Influences of cation and anion substitutions on oxidative coupling of methane over hydroxyapatite catalysts

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HIGHLIGHTS

- Pb^{2+}, CO_3^{2-} and both substitutions in hydroxyapatite (HAP) were studied.
- Structural properties and performance of HAP catalysts in OCM reactions were revealed.
- Pb-HAP-CO_3 exhibits the best stability and C_2 yield under optimized conditions.
- Tuning compositions of HAP by ion substitutions tailors its OCM performances.

GRAPHICAL ABSTRACT
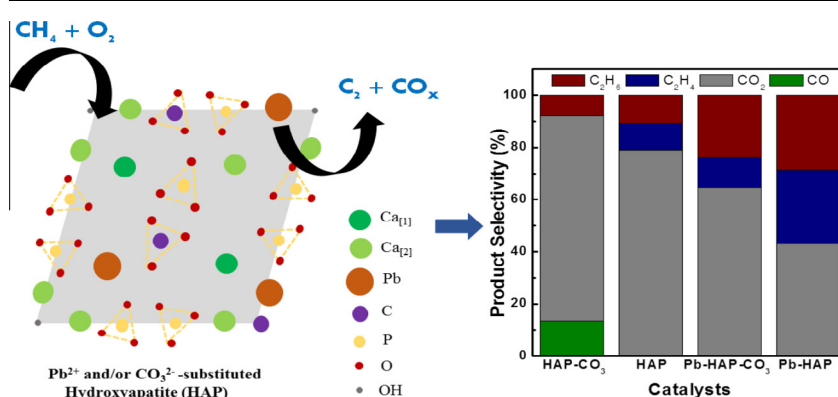
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ABSTRACT

Lead substituted hydroxyapatite (Pb-HAP) has been an active catalyst for oxidative coupling of methane (OCM) reactions. CO_3^{2-} substituted HAP (HAP-CO_3) has showed enhanced oxide ion conductivity than bare HAP in high temperature solid oxide fuel cells. Substitutions for both cations and anions in HAP structure (Pb-HAP-CO_3) are promising to integrate the catalytic property of Pb-HAP and oxide ion conductive property of HAP-CO_3 into one apatite-based ceramic material that can be manufactured into membrane reactors for possessing CH_4 activation and O_2 permeation capabilities for efficient OCM reactions. In this work, the effects of substitutions for both cation (Pb^{2+}) and anion (CO_3^{2-}) in HAP structure on OCM reactions were studied. The composition and physicochemical properties of HAP catalysts were changed by the cation and anion substitutions, respectively, and as consequences, they influenced the catalytic performances of HAP structure in OCM reactions. The selectivity to C_2 (ethylene and ethane) products increased in the order of HAP-CO_3 < HAP < Pb-HAP-CO_3 < Pb-HAP, while Pb-HAP-CO_3 showed the best stability and comparable C_2 yield (under optimized reaction conditions) to Pb-HAP catalyst. Under different reaction temperature and/or CH_4/O_2 ratio in the OCM reactions, the CH_4 conversion and C_2 or CO_x (CO and CO_2) selectivity showed a strong dependence on the composition of HAP-based catalysts. The present study forms a basis for understanding of the correlations between the composition, structure, and catalytic performance of HAP and other apatite structured catalysts, which are potential membrane materials for OCM reactions in membrane reactors.

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1. Introduction

The depletion of crude oil is shifting the market attention to natural gas that is still of great abundance [1,2]. Natural gas is made up of mainly methane (CH_4), which can substitute liquid petroleum for power generation and be a raw material in petrochemical industries. Rigorous research efforts have been made to convert methane into liquid fuels or chemicals. The most widely studied methane conversion processes include dry and steam reforming of methane to synthesis gas ($CO + O_2$) followed by Fischer–Tropsch synthesis of higher hydrocarbons [3], non-oxidative direct methane conversion to aromatics [4,5], and direct oxidative coupling of methane (OCM) to C_2 hydrocarbon [6,7]. In comparison with the first two processes, OCM is potentially more selective and economical given its unique capability in forming C_2 (C_2H_4 and C_2H_6) hydrocarbons while circumventing the intermediate energy intensive steps in synthesis gas approach and fast catalyst deactivation by coke deposition in methane-to-aromatics approach. The more reactive nature of C_2 products than methane in OCM reactions, however, leads to the sequential oxidation of C_2 to CO_x (CO or CO_2). The attainable C_2 yield in the OCM process is limited to 28% under a fixed-bed, continuous-feed reaction condition [8].

Membrane reactors comprised of active catalysts and O_2 permeable membranes have potential to mitigate the limit on C_2 yield in the OCM process [9]. The OCM reaction by catalytic membrane reactors involves both surface and gas-phase reactions. The O_2 permeable membranes serve as O_2 distributors to regulate gaseous O_2 concentration in the reactor, which restricts the consecutive oxidation of C_2 to CO_x. Although a substantial enhancement of the C_2 yield has been predicted when an O_2 permeable membrane was used in conjunction with an active OCM catalyst [10,11], the parallel experimental studies on the OCM process in membrane reactors were not favorable due to lack of membranes with sufficient and harmonized catalytic and O_2 permeable properties, and lack of rigorous description of the O_2 kinetic effects on the OCM process in membrane reactors.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a type of calcium phosphate crystal more commonly studied in biomaterials because it is a major constituent of teeth and bones [12]. HAP has a hexagonal structure which is stable up to 1273 K, and is comprised of 10 Ca^{2+} ions located on two sets of non-equivalent sites, 4 $Ca_{[1]}$ on site 1 and 6 $Ca_{[2]}$ on site 2 in one unit cell [13]. The $Ca_{[1]}$ is coordinated to 6 oxygen atoms belonging to different PO_4 tetrahedra and also to 3 oxygen atoms at a larger distance. The $Ca_{[2]}$ is found in cavities in the walls of the channels formed between the Ca and O atoms [14]. The Ca^{2+} cation and the anion, either PO_4^{3-} in the B-site or OH^- in the A-site, can be substituted by other cation or anions using co-precipitation of a mixed cation and anion precursor solutions [15–17], sorption of cation solution onto HAP structure [18], as well as simple mixing of calcium hydroxide with a cation containing orthophosphoric acid solution [19]. These synthesis methods endow HAP with tunable thermal and chemical stability [20], catalytic properties [21,22], and ion/electronic conductive properties [23]. Pb can substitute either $Ca_{[1]}$ or $Ca_{[2]}$, or both depending on the Pb concentrations in the structure, and Pb-HAP were able to increase C_2 selectivity by a factor of 5 compared to bare HAP [24]. Recent report on B-site substituted HAP-CO_3, in which the PO_4^{3-} of HAP was partially substituted by CO_3^{2-}, showed that the oxide ion conduction was comparable to the yttria-stabilized-zirconia superionic conductor at 973 K [25]. Given the catalytic property of Pb-HAP and oxide ion conductive property of HAP-CO_3, Pb-HAP-CO_3 is a promising apatite-based ceramic membrane material possessing CH_4 activation and O_2 permeation capabilities for efficient OCM reactions. Systematic investigation on both cation and anion substituted HAP in OCM reactions, however, is rarely accessible.

In the present work, we report the synthesis of HAP catalysts with cation (Pb-HAP), anion (HAP-CO_3), and both cation and anion (Pb-HAP-CO_3) substitutions. The effects of substitutions on physicochemical and acidity/basicity properties, and catalytic behaviors of HAP-based catalysts were assessed. X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption, Fourier transform infrared (FTIR) and Raman spectroscopy, temperature programmed desorption of ammonia (NH_3-TPD), X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure spectroscopy (XAFS) were used to characterize the structural and physicochemical properties of the HAP-based catalysts. The catalytic behaviors of the HAP-based catalysts in OCM reactions were examined. It is shown that cation or anion substitution can change the composition and physicochemical properties of the HAP-based catalysts, and as consequences, the catalytic behaviors of HAP-based materials in OCM reactions.

2. Experimental

2.1. Materials

Ammonium phosphate dibasic ((NH_4)$_2$HPO$_4$, $\geqslant$99.0%), ammonium chloride (NH_4Cl, $\geqslant$99.5%) and ammonia hydroxide solution (NH_4OH, 28–30%) were supplied from Sigma–Aldrich. Lead nitrate ($Pb(NO_3)_2$, A.C.S. Reagent) was purchased from J.T. Baker. Sodium bicarbonate ($NaHCO_3$, 99.7–100.3%) was provided by BDH. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, >99.5 purity) was purchased from Alfa-Aesar.

2.2. HAP-based catalysts preparation

The synthesis of bare HAP was carried out by first preparing a solution of (NH_4)$_2$HPO$_4$ (0.25 M, 480 mL) in one flask and a solution of $Ca(NO_3)_2$ (0.42 M, 320 mL) in a second flask. After pH of each solution was raised to ~10 with NH_4OH, the two source solutions were mixed together by adding (NH_4)$_2$HPO$_4$ solution via a syringe pump (4 mL min^{-1}) to $Ca(NO_3)_2$ solution that was preheated to 363 K in an oil bath and was equipped with a reflux condenser. After addition of the (NH_4)$_2$HPO$_4$ solution, a milky white suspension was obtained and the suspension was kept at 363 K under magnetic stirring overnight followed by aging for 24 h at room temperature. Finally, the product was collected by centrifugation at 6000 rpm for 5 min and washed by dispersing in deionized (DI) water. The water washing and centrifugation steps were repeated 5 times. A vacuum oven was utilized to dry the wet product at 343 K overnight.

In the synthesis of HAP-CO_3 catalyst, the same procedure as that for HAP was employed except that a solution consisting of (NH_4)$_2$HPO$_4$ (0.25 M) and $NaHCO_3$ (0.17 M) was prepared to replace 0.25 M (NH_4)$_2$HPO$_4$ solution in HAP synthesis. For synthesis of Pb-HAP-CO_3 catalyst, the $Ca(NO_3)_2$ solution in the second flask was replaced with a solution of $Ca(NO_3)_2$ (0.34 M) and $Pb(NO_3)_2$ (0.08 M). The rest of procedure was the same as that for synthesis of HAP-CO_3 catalyst. The synthesis of Pb-HAP catalyst followed a reported procedure [16], which was similar to synthesis of bare HAP above except that an aqueous solution of $Pb(NO_3)_2$ (0.08 M), $Ca(NO_3)_2$ (0.34 M) and NH_4Cl (1.3 M) was prepared to replace $Ca(NO_3)_2$ (0.42 M) in HAP synthesis.

Finally, the vacuum dried HAP-based samples were calcined in flowing air (150 mL min^{-1}, ultrapure, Airgas) at 823 K for 5 h at a ramp rate of 17.5 K min^{-1} from ambient temperature. All the samples were pelleted, crushed, and sieved to retain particle sizes between 180 and 425 μm (40–80 mesh) for the following characterization and catalysis experiments.