Influences of Cation and Anion Substitutions on Oxidative Coupling of Methane over Hydroxyapatite Catalysts

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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 $\text{HAP-}\text{CO}_3 < \text{HAP} < \text{Pb-HAP-}\text{CO}_3 < \text{Pb-HAP}$, 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.

Keywords: Hydroxyapatite; membrane reactor; anion and cation substitution; methane; oxidative coupling.

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 ($\text{CO} + \text{O}_2$) 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 O₂ permeable properties, and lack of rigorous description of the O₂ kinetic effects on the OCM process in membrane reactors.

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) 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 $\text{Ca}_{[1]}$ on site 1 and 6 $\text{Ca}_{[2]}$ on site 2 in one unit cell [13]. The $\text{Ca}_{[1]}$ is coordinated to 6 oxygen atoms belonging to different PO_4 tetrahedra and also to 3 oxygen atoms at a larger distance. The $\text{Ca}_{[2]}$ 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 $\text{Ca}_{[1]}$ or $\text{Ca}_{[2]}$, or both depending on the Pb concentrations in the structure, and Pb-HAP were able to increase C₂ selectivity by a factor of 5 compared to bare HAP [24]. Recent report on B-site substituted HAP-CO₃, 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-CO₃, Pb-HAP-CO₃ is a promising apatite-based ceramic membrane material possessing CH₄ activation and O₂ 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-CO₃), and both cation and anion (Pb-HAP-CO₃) 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 (NH₃-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 ((NH₄)₂HPO₄, ≥99.0%), ammonium chloride (NH₄Cl, ≥99.5%) and ammonia hydroxide solution (NH₄OH, 28-30%) were supplied from Sigma-Aldrich. Lead nitrate (Pb(NO₃)₂, A.C.S. Reagent) was purchased from J.T. Baker. Sodium bicarbonate (NaHCO₃, 99.7-100.3%) was provided by BDH. Calcium nitrate tetrahydrate (Ca(NO₃)₂ · 4H₂O, >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 (NH₄)₂HPO₄ (0.25 M, 480 mL) in one flask and a solution of Ca(NO₃)₂ (0.37 M, 320 mL) in a second flask. After pH of each solution was raised to ~10 with NH₄OH, the two source solutions were mixed together by adding (NH₄)₂HPO₄ solution via a syringe pump (4 mL min⁻¹) to Ca(NO₃)₂ solution that was preheated to 363 K in an oil bath and was

equipped with a reflux condenser. After addition of the $(\text{NH}_4)_2\text{HPO}_4$ solution, a milky white suspension was obtained and the suspension was kept at 363 K under magnetic stirring overnight followed by aging for 24 hours 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 $(\text{NH}_4)_2\text{HPO}_4$ (0.25 M) and NaHCO_3 (0.17 M) was prepared to replace 0.25M $(\text{NH}_4)_2\text{HPO}_4$ solution in HAP synthesis. For synthesis of Pb-HAP- CO_3 catalyst, the $\text{Ca}(\text{NO}_3)_2$ solution in the second flask was replaced with a solution of $\text{Ca}(\text{NO}_3)_2$ (0.4 M) and $\text{Pb}(\text{NO}_3)_2$ (0.1 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 $\text{Pb}(\text{NO}_3)_2$ (0.1 M), $\text{Ca}(\text{NO}_3)_2$ (0.4 M) and NH_4Cl (1.3 M) was prepared to replace $\text{Ca}(\text{NO}_3)_2$ (0.25 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 hours 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.

2.3 Catalysts characterization. The morphologies of the HAP-based catalysts were observed by scanning electron microscopy (SEM) on a Hitachi SU-70 electron microscope. The crystallinity of the catalysts were examined by powder X-Ray diffraction (XRD) patterns using a Bruker D8 Advance Lynx Powder Diffractometer (LynxEye PSD detector, sealed tube, $\text{Cu } K_\alpha$ radiation with $\text{Ni } \beta$ -filter). N_2 adsorption-desorption isotherms of the samples were measured

using an Autosorb-iQ analyzer (Quantachrome Instruments) at 77 K. The specific surface areas of the samples were determined using (Brunauer, Emmett and Teller) (BET) method. Thermogravimetric analysis (TGA) of the catalyst samples was performed in a TGA instrument (2950, TA Instruments, Inc.) under a mixed air and N₂ flow of 100 mL min⁻¹ (40% air, 60% N₂) with a heating rate of 10 K min⁻¹ from 308 K to 1273 K. Elemental composition of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-EOS, Optima 4300DV Instrument, Perkin-Elmer). The FTIR spectra of the samples were recorded with a spectrometer (Nicolet Magna-IR 560) in the range of 400-4000 cm⁻¹. The Raman spectra of the catalysts were collected with a Raman spectrometer (LabRAM Aramis, Horiba Scientific) in the range of 200-2000 cm⁻¹. XPS data was measured over a Kratos AXIS 165 spectrometer equipped with 165 mm radius hemispherical analyzer and eight channelstron detection system coupled with monochromatic Al radiation. The X-ray absorption fine structure spectroscopy (XAFS) measurements at the Pb L₃ edge (~ 13.036 keV) were conducted on the bending-magnet beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon source in Argonne National Laboratory. XAFS data were collected in the transmission mode under ambient condition. PbO, PbO₂ and Pb foil were considered as references and measured at the beamline. The Pb species fraction was calculated by conducting Pb X-ray absorption near edge spectroscopy (XANES) linear combination fittings using Athena in the IFEFFIT software package.

2.4 Determination of acidity of catalysts. The surface acidity of the HAP-based catalysts was evaluated by NH₃-TPD using an Autosorb-iQ instrument (Quantachrome, ASIQM0000-4) equipped with a thermal conductivity detector (TCD). In the measurement, 0.1 g catalyst sample was loaded into a quartz reactor and heated at a rate of 10 K min⁻¹ to 973 K under He (40 mL

min⁻¹) and maintained at this temperature for 2 hours in order to remove the surface impurities. After being cooled to room temperature under He stream, the catalyst sample was exposed to NH₃ (30 mL min⁻¹, ultrapure, Airgas) stream for 0.5 hours. Physisorbed NH₃ was then removed by flowing He gas (30 mL min⁻¹) for 2 hours. Afterwards, the catalyst sample was ramped to 1100 K at a ramp rate of 10 K min⁻¹, and the NH₃-TPD profile was recorded during this step.

2.5 OCM catalytic test. The catalytic reaction was performed in the reactor system that has been described in our previous work [26]. Typically, 0.3 g of catalyst sample was loaded in a U-shape tubular quartz reactor (10 mm inner diameter) which was placed inside a temperature controlled furnace (National Electric Furnace FA120 type). The temperature of the furnace was controlled by a Watlow Controller (96 series). A K-type thermocouple was attached to the outer wall of the reactor to monitor the temperature of the catalyst environment. The sample was pretreated in He and O₂ atmosphere (33 mL min⁻¹, volume ratio: 91% He, 9% O₂) at 823 K for 4 hours prior to the OCM reactions. Afterwards, the catalyst was heated to the desired reaction temperature. The CH₄ (8 mL min⁻¹, 99.999% purity, Airgas) and O₂ (3 mL min⁻¹, 99.9993% purity, Airgas) diluted in N₂ (5 mL min⁻¹, 99.95% purity, Airgas) and He (30 mL min⁻¹, 99.9993% purity, Airgas) were sent via heated transfer lines hold at 343 K to the reactor. The reactant and product gases were analyzed using gas chromatograph (Agilent Technologies, 6890N) equipped with ShinCarbon ST packed column connected to a TCD. Dependency of CH₄/O₂ ratios was studied by changing the flow rates of O₂ and the balance He gases while keeping constant flow rate in CH₄. The blank test in the reactor without catalysts showed that the methane conversion was less than 1%, suggesting that the gas phase reaction between CH₄ and O₂ was not favored under studied conditions.

3. Results and discussion

3.1 Textural and structural properties of catalysts. Figure 1 shows the SEM images of the HAP-based catalysts. The bare HAP catalyst (Figure 1(A)) consists of uniform nanoparticles with sizes between 10 nm to 20 nm. The particle sizes were determined by observing SEM images captured at multiple positions of the sample after loaded into SEM chamber. The nanoparticles tend to form irregular agglomerates. For HAP-CO₃ catalyst in Figure 1(B), capsule-like particles are observed. Upon Pb substitution into HAP (Pb-HAP), the sample turned into rod-shaped clusters, as shown in Figure 1(D). These rod-shaped clusters stacked on each other to form agglomerates. In the case of both cation and anion substituted HAP (Pb-HAP-CO₃), a mixture of these morphologies were observed, as shown in Figure 1(C). The cation and anion,

Table 1. Chemical compositions and surface areas of HAP-based catalysts for OCM reactions.

Catalyst	Composition ^a			Composition ^b			Surface area ^c (m ² /g)
	Pb/Ca	C/P	(Ca+Pb)/(P+C)	Pb/Ca	C/P	(Ca+Pb)/(P+C)	
HAP-CO ₃	0.00	0.48	1.64	0.00	0.29	1.56	36
HAP	0.00	0.00	1.65	0.00	0.00	1.59	39
Pb-HAP-CO ₃	0.17	0.44	1.73	0.33	0.34	1.64	37
Pb-HAP	0.16	0.00	1.60	0.47	0.00	1.63	49

^a Determined by elemental analysis (ICP-OES). ^b Determined from XPS measurement. ^c Determined by BET method.

or both cation and anion substitutions did not dramatically change the particle sizes of HAP catalysts. The surface areas of the HAP-based catalysts were determined from N₂ adsorption-desorption isotherms and the results are listed in Table 1. Consistent with SEM results, there is no significant change in surface areas across these four HAP-based catalysts.

XRD, FTIR and Raman spectra were used to study crystal polymorphs of the HAP-based catalysts, and the results are shown in Figure 2(A)-(C). In Figure 2(A), all peaks of the XRD spectrum for HAP, HAP-CO₃, Pb-HAP and Pb-HAP-CO₃, respectively, are consistent with the

crystalline HAP phase. This result indicates that HAP crystalline structure was well-preserved after the incorporation of cation (Pb^{2+}), anion (CO_3^{2-}), or both cation and anion (Pb^{2+} and CO_3^{2-}),

Figure 1. SEM images showing morphologies of HAP-based catalysts: (A) HAP, (B) HAP- CO_3 , (C) Pb-HAP- CO_3 , and (D) Pb-HAP, respectively.

respectively. A further examination on the XRD spectra shows that the peak position and width are slightly different across the HAP-based catalysts. Firstly, the diffraction peaks of Pb-HAP and Pb-HAP- CO_3 are shifted to lower diffraction angles compared to HAP and HAP- CO_3 samples. The left-shift of the diffraction peaks was caused by Pb^{2+} substitution, which has larger size than Ca^{2+} ions. It is reported that the incorporation of larger cations in the apatite materials expands the lattice parameters of the hexagonal structure and thus leads to an increase in unit cell volume, which in turns causes a downward shifting in 2θ diffraction angles [16]. Secondly, the

diffraction peaks broaden from HAP to HAP-CO₃ and further to Pb-HAP-CO₃ and Pb-HAP, suggesting that the crystallinity of HAP-based catalysts decreased with incorporation of cation, anion, or both type of ions into the crystalline HAP material. The broadening and left-shifting of the diffraction peaks in Pb-HAP and Pb-HAP-CO₃ samples might also be resulted from the presence of trivial amount of other crystalline phases such as hydroxypyromorphite (HPY). It is reported that HPY can be precipitated from the synthesis mixture similar to that of HAP used in the present study [27, 28]. The concurrent precipitation of HPY should be insignificant since no obvious diffraction peaks of HPY are observed in Figure 2(A).

Figure 2. XRD patterns (A), FT-IR spectra (B), Raman spectra (C), and TGA curves (D) of HAP-based catalysts, respectively, used for OCM reactions.

Figure 2(B) illustrates the FTIR spectra of HAP-based catalysts. The spectrum of bare HAP shows all absorption bands characteristic for HAP [29]. For PO_4^{3-} group, the ν_1 vibration (symmetric stretching) occurred at 942 cm^{-1} , the ν_3 vibration (asymmetric stretching) centered at 1000 cm^{-1} and 1100 cm^{-1} , while ν_2 vibration (asymmetric bending) located at 563 cm^{-1} , 600 cm^{-1} , 942 cm^{-1} , are all observed. The librational mode of OH^- groups appears at 631 cm^{-1} , suggesting the presence of hydroxyl groups in the bare HAP sample. Absence of any distinct bands in the range of $1400\text{--}1550\text{ cm}^{-1}$ indicates that bare HAP does not contain detectable carbonate (CO_3^{2-}) groups. The vibrational modes of PO_4^{3-} groups are also observed in HAP- CO_3 , Pb-HAP- CO_3 , and Pb-HAP samples (Figure 2(B)). This result suggests that the HAP structure was preserved upon cation, anion, or both substitutions, in agreement with the XRD results. The presence of broad vibrational bands centered at 1450 cm^{-1} (ν_3 symmetric stretching of CO_3^{2-}), characteristic for substitution of PO_4^{3-} by CO_3^{2-} (B-type) [30, 31], in both HAP- CO_3 and Pb-HAP- CO_3 samples indicates the incorporation of CO_3^{2-} into the HAP structure. The absorption band at 631 cm^{-1} disappears in HAP- CO_3 and Pb-HAP- CO_3 , which resulted from the substitution of OH^- by CO_3^{2-} groups to form A-type substituted HAP. The FTIR spectra of HAP- CO_3 and Pb-HAP- CO_3 overall suggest that AB-type CO_3^{2-} substituted HAP was formed. The band at 872 cm^{-1} in the FTIR spectra of these two samples result from both CO_3^{2-} (ν_2 in-plane bending of CO_3^{2-}) and HPO_4^{2-} groups. It is reported that HPO_4^{2-} groups are created to counterbalance the ionic charge when the OH^- groups are replaced by CO_3^{2-} in HAP, which overlaps with the CO_3^{2-} band at 872 cm^{-1} . The absence of CO_3^{2-} bands and appearance of OH^- band at 631 cm^{-1} in Pb-HAP catalyst suggests no detectable CO_3^{2-} groups in this sample. A slight shift of the vibration modes at 563 cm^{-1} and 600 cm^{-1} of PO_4^{3-} groups toward lower wavenumbers in Pb-HAP and Pb-HAP- CO_3 reveals the presence of Pb^{2+} ions [32], consistent with left-shift of 2θ angles observed from XRD

spectra. The features of FTIR spectra overall indicate that successful synthesis of cation (Pb^{2+}), anion (CO_3^{2-} , AB-type), and cation and anion (Pb^{2+} and CO_3^{2-}) substituted HAP catalysts.

Raman spectra in Figure 2(C) are further used to understand the structural properties of the HAP-based catalysts. The vibration modes of PO_4^{3-} groups in HAP structure, ν_1 (~ 960 to 961 cm^{-1}), ν_2 (~ 430 to 450 cm^{-1}), ν_3 (~ 1035 to 1048 cm^{-1} and ~ 1070 to 1075 cm^{-1}), ν_4 (~ 587 to 604 cm^{-1}), confirm the apatite structure of all the catalysts [33]. The vibrational modes of the CO_3^{2-} group are detected at 1073 cm^{-1} in HAP- CO_3 and Pb-HAP- CO_3 (ν_1 mode of B-type carbonate) [33], suggesting the presence of CO_3^{2-} groups in these two samples, consistent with FTIR results above. The Raman peak at 960 cm^{-1} undergoes a shift to lower wavenumber (928 cm^{-1}) when the bare HAP was substituted with Pb^{2+} ions, which is attributed to the stronger Pb-O interactions compared with the Ca-O ones in HAP catalysts [24]. The absence of vibrational band at $\sim 700 \text{ cm}^{-1}$ in Figure 2(C), which is assigned to an asymmetric $\text{P}=\text{O}$ stretching mode of PO_4^{3-} groups in the stoichiometric HAP, indicates that all the as-synthesized HAP-based catalysts are non-stoichiometric [21, 34].

The thermal stability of the pre-calcined HAP-based catalysts was examined by TGA data presented in Figure 2(D). The TGA measurement was conducted on the as-synthesized HAP samples after the drying step in vacuum oven. The slight decrease in weight for all the samples at temperature from 300-750 K is assigned to the evaporation of water bound to the catalyst surface or decomposition of adsorbed ammonium or nitrate ions used in the catalyst synthesis. The weight loss at the temperature above 1100 K was caused by the structure decomposition such as dehydroxylation since the temperature approaches the thermal stability limit of the HAP material [35]. In the temperature range of 750-1100 K, these four HAP-based catalysts showed different thermal decomposition behaviors. The bare HAP is stable, but HAP- CO_3 has two weight losses.

The first weight loss at 1030 K was due to the removal of CO_3^{2-} groups from A-type substitution, while the second loss at 1100 K was resulted from the decomposition of B-type substituted CO_3^{2-} groups [36]. Pb-HAP also has two weight losses in this temperature range. The first one at 830 K is assigned to the loss of chlorine component used in the catalyst preparation [21]. The second one at 1030 K can be attributed to the decomposition of HAP into a Pb-containing β -tricalcium phosphate. Compared to Pb-HAP and HAP-CO_3 , Pb-HAP- CO_3 has much better thermal stability in the temperature range of 750-1100 K.

3.2 Composition analysis of HAP-based catalysts. The bulk and surface stoichiometry of the HAP-based catalysts were determined using ICP-OES and XPS analyses, respectively, and the results are listed in Table 1. The Pb/Ca molar ratios in the synthesized samples are lower than the theoretical ratios ($\text{Pb/Ca} = 0.25$) used in catalyst synthesis. The cation/anion (i.e., $(\text{Ca+Pb})/(\text{P+C})$) molar ratios are slightly different, but close to the stoichiometric ratio of 1.67. The substitution of Pb^{2+} cation or CO_3^{2-} anion or both into the apatite structure did not alter the stoichiometry of HAP significantly. The surface element composition of the HAP-based catalysts in Table 1 shows that Pb/Ca ratios and $(\text{Ca+Pb})/(\text{P+C})$ ratios are higher and lower, respectively, than those determined from ICP-OES analysis for these four catalyst samples. This result suggests that Pb content is rich on the surface of the Pb-HAP and Pb-HAP- CO_3 samples.

The basicity/acidity of the HAP catalyst and thus their catalytic performance in OCM reactions are known to depend strongly on the chemical state of the cationic sites. XPS data was therefore measured to identify the chemical states of the cationic species (Pb and Ca) in these post-calcined HAP-based catalysts. The presence of the desired elements (Ca, Pb, P and O)

Figure 3. XPS spectra (A), Pb 4f spectra (B), Ca 2p (C) and XANES spectra (D) of HAP-based catalysts, respectively, used for OCM reactions.

in the final product (Figure 3(A)) indicates the successful preparation of the HAP-based catalysts. The binding energies of Pb 4f_{7/2} and Pb 4f_{5/2} of Pb-HAP are lower than those of Pb-HAP-CO₃ (Figure 3(B)), which suggests Pb²⁺ cations of Pb-HAP were positioned in a more electronegative environment than those of Pb-HAP-CO₃. There are two types of Ca sites in HAP materials: 9-coordinated Ca_[1] and 7-coordinated Ca_[2]. The basicity of an atom is well known to increase with

increase in its coordination number [37, 38]. It is expected that Pb^{2+} ions substitution for $\text{Ca}_{[1]}$ would possess more basicity compared to $\text{Ca}_{[2]}$, and thus, Pb-HAP had more Pb^{2+} ions positioned at the $\text{Ca}_{[1]}$ sites and higher basicity than Pb-HAP- CO_3 catalyst. The binding energies of Ca $2p_{3/2}$ and Ca $2p_{1/2}$ in the HAP-based catalysts, however, are almost identical (Figure 3(C)). The XPS data suggests that the surface basicity of the catalyst is mainly related to the Pb^{2+} ions and their chemical states. The oxidation state and possible phases of Pb ions in Pb-HAP and Pb-HAP- CO_3 were studied using Pb L_3 XANES spectra of Pb-HAP and Pb-HAP- CO_3 . Figure 3(D) shows that both Pb-HAP and Pb-HAP- CO_3 exhibited similar adsorption energies at 13039 eV. The ~ 3 eV shift to higher energy than the metallic Pb foil indicates that Pb-HAP is in higher oxidation state than zero. Pb L_3 edge represents mainly the $2p \rightarrow 6p$ transition for Pb^{2+} -containing structures. On the other hand, a pre-edge at ~ 13027 eV representing $2p \rightarrow 6s$ transition can be observed for Pb^{4+} ions (e.g., PbO_2). The absence of pre-edge features in Pb-HAP and Pb-HAP- CO_3 XANES spectra indicates that most Pb ions in the catalysts are in the Pb^{2+} state. There is no overlapping between Pb-HAP and PbO reference, indicating that Pb^{2+} ions exist in the phase other than PbO.

3.3 Surface acidity of HAP-based catalysts. The surface acidity and acid strength of the HAP-based catalysts were investigated using NH_3 -TPD. Phosphate groups in bare HAP are responsible for the acidity of the catalyst, whereas the Ca^{2+} ions are responsible for the basicity [36]. An increase in the basicity and acidity is expected upon Pb^{2+} and CO_3^{2-} substitution into the HAP structure, respectively. Figure 4 shows NH_3 -desorption peaks exist in the regions of lower temperatures (< 600 K), medium temperatures (750 – 930 K), and also at higher temperatures (> 930 K), respectively. This indicates the presence of weak, medium and strong acid sites in the HAP-based catalyst samples. The broad variation in peak intensity across these four HAP-based catalyst samples reveals that the catalysts differ from each other widely in their total number of

acid sites and also in the strength of the acid sites. In the low temperature region in Figure 4, bare HAP exhibits a broad peak centered at 440 K. This desorption peak is split into two peaks, one shifted downwards to 400 K and the other shifted upwards to 520 K in the sample of HAP-CO₃. When Pb²⁺ ions were incorporated into the HAP-CO₃ to form Pb-HAP-CO₃, the acidity of the catalyst is significantly decreased, as reflected by the reduced intensity of the NH₃-TPD peaks below 600 K. Pb-HAP shows similar NH₃-desorption peak to that of Pb-HAP-CO₃. The weak acidity in the catalysts follows the order of HAP-CO₃ > HAP > Pb-HAP ~ Pb-HAP-CO₃. The medium acidity in these four catalysts shows the same trend to that of weak acidity. In the high temperature range (750 - 930 K), HAP-CO₃ and HAP have higher peak intensity than that of Pb-HAP and Pb-HAP-CO₃. The order of NH₃-TPD peak intensity is HAP-CO₃ > Pb-HAP-CO₃ > HAP > Pb-HAP.

Figure 4. NH₃-TPD Profiles of HAP, HAP-CO₃, Pb-HAP and Pb-HAP-CO₃ catalysts.

The liberation of NH₃ in the low temperature range in Figure 4 is mainly attributed to the PO₄³⁻ groups present in the HAP catalysts [39]. The medium and high temperature NH₃-desorption peaks are caused by the co-existed PO₄³⁻, CO₃²⁻ and HPO₄²⁻ groups. The AB-type CO₃²⁻ substituted HAP, as suggested by FTIR data, contains both CO₃²⁻ groups in the A and B sites and HPO₄²⁻ that is resulted from substitution of OH⁻ groups by CO₃²⁻ [39]. The broad and

strong high temperature desorption peak in HAP-CO₃ and Pb-HAP-CO₃ might also be caused by the release of CO₂ from CO₃²⁻ groups in the apatite structure [40]. It is generally accepted that the strength and quantity of the acid sites are directly related to desorption temperature and intensity in NH₃-TPD analysis. Therefore, the NH₃-TPD data confirms that the acidity HAP-based catalysts was tuned upon Pb²⁺, CO₃²⁻, or both substitutions. The absence of CO₃²⁻ from Pb-HAP-CO₃ catalyst further reduced the acidity of the catalyst since Pb-HAP only showed very weak NH₃ desorption peaks. The reduction and enhancement in acidity upon Pb²⁺ and CO₃²⁻ substitution, respectively, are consistent with composition and XPS analyses discussed above.

3.4 Performance of HAP-based catalysts in OCM reactions. The activity, stability and selectivity of the HAP-based catalysts in OCM reactions were firstly examined at 973 K and 101 kPa pressure. Figure 5(A) shows that the methane conversion followed a sequence of Pb-HAP-CO₃ > HAP > Pb-HAP > HAP-CO₃. In addition, HAP and Pb-HAP-CO₃ were more stable than Pb-HAP and HAP-CO₃. The slight decrease in activity of Pb-HAP with time on steam (TOS) and abrupt drop in activity of HAP-CO₃ in the beginning of the reaction was resulted from their structural instability, as shown by the TGA data in Figure 2(D). It should be noted that Pb-HAP-CO₃ maintained its activity and stability in the OCM reaction conditions. Figure 5(B) shows the product selectivity of the HAP-based catalysts with TOS of 6 h and methane conversion of 23%. The C₂ selectivity monotonically increases from HAP-CO₃, HAP, Pb-HAP-CO₃ to Pb-HAP catalysts. The activity and selectivity of these four HAP-based catalysts follows the reverse order of low and medium temperature desorption peak intensity in NH₃-TPD profiles. Pb-HAP and Pb-HAP-CO₃ are more active and selective in C₂ formation. **It is reported that Pb²⁺ ions form covalent bonds with carbon, which can stabilize methyl radicals and enable pairwise reaction of methyl radicals to form C₂ products [17, 24, 41-43].** In HAP and HAP-CO₃ catalysts, the acidic

environment promotes dissociative adsorption and builds up a strong interaction between the catalyst surfaces and C_2 products. C_2 products tend to stay on the surface of the catalyst which then undergoes secondary oxidation process to form CO and CO_2 [44]. The trend of C_2 selectivity across these catalysts is consistent with their surface composition and acidity changes. This result suggests that the tunable composition of the HAP-based catalysts by ion substitutions influences their physicochemical properties and consequently the selectivity in OCM reactions.

Figure 5. (A) Methane conversion with time-on-stream in OCM reactions and (B) Product selectivity for OCM reactions over HAP-based catalysts at 23% conversion under 973 K and 101 kPa pressure conditions and a space velocity of $8800 \text{ mL g}_{\text{cat}}^{-1} \cdot \text{hr}^{-1}$.

Methane conversion and product selectivity in OCM reactions over the HAP-based catalysts at different temperatures were studied. As shown in Figure 6(A), the methane conversion over Pb-HAP and Pb-HAP- CO_3 increased significantly with increasing temperature, while the conversion increased only slightly over HAP- CO_3 and HAP catalysts. This suggests that Pb species is the active component in the HAP-based catalyst for methane activation in OCM reactions, consistent with previous report [16]. Figure 6(B)-(D) shows the selectivity to

Figure 6. Methane conversion (A) and product selectivity (C₂ (B); CO₂ (C); CO (D)) of OCM reactions over HAP-based catalysts at different temperatures. ($P_{\text{CH}_4} = 27.1$ kPa, $P_{\text{O}_2} = 11.0$ kPa, total flow = 46 ml min^{-1} , He was used as the balance gas).

C₂, CO₂, and CO products across these four catalysts at different reaction temperatures. C₂ production was favored with increasing temperature, CO₂ formation was inhibited, while CO formation was kept almost constant. It should be noted that HAP-CO₃ generated more CO than other HAP-based catalysts (Figure 5(B) and 6(D)). The methane reforming or reverse water gas

shift reactions, caused by the acidity of HAP-CO₃ catalyst, can potentially contribute to the CO product.

Figure 7. Effect of methane-to-oxygen (CH_4/O_2) ratio on C_2 selectivity and CH_4 conversion at (A) 923 K, (B) 943 K and (C) 973 K at a constant CH_4 partial pressure of 25 kPa. (Total flow rate = 46 mL min^{-1}) (Filled symbol represents C_2 selectivity, unfilled symbol represents CH_4 conversion)

The effects of methane to oxygen ratio in OCM reactions was studied on the selected Pb-HAP and Pb-HAP-CO₃ catalysts at different temperatures. Figure 7 shows the methane to oxygen ratio is tuned by varying oxygen partial pressure (8.1/11.3/21.0/32.0/40.7 kPa, respectively) while keeping a constant methane partial pressure of 25 kPa, and helium was used as the balance gas. CH_4 conversion decreased with increasing CH_4/O_2 ratio while C_2 selectivity increased with increasing CH_4/O_2 ratio at all the studied temperatures for both catalysts. Higher CH_4/O_2 ratio indicates lower O_2 concentration in the gas phase in the reaction, which in turns promotes C_2 formation since most of the O_2 are activated on the surface of the catalyst. On the other hand, higher CH_4/O_2 ratio, i.e., lower O_2 concentration, leads to lower CH_4 conversion. Figures 7(A) also demonstrates that CH_4 conversion over Pb-HAP-CO₃ catalyst was higher than Pb-HAP catalysts when the reaction temperature was low (923 K). With an increase in reaction temperature to 943 K (Figure 7(B)) or 973 K (Figure 7(C)), Pb-HAP and Pb-HAP-CO₃ showed similar methane conversion. The selectivity to C_2 product, however, showed opposite trend with

the reaction temperature. At the temperature of 923 K (Figure 7(A)), both catalysts have similar C₂ selectivity in OCM reactions. With increasing reaction temperature to 943 K (Figure 7(B)), Pb-HAP has higher C₂ selectivity than that of Pb-HAP-CO₃. The differences in C₂ selectivity is more evident when the temperature was further increased to 973 K (Figure 7(C)). With the available C₂ selectivity and CH₄ conversion data, the C₂ yield, which is product of C₂ selectivity and CH₄ conversion, can be accessed. At lower reaction temperature (923 K), Pb-HAP-CO₃ showed higher C₂ yield than that of Pb-HAP catalyst. When the reaction temperature was increased to 973 K, the C₂ yield was higher in Pb-HAP than Pb-HAP-CO₃. These results suggest that the C₂ production over Pb-HAP-CO₃ can be optimized under certain reaction conditions. Overall, the OCM reaction data indicate that the catalytic performance of the HAP-based catalysts can be tuned upon cation or anion substations in the apatite structure. Given the catalyst stability, activity, selectivity and O₂ permeable properties under optimized reaction condition, Pb-HAP-CO₃ can be a potential catalyst to be integrated in membrane reactor to enable effective OCM reactions with side feeding of O₂ through the membrane.

The crystallinity and structure of Pb-HAP-CO₃ were studied after OCM reactions. Figure 8 shows the XRD, FTIR and Raman data, respectively, collected on Pb-HAP-CO₃ sample after TOS of 10 hours. For comparison purpose, the XRD patterns of three other catalyst samples (HAP, Pb-HAP and Pb-HAP-CO₃) were measured and included in Figure 8(A). In comparison with Figure 2(A), the sharpness of the XRD peaks in all the samples was decreased, which indicates that crystallinity of the HAP-based catalyst might be reduced after OCM reaction. The HAP, Pb-HAP and HAP-CO₃ still maintain their initial diffraction peak positions. The Pb-HAP-CO₃, however, formed a new diffraction peak centered at $2\theta \sim 30^\circ$. This diffraction peak can be indexed to the HPY structure. HPY has been reported to be synthesized from mixture of lead and

phosphate precursor solutions [27, 28]. In the OCM reaction condition, acidic environment of Pb-HAP- CO_3 may facilitate the transformation of the HAP to HPY structure. It should be noted that the catalytic performance of Pb-HAP- CO_3 did not decrease with time on stream of the OCM reaction (Figure 5). The FTIR (Figure 8(B)) spectra of Pb-HAP- CO_3 sample after OCM reaction shows that the vibrational bands centered at 1450 cm^{-1} , which corresponds to ν_3 symmetric stretching of CO_3^{2-} . The band at 872 cm^{-1} , which results from CO_3^{2-} (ν_2 in-plane bending of CO_3^{2-}) group, can still be observed after 10 hours of reaction, implying that CO_3^{2-} group was still present in the HAP structure. In the case of Raman spectra (Figure 8(C)) of Pb-HAP- CO_3 , the vibrational modes of the CO_3^{2-} group are detected at 1073 cm^{-1} after 10 hour of OCM reaction, again indicating that Pb-HAP- CO_3 still maintained the carbonate group inside the structure.

Figure 8. XRD pattern (A), FTIR (B) and (C) Raman of Pb-HAP- CO_3 after 10-hour of OCM reaction. For comparison purpose, XRD patterns of HAP, HAP- CO_3 and Pb-HAP samples after 10 hour OCM reaction have also been presented in (A).

4. Conclusions

The HAP apatite structure with cation (Pb^{2+}), anion (CO_3^{2-}), or both (Pb^{2+} and CO_3^{2-}) substitutions have been synthesized. The physicochemical properties and catalytic behaviors of the HAP-based catalysts were assessed by a variety of characterizations and OCM catalysis tests. The Pb^{2+} and CO_3^{2-} substitutions changed the composition and physicochemical properties of the HAP catalyst. The Pb-HAP- CO_3 with both Pb^{2+} and CO_3^{2-} substitutions exhibited the best thermal structural stability. The tunable composition of the HAP-based catalysts, and thus the tunable surface acidity environment, influences the catalytic behaviors of the catalysts in OCM reactions. The OCM catalysis studies showed that C_2 selectivity increased with Pb^{2+} substitution in the catalysts whereas Pb-HAP- CO_3 exhibited better stability in comparison with Pb-HAP. At the examined reaction temperatures of 923, 943, and 973 K, the CH_4 conversion and C_2 selectivity decreased and increased, respectively, with increasing CH_4/O_2 ratios. The C_2 yield showed a strong dependence on the composition of HAP-based catalysts and reaction conditions. The present work is for the first time a systematic examination of the effects of composition of HAP-based apatite materials on OCM reactions. The synthesis method, understating of the correlations between the composition, property, and catalytic performance of HAP-based catalysts are applicable to a range of apatite structured ceramic materials, which are potential membrane materials for OCM reaction in membrane reactors.

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Graphical abstract