (Figure 2), suggesting that tunable active site can be achieved by cation and anion substitution.

![Figure 1](image1.png) (A) NH3−TPD and (B) CO2−TPD of carbonate-based HAP catalysts, respectively.

![Figure 2](image2.png) Product selectivity of OCM reactions over carbonate-based HAP catalysts.

Significance

The present study contributes to the further understanding of the effects of cation and anion substitution in HAP on OCM reactions, which provides reference for future designed synthesis of effective oxide ion conducting catalyst for methane conversions in membrane reactor conditions.

References