

Investigations of Fe-MAI₂O₄ (M = Ca, Mg, Sr, Ba) Catalysts for Catalytic Decomposition of Methane

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Catalytic decomposition of methane is a more sustainable alternative for hydrogen production compared to established technologies like steam methane reforming and coal gasification. This study reports iron-based catalysts supported on MAI₂O₄ (M = Ca, Mg, Sr, Ba) prepared via a *ball-milling* or one-pot modified Pechini (*sol-gel*) method. The synthesized catalysts were evaluated for their CDM performance in the range of 750–800 °C. In general, we show that ball-mill synthesis leads to higher CDM activities than sol-gel synthesized samples, which undergo quick deactivation. Raman spectroscopy and H₂-TPR indicate that synthesizing the Fe-MAI₂O₄ catalysts via the sol-gel method results in iron coordination with cations (i.e., M) and with alumina to decrease iron's reducibility and its overall catalytic activity. For the ball-mill synthesized samples, we find that a 30 wt% Fe-CaAl₂O₄ catalyst tested at optimized reaction conditions of $T_{red} = 700^{\circ}\text{C}$, $T_{rxn} = 750^{\circ}\text{C}$, $y_{\text{CH}_4} = 0.9$, and $GHSV = 1.25 \text{ L} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ obtained a competitive carbon yield of 17.86 g_C/g_{Fe} (5.06 g_C/g_{Cat}). TEM and SEM of the spent product indicate that the carbon product forms primarily via a tip-growth mechanism, with both filamentous and nano-onion-type carbon being generated. Raman spectroscopy of the spent product determined most of the carbon formed on the ball-milled Fe-MAI₂O₄ catalysts was graphitic in nature with I_D/I_G ratios ranging between 0.400 and 0.500. Overall, *ball-milling* appears to be a simple yet effective strategy to prepare dispersed iron catalysts for CDM.

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I. INTRODUCTION

Today's energy consumption largely derives from fossil fuels, including petroleum, natural gas, and coal [1]. The consumption of these carbonaceous resources is a primary driver behind anthropogenic CO₂ emissions, which have resulted in an increase in atmospheric CO₂ concentrations by ~150% (i.e., 280–430 ppm) from preindustrial levels [2]. CO₂ itself is a potent greenhouse gas, and the projected implications of its continued, unconstrained emissions have been well documented by both government and independent agencies [3]. In general, a shift toward renewable energy sources to address the world's energy needs is becoming increasingly attractive. Hydrogen gas as an energy source has recently been of interest because when combusted, it generates only water as a byproduct and has a superior mass-based energy density of 120–142 MJ kg^{−1} compared to traditional sources.

Currently, the world's supply of hydrogen (~100 MT, 2024) is largely derived from methane reforming or coal gasification processes, whereas a limited share is produced from green or renewable technologies [4]. It is notable that even with a constant expansion of global production (e.g., 3% growth from 2024 to 2100), the energy obtainable from hydrogen (~945 MT, 37 200 TWh in 2100 assuming $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$, $\Delta H_{\text{rxn}} = 285.8 \text{ kJ/mol}$ HHV) would still represent a small portion of present-day energy consumption (i.e., 183 000 TWh in 2023) [5]. Therefore, it is unlikely that a true hydrogen economy can be established without aggressive innovation in hydrogen production technologies combined with suitable storage and transportation mechanisms [5].

There are several mature H₂ production technologies, the dominant processes today being steam reforming (SMR) and coal gasification (CG) [6]. While effective, SMR and CG produce sizable CO₂ emissions (5.1–13.7 and ~25.6 kg CO₂/kg H₂, respectively) and typically require additional gas postprocessing (i.e., pressure swing adsorption) to generate a pure stream of hydrogen [7]. In contrast, catalytic decomposition of methane (CDM) is an alternative hydrogen production technology capable of producing H₂ with *in situ* carbon capture [8]. The CDM process has a comparable enthalpy of reaction requirement

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compared to SMR after the water-gas-shift reaction (37.5 vs 41.4 kJ/mol H_2), and no theoretical CO_2 generation (i.e., $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) outside of secondary emissions associated with unit heating [9]. Thermal pyrolysis of methane without a catalyst requires temperatures $>1200^\circ\text{C}$ to achieve viable methane conversions due to the high activation energy ($E_a = 347\text{--}420$ kJ/mol) [10,11]. To overcome this limitation, a catalyst is typically utilized to lower the energy barrier for methane dissociation. Several different types of catalyst systems have been explored in the CDM field, including supported metals [7], molten metals or salts [12,13], and carbon catalysts [14,15]. Additional field enhancement effects (i.e., microwave, induction heating, and plasma-assisted approaches) [16–19] and co-feed schemes (i.e., utilizing diluted CO_2 or H_2O along with CH_4) [20,21] have also been investigated. Supported metal systems (i.e., transition metals supported by an oxide material) are highly active and produce filamentous carbon, which may greatly influence the economics of the produced hydrogen assuming adequate carbon quality and an existing carbon market [22–24]. It is notable that, for most approaches, catalyst stability and longevity challenges remain a critical challenge.

For supported metal systems, the primary transition metals utilized for CDM are Ni, Co, and Fe, dispersed on an oxide support like Al_2O_3 , SiO_2 , and MgO [25]. Additional studies have also shown that these metals can be doped into a parent structure (e.g., LaNiO_3 or hexaaluminates) and exsolved to the surface of the oxide to be catalytically active [26–28]. Ni and Co are particularly active at lower temperatures of $500\text{--}600^\circ\text{C}$ but undergo facile deactivation above 600°C due to sintering or imbalance in reaction rate vs carbon diffusion rate on the surface of the catalyst particle. Fe is typically active at a higher temperature range of $700\text{--}900^\circ\text{C}$, however, still mainly faces deactivation issues due to fragmentation or metal dusting [7].

In this study, we support monometallic iron on MAl_2O_4 materials (i.e., Fe- MAl_2O_4) with M representing Ba, Ca, Mg, or Sr, respectively. Per the literature, MAl_2O_4 materials have not been thoroughly explored or tested with iron as a support for their catalytic activity in CDM. However, a Ni-supported catalyst system was previously reported where NiO was deposited on various MAl_2O_4 materials ($M = \text{Ba}, \text{Ca}, \text{Fe}, \text{Mg}, \text{and Zn}$), which showed reasonable CDM activity in the range of $500\text{--}650^\circ\text{C}$ [29]. As previously mentioned, although Fe-based catalysts face several issues, they are cheaper, more abundant, and environmentally benign when compared to Ni or Co, making Fe an attractive metal catalyst for CDM. We particularly explored two low-complexity synthesis methods and their impact on the resulting iron activity for CDM. The effect of sample pretreatment, reaction temperature, and GHSV was explored to maximize the productivity of the samples.

II. METHODS

A. MAl_2O_4 support synthesis

A modified Pechini method was utilized to synthesize BaAl_2O_4 , CaAl_2O_4 , MgAl_2O_4 , and SrAl_2O_4 supports. In this process, stoichiometric amounts of barium nitrate (Sigma-Aldrich, ACS Reagent, $\geq 99\%$), calcium nitrate tetrahydrate (Sigma-Aldrich, $\geq 99\%$), strontium nitrate (Sigma Aldrich, ACS Reagent, $\geq 99\%$), and alumina nitrate nonahydrate (Thermo Scientific, $\geq 99\%$) were combined in a clean plastic synthesis container with approximately 30 mL of deionized water. A stir bar was added to the mixture, and the container was placed on a hot plate. The temperature of the hotplate was initially set at 40°C and the RPM to 300. After ~ 20 min, citric acid (Sigma-Aldrich, $\geq 99\%$) was added and mixed for ~ 20 min at 40°C . After this period, ethylene glycol (Sigma-Aldrich, ReagentPlus®, $\geq 99\%$) was added to the mixture. The molar ratio of citric acid to the total molar amount of cations and the moles of ethylene glycol to citric acid are 2.5:1 and 1.5:1, respectively. The hotplate temperature setpoint was changed to 80°C . Over the next 2–3 h solvent evaporation occurred until gelling of the ethylene glycol occurred. The gel was subsequently removed from the hotplate and placed in a drying oven. The gel was dried overnight at 85°C . The resulting solid precursor material obtained from the sol-gel synthesis was then crushed using a pestle and mortar until it reached the consistency of a fine powder. The powder is transferred into a clean alumina crucible and loaded into a high-temperature tube furnace (GSL-1500X). The powder was then calcined in air at 1250°C for 10 h with a ramp-up and ramp-down rate of $3^\circ\text{C}/\text{min}$.

B. Preparation of FeAl_2O_4 -CM samples via ball milling

To disperse iron onto the catalyst, a ball-mill mixing method was utilized. In this method, a portion of the calcined support and iron (III) oxide (Sigma Aldrich, $\geq 96\%$) were measured and loaded according to the desired iron wt% into a stainless-steel ball-mill container. The desired iron wt% was chosen on a metal-only basis (i.e., 10 wt%Fe + 90% MAl_2O_4). The associated mass of Fe_2O_3 ($M_{\text{Fe}_2\text{O}_3}$) to be loaded into the ball-mill apparatus was estimated based on stoichiometry (i.e., $M_{\text{Fe}_2\text{O}_3} = 0.5M_{\text{Fe}}(159.69/55.85)$). After both powders are loaded into the ball-mill container, 3 mm zirconia beads are added to the container in the ratio of 5:1 Zr beads to catalyst powder on a mass basis. Ethanol (Thermo Scientific, 200 Proof, 99.5 + %, ACS Reagent) was used as a solvent and was only added to cover the powder contents in the container. The container was then ball milled for 3 h in a Vivtek Instruments VBM-V80 Ball Mill at 1200 RPM (1200 cycles per min).

C. Preparation of Fe-MAl₂O₄-SG samples via Pechini sol gel

The preparation of the Fe-MAl₂O₄-SG samples followed the same synthesis method described in Sec. II A except for the addition of iron (III) nitrate nonahydrate (Sigma Aldrich, 99% + analytical grade) in the required amount.

D. Reactor configuration and isothermal testing

Catalytic evaluation of the supported iron catalysts was carried out utilizing a large-bottom quartz U-tube (Fig. S1 in Supplemental Material [30]). In this setup, approximately 250 mg of Fe-MAl₂O₄ powder was loaded into a quartz U-tube, which was placed into a vertical furnace integrated with a temperature controller. The quartz U-tube inlet was attached to a gas manifold equipped with Alicat mass-flow controllers, which allowed for the feeding of methane, hydrogen, carbon dioxide, and argon. The outlet from the reactor was connected to an Agilent MicroGC 490 equipped with a 10 m 5 Å mol-sieve column for effluent composition analysis. The settings for the MicroGC column were 100 °C injector temperature, 40 ms injection time, 150 kPa column head pressure, 80 °C column temperature, and 8 s backflush. The catalysts were activated in 80% H₂ (balance N₂) for 1 h at between 700 and 800 °C. The CDM reaction was conducted at atmospheric pressure, with the partial pressures of CH₄ and N₂ fixed at 0.9 and 0.1 atm, respectively, for a total of 1 atm. The feed flowrates varied between 10 and 20 sccm based on the desired GHSV ranging between 1.25 and 5 L · g⁻¹ · h⁻¹. The reaction tests were performed at atmospheric pressure and between 750 and 850 °C.

The methane conversion (X_{CH_4}) is estimated with the aid of a 10 vol % N₂ inert tracer to estimate the total product flowrate (which is independently validated with a flow-measurement device). In this case, the X_{CH_4} and X_{CO_2} are determined via:

$$X_{\text{CH}_4} = \frac{y_{\text{CH}_4} \left(\frac{F_{\text{N}_2, \text{feed}}}{y_{\text{N}_2}} \right)}{F_{\text{CH}_4, \text{feed}}},$$

where y_{H_2} and y_{N_2} are the real-time concentrations in vol % measured from our calibrated GC during the reaction. $F_{\text{CH}_4, \text{feed}}$ and $F_{\text{N}_2, \text{feed}}$ are the known feed volumetric flowrates of the inert tracer (i.e., N₂) and methane. The instantaneous hydrogen balance (ϕ_{H_2}) is also utilized to show the hydrogen gas is the primary gaseous product with residual methane and inert N₂ gas tracer:

$$\begin{aligned} \phi_{\text{H}_2} &= \frac{2F_{\text{out, total}} y_{\text{H}_2} + 4F_{\text{out, total}} y_{\text{CH}_4}}{4F_{\text{CH}_4, \text{feed}}} \\ &= \frac{F_{\text{out, total}}}{4F_{\text{CH}_4, \text{feed}}} (2y_{\text{H}_2} + 4y_{\text{CH}_4}). \end{aligned}$$

A deactivation extent (Θ) was defined to compare the deactivation rate between the 10, 20, and 30 wt % Fe-CaAl₂O₄ catalysts. $X(t)$ represents the observed methane conversion, and X_{Max} represents the maximum conversion observed during the testing period:

$$\Theta = 1 - \frac{X(t)}{X_{\text{max}}}$$

E. Catalyst characterization

Note: supporting catalyst characterization can be located in Supplemental Material files [30].

1. Ex situ x-ray diffraction (XRD)

XRD patterns were taken using an X'Pert Pro x-ray diffractometer. The diffractometer was equipped with a Cu K α x-ray source (45 kV beam voltage, 40 mA current). Samples were mounted on a flat stage and scanned across a 2θ range of 10°–90° (8°/min scanning rate), with a 0.2177° divergence slit, a 1° scattering slit, and a 0.3 mm receiving slit. Material identification was conducted using HighScore integrated with the PDF-4 material database.

2. In situ x-ray diffraction (XRD)

High-temperature experiments were recorded using a PANalytical Empyrean x-ray diffractometer fitted with a copper (anode) x-ray generator ($\lambda = 1.5406$ Å) in the continuous scanning mode (generator voltage: 45 kV, tube current: 40 mA) using a HTK2000 heating stage. A schematic of the XRD and gas manifold utilized is shown in Fig. S2 in Supplemental Material [30]. For the reduction studies, a scan range of 20°–70° and a step size of 0.026° were utilized; 50 sccm of 3 vol % H₂ in balance N₂ was used as the reducing gas. A heating rate of 5 °C min⁻¹ from 25 to 700 °C was utilized.

3. Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (SEM-EDS)

SEM images of calcined, reduced, and postreaction samples were collected using a Hitachi SU8700 field-emission (FESEM). The primary detector utilized for imaging was the upper secondary electron detector (UD). The analyzer tension, amperage, and working distance were set at 2.00 kV, a spot size of 30, and ~4–5 mm, respectively. EDS was performed on the samples using an Oxford energy dispersive x-ray spectrometer. For EDS measurements, the FESEM analyzer tension, amperage, and working distance were set between 10.00 and 20.00 kV, a spot size of 60–90, and ~6 mm, respectively, depending on the sample.

4. High-resolution transmission electron microscopy (HRTEM) with energy dispersive x-ray spectroscopy (EDX)

HRTEM and scanning transmission electron microscopy (STEM) with high-angle annular dark-field imaging coupled with EDX tomography were utilized to further characterize the morphology and elemental composition of the catalytic samples (Fischer Scientific Talos, operating at 200 kV).

Temperature programmed reduction (TPR): TPR- H_2 was performed using a Micromeritics AutoChem II 2920 to assess the reducibility of the catalyst. Approximately 40–50 mg of calcined catalyst was loaded into the AutoChem II unit. The sample was then heated from 20 to 900 °C at a ramp rate of 10 °C/min, in 5% H_2 in balance argon at a flow rate of 50 cc/min. Hydrogen consumption was monitored via the TCD signal, and the processed data were normalized based on the highest peak intensity measured during analysis.

Raman spectroscopy: For the *ex situ* Raman experiments, a Horiba XploRA PLUS Confocal Raman microscope equipped with a 532 nm excitation wavelength laser source was utilized. The laser was focused onto the samples with a 50× objective (Olympus LMPlanFL N), while the spectrometer was used with a 750 nm grating, 500 μ m hole, and 200 μ m slit resulting in a spectral resolution of $\sim 2.52 \pm 0.20$ cm^{-1} in the range between 1000 and 3000 cm^{-1} . The acquisition time was set to 1 s and total accumulations per spectra set at 50 with a filter setting at 1%. The 520.7 cm^{-1} band of a silicon wafer standard was used to calibrate the spectrometer before spectral acquisition.

III. RESULTS AND DISCUSSION

A. Catalyst synthesis and characterization

The preparation of the 10Fe- MAI_2O_4 catalysts was accomplished utilizing two synthesis methods. First, a ball-mill method where the supports (i.e., MAI_2O_4) were first synthesized using a Pechini sol-gel method followed by ball milling with Fe_2O_3 we hereafter refer to as Fe- MAI_2O_4 -BM. Second, the 10Fe- MAI_2O_4 catalysts were synthesized using a one-pot Pechini sol-gel method hereafter referred to as Fe- MAI_2O_4 -SG samples.

After calcination of the MAI_2O_4 supports, XRD was utilized to evaluate the phase purity of each synthesized support. Each material was matched to an existing powder diffraction file and shows good agreement between both the intensity and 2θ position of the expected peaks [Fig. 1(a)]. $BaAl_2O_4$ (PDF No. 00-017-0306) was found to have a hexagonal structure ($P6_322$), $CaAl_2O_4$ (PDF No. 04-013-0779) a monoclinic structure ($P2_1/n$), $MgAl_2O_4$ (PDF No. 01-072-7248) a cubic structure ($Fd\bar{3}m$), and $SrAl_2O_4$ (PDF No. 01-084-4281) possessed a monoclinic structure ($P2_1$).

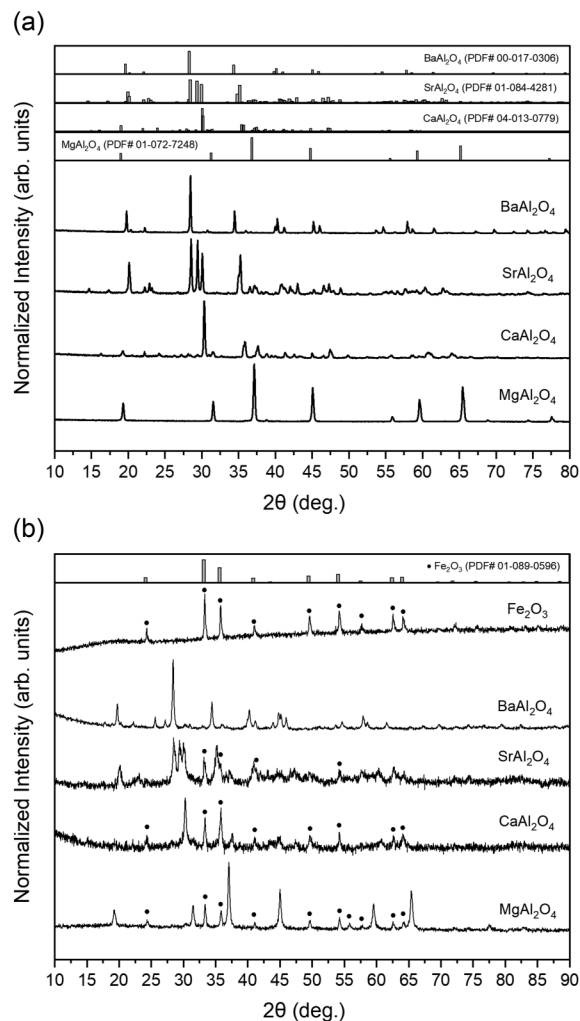


FIG. 1. Powder diffraction profiles of (a) calcined MAI_2O_4 supports and (b) the post-ball-milling 10Fe- MAI_2O_4 -BM samples.

Each MAI_2O_4 was subsequently ball milled with an appropriate amount of Fe_2O_3 powder to give 10 wt % Fe + MAI_2O_4 on an iron-only basis [Fig. 1(b)]. In general, the XRF results are generally consistent with nominal loading (wt %) except for 10Fe- $MgAl_2O_4$ -BM and 10Fe- $CaAl_2O_4$ -BM samples (Table I). XRD patterns of the ball-milled materials clearly show the original MAI_2O_4 diffraction patterns in addition to rhombohedrally centered hexagonal ($R\bar{3}c$) α - Fe_2O_3 (PDF No. 01-089-0596). Notably, the structure of (Mg, Ca, Sr) Al_2O_4 supports appeared to remain intact during the ball milling.

For the samples prepared via sol gel (i.e., Fe- MAI_2O_4 -SG), it can be observed that 10Fe-(Ca, Ba, Sr) Al_2O_4 -SG appear to be structurally similar to original MAI_2O_4 support diffraction patterns (Figs. S3(a)–S3(d) in Supplemental Material [30]). Notably, there is no significant presence of Fe_2O_3 observed. In the case of 10Fe- $CaAl_2O_4$ -SG, the main identified phase was monoclinic ($P2_1/n$) $CaAl_{1.817}Fe_{0.183}O_4$ (PDF No. 01-070-7252)

TABLE I. Nominal and measured iron content of Fe-MAI₂O₄ samples.

Sample name	Fe (Nom.) ^a	Fe (Meas.) ^b
10Fe-MgAl ₂ O ₄ -BM	10	15.03
10Fe-CaAl ₂ O ₄ -BM	10	13.08
10Fe-SrAl ₂ O ₄ -BM	10	11.05
10Fe-BaAl ₂ O ₄ -BM	10	11.24
10Fe-MgAl ₂ O ₄ -SG	10	7.42
10Fe-CaAl ₂ O ₄ -SG	10	9.00
10Fe-SrAl ₂ O ₄ -SG	10	8.67
10Fe-BaAl ₂ O ₄ -SG	10	10.55
20Fe-CaAl ₂ O ₄ -BM	20	22.03
30Fe-CaAl ₂ O ₄ -BM	30	27.80

^aNominal wt % Fe from synthesis.^bMeasured wt % Fe from XRF.

and a small portion of monoclinic (*C2/c*) CaAl₄O₇ (PDF No. 00-046-1475). For 10Fe-MgAl₂O₄-SG, significant crystal structure differences were observed. The dominant crystal phases identified were hexagonal (*R3c*) α -Al₂O₃ (PDF No. 04-015-8609) and cubic (*Fd3m*) MgFe₂O₄ (PDF No. 04-012-1077). The diffraction profile for 10Fe-SrAl₂O₄-SG consisted of monoclinic (*P* * */**) SrAl₂O₄ (PDF No. 00-034-0379) and hexagonal (*P*_{6₃}/*mmc*) SrFe_{3.44}Al_{8.56}O₁₉ (PDF No. 04-009-8629). There are no separate detectable phases for 10Fe-BaAl₂O₄-SG sample besides hexagonal (*P*_{6₃}22) BaAl₂O₄ (PDF No. 04-020-7786). XRF indicates that the nominal and expected iron content is slightly lower than the targeted 10 wt % (Table I). SEM was used to image the surface morphology of the different catalytic materials. For the 10Fe-CaAl₂O₄-BM catalysts, the images of the calcined MAI₂O₄ supports (Figs. S4(a)–S4(d) in Supplemental Material [30]) are relatively smooth in comparison to the samples post-ball-milling with Fe₂O₃, which clearly show the expected breakage of the support structure (Figs. S4(e)–S4(f) in Supplemental Material [30]). By comparison, the 10Fe-MAI₂O₄-SG catalysts possessed a similar smooth surface morphology comparable to the calcined MAI₂O₄ supports (Figs. S4(i)–S4(l) in Supplemental Material [30]).

The nature of the iron after these two synthesis methods was further evaluated via Raman spectroscopy (Table S1 in Supplemental Material [30]). Characteristic vibrational modes of the various MAI₂O₄ supports were observed, which consisted of the E_g band for MgAl₂O₄ (405.3 cm^{−1}), [31] AlO^{4−} vibrations CaAl₂O₄ (519.4 cm^{−1}), as well as characteristic O-Al-O vibrations for SrAl₂O₄ (461.2 cm^{−1}) and BaAl₂O₄ (417.2 cm^{−1}) respectively (Fig. S5(a) in Supplemental Material [30]) [32–34]. For the 10Fe-MAI₂O₄-BM catalysts, the A_{1g} and E_{2g} bands of Fe₂O₃ were present between 220.6–221.8 and 287.6–291.1 cm^{−1}, respectively, for each sample. This is consistent with the expected Raman-active vibrational

modes of the rhombohedrally centered hexagonal (*R3c*) space group for Fe₂O₃ [35]. Collectively, these vibrational modes are an indication of free hematite supported on the aluminate spinel species (Fig. S5(b) in Supplemental Material [30]). Conversely, for the 10Fe-MAI₂O₄-SG catalysts, significant changes in iron coordination were observed. A peak at 650.85 cm^{−1} was observed for 10Fe-MgAl₂O₄-SG which we assign to the A_{1g} vibrational mode of magnetite (i.e., Fe₃O₄ or (Fe²⁺Fe³⁺)O₄) which typically exhibits the A_{1g} vibration near 660 cm^{−1} [35,36]. Peaks at 737.4 and 754.3 cm^{−1} were observed for 10Fe-SrAl₂O₄-SG and 10Fe-BaAl₂O₄-SG, respectively, which are attributed to a hercynite spinel (i.e., FeAl₂O₄). [37] The 10Fe-CaAl₂O₄-SG sample appeared to possess no significant iron vibrational modes but rather a slightly broadened AlO^{4−} vibrational band for CaAl₂O₄ near 520 cm^{−1} (Fig. S5(c) in Supplemental Material [30]). Overall, the 10Fe-MAI₂O₄-SG compounds appear to possess a slightly more reduced form of iron in the structure from its coordination with other cations (i.e., Mg, Ca, Sr, Ba, and Al), which we hypothesize likely make it more difficult to reduce to metallic iron compared to the 10Fe-MAI₂O₄-BM samples.

The reducibility of the Fe-MAI₂O₄-BM samples was evaluated using H₂-TPR [Fig. 2(a)]. For each 10 wt % Fe-MAI₂O₄ (*M* = Mg, Ca, Sr, Ba), a maximum H₂ consumption peak was observed in the temperature range between 512 and 533 °C. There were minor differences between iron dispersed on the CaAl₂O₄, SrAl₂O₄, and BaAl₂O₄ supports. Both SrAl₂O₄ and CaAl₂O₄ exhibited a shoulder peak at 576 and 620 °C, respectively, while BaAl₂O₄ exhibited a single broad peak with no observable higher H₂ consumption shoulder peak. Notably, the 10 wt % Fe-MgAl₂O₄ exhibited additional consumption peaks at 583 and 652 °C, respectively. From the H₂-TPR data, it is apparent that MgAl₂O₄ leads to a less facile reduction of surface iron species compared to CaAl₂O₄, SrAl₂O₄, and BaAl₂O₄. This was separately confirmed by the residual Fe₂O₃ present in the *ex situ* postreduction XRD patterns. In contrast to bulk Fe₂O₃ which shows a max hydrogen consumption at 711 °C and complete reduction after 850 °C, all catalyst samples exhibit a decrease in their peak reduction temperature [38].

H₂-TPR of the Fe-MAI₂O₄-SG samples was conducted and shows clear differences in reducibility compared to their BM counterparts [Fig. 2(b)]. In general, the catalyst samples prepared via a sol-gel method are less reducible, as indicated by the hydrogen consumption peaks shifting toward higher temperatures in all cases. As previously mentioned, all maximum H₂ consumption peaks for the Fe-MAI₂O₄-BM samples ranged between 512 and 533 °C. For the sol-gel synthesized samples, the 10Fe-CaAl₂O₄-SG peak shifted to 790.8 °C. For 10Fe-SrAl₂O₄-SG and 10Fe-BaAl₂O₄-SG a progressive H₂ evolution shoulder was evident up to 900 °C. Specifically for

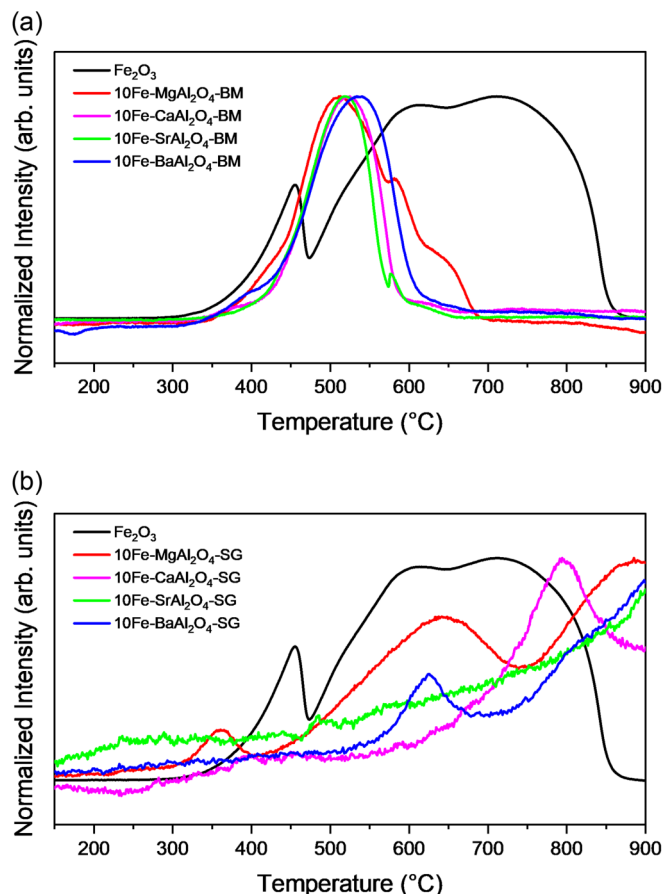


FIG. 2. Hydrogen consumption from H₂-TPR for (a) 10Fe-MAl₂O₄-BM samples and (b) 10Fe-MAl₂O₄-SG samples compared to free Fe₂O₃.

10Fe-BaAl₂O₄-SG, a local maximum was observed around 625.6 °C. For 10Fe-MgAl₂O₄-SG, the three peaks observed in the ball-milled sample were notably spread out at 359.7, 641.5, and ~891 °C, respectively. Overall, despite slight

differences in iron loading from XRF between the different synthesis methods (Table I), the dispersion of iron on MAI₂O₄ supports via ball milling (i.e., Fe-MAI₂O₄-BM) appears to be an effective strategy for increasing the overall reducibility of the iron.

B. Isothermal CDM evaluation

1. Initial screening of ball-milled 10Fe-MAI₂O₄ catalysts

Initial CDM screening of the as-prepared 10Fe-(Ba, Ca, Mg, Sr)Al₂O₄-BM catalysts was conducted at 800 °C under 90 vol % CH₄ balance N₂ and GHSV = 5 L · g⁻¹ · h⁻¹ after an 800 °C reduction in 80 vol % H₂ [Fig. 3(a)]. Generally, all catalysts exhibited a quick deactivation profile, losing appreciable amounts of their initial activity within 1 h TOS. In terms of comparative performance, Fe-CaAl₂O₄-BM exhibited the highest average conversion rate of 28.16% over 250 min, followed by Fe-SrAl₂O₄-BM at 27.91% over 235 min, then Fe-BaAl₂O₄-BM at 23.75% over 96 min, and finally Fe-MgAl₂O₄-BM at 14.30% over 270 min. Further, the carbon yields reflect the observed performance, with 10Fe-CaAl₂O₄-BM yielding 9.12 g_C/g_{Fe} (0.91 g_C/g_{Cat}), Fe-BaAl₂O₄-BM with 6.42 g_C/g_{Fe} (0.64 g_C/g_{Cat}), Fe-SrAl₂O₄-BM with 7.08 g_C/g_{Fe}, and finally Fe-MgAl₂O₄-BM with 3.63 g_C/g_{Fe} (0.36 g_C/g_{Cat}), respectively. The average instantaneous hydrogen balance for all of the screened 10Fe-MAI₂O₄-BM catalyst samples was > 94.6% confirming their ability to generate CO₂-free hydrogen (Fig. S6(a) in Supplemental Material [30]). The normalized activity for the Fe-MAI₂O₄-BM catalysts based on the average CH₄ conversion from 0 to 90 min was comparable for the (Ca, Sr, Ba)MAI₂O₄-BM catalysts, which ranged between 421.35 and 503.01 mmol · g⁻¹ · h⁻¹ (Table S2 in Supplemental

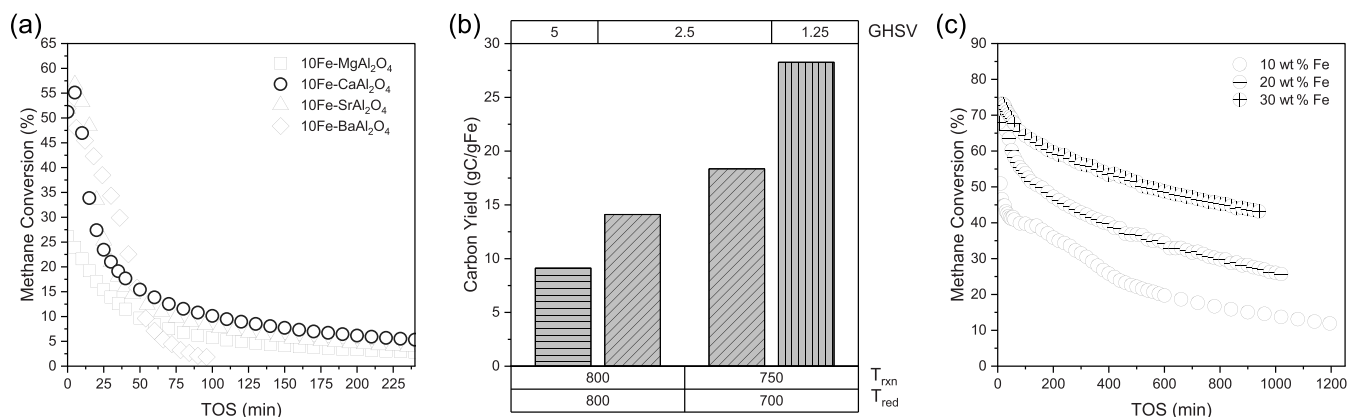


FIG. 3. CDM performance data for (a) screening tests on 10Fe-MAI₂O₄-BM catalyst samples tested at $T_{red} = 800$ °C, $T_{rxn} = 800$ °C, $y_{CH_4} = 0.9$ and $GHSV = 5$ L · g⁻¹ · h⁻¹, (b) pretreatment and reaction condition optimization on 10Fe-CaAl₂O₄-BM with $y_{CH_4} = 0.9$, and (c) iron-loading variation on XFe-CaAl₂O₄-BM with $X = 10, 20$, and 30 wt % at $T_{red} = 700$ °C, $T_{rxn} = 750$ °C, $y_{CH_4} = 0.9$, and $GHSV = 1.25$ L · g⁻¹ · h⁻¹.

Material [30]). For MgAl₂O₄-BM, the normalized activity was 203.67 mmol · g_{Fe}⁻¹ · h⁻¹.

2. Testing of ball-milled 10Fe-CaAl₂O₄ and sol-gel synthesized 10Fe-MAI₂O₄ catalysts at optimized reaction conditions

It was found that the 10Fe-CaAl₂O₄-SG exhibited the highest carbon yield of 9.12g_C/g_{Fe} and further appeared to have a slightly higher conversion at the end of the isothermal screening tests [Fig. 3(a)]. Therefore, reduction and reaction conditions to optimize catalytic activity were explored on 10Fe-CaAl₂O₄-BM [Fig. 3(b)]. The effect of GHSV was first explored, keeping the same reaction and reduction temperatures as in the screening phase (i.e., $T_{rxn} = T_{red}$). When the GHSV was lowered from 5 to 2.5 L · g⁻¹ · h⁻¹ the overall carbon yield for 10Fe-CaAl₂O₄-BM increased by x1.54 from 9.12g_C/g_{Fe} (0.91g_C/g_{Cat}) to 14.11g_C/g_{Fe} (1.41g_C/g_{Cat}). The reduction temperature and reaction temperatures were changed to 700 and 750 °C, respectively, while keeping the GHSV fixed at 2.5 L · g⁻¹ · h⁻¹. The lowering of both temperatures had an additional positive impact on the associated carbon yield of the 10Fe-CaAl₂O₄-BM system reaching 18.35g_C/g_{Fe} (1.83g_C/g_{Cat}). Further lowering the GHSV to 1.25 L · g⁻¹ · h⁻¹ at 700 °C reduction and 700 °C reaction temperatures increased the carbon yield to 28.25g_C/g_{Fe} (2.83g_C/g_{Cat}). The average instantaneous hydrogen balance for the screened samples was > 95.5% except for 10Fe-CaAl₂O₄-BM tested at $T_{red} = 700$ °C, $T_{rxn} = 750$, and $GHSV = 1.25$ L · g⁻¹ · h⁻¹ which had an average hydrogen balance of 84.5% (Fig. S6(b) in Supplemental Material [30]). Overall, compared to the screening conditions, the carbon yield was improved by a factor of 3.1x. From these results, it was established that lower GHSVs combined with lower reduction and reaction temperatures enable higher overall CDM productivity. The sol-gel synthesized 10Fe-MAI₂O₄-SG catalysts ($M = \text{Mg, Ca, Sr, Ba}$) were evaluated for CDM at the optimized conditions of $T_{red} = 700$ °C, $T_{rxn} = 750$, and $GHSV = 1.25$ L · g⁻¹ · h⁻¹ (Fig. S7 in Supplemental Material [30]). It can be generally observed that the sol-gel synthesized materials exhibited limited activity, with initial CH₄ conversions being < 3.5% except for 10Fe-MgAl₂O₄-SG which had an initial CH₄ conversion of 27.59%, but this activity attenuated < 5% within 1 h TOS. The average instantaneous hydrogen balances for the 10Fe-MAI₂O₄-SG samples ranged between 89.3% and 98.5% (Fig. S6(d) in Supplemental Material [30]). We hypothesize that the low observed CH₄ conversions and catalyst stability of the 10Fe-MAI₂O₄-SG catalysts can be attributed to a reduction in the available reduced surface iron readily available to react with CH₄. As we have demonstrated in the catalyst synthesis and characterization section, the iron in the 10Fe-MAI₂O₄-SG formulations exhibited Raman

vibrational modes consistent with either magnetite (Fe₃O₄) or likely FeAl₂O₄-type vibrations as opposed to the characteristic vibrations of Fe₂O₃. This implies Fe is likely coordinated with the other cations (i.e., $M = \text{Mg, Ca, Sr, Ba}$) or the alumina, which may decrease the reducibility of Fe_xO_y → Fe. As the H₂-TPR of the sol-gel samples showed, compared to the 10Fe-MAI₂O₄-BM formulations, the maximum H₂-consumption peak shifts to higher temperatures, implying less facile reducibility of the iron. Quantitative hydrogen consumption data from H₂-TPR also reflects reducibility differences between sample preparation methods (Table S3 in Supplemental Material [30]), with BM samples generally showing higher hydrogen consumption. The reducibility of iron coordinated with alumina compounds like FeAl₂O₄ or even low iron SrFe_xAl_{12-x}O₁₉ (where $x \leq 3$) has been shown to drastically decrease iron reducibility [39]. The ultimate effect is less available reduced iron to facilitate the reaction, which results in lower observed catalytic performance.

3. Increased iron loading on CaAl₂O₄

The impact of increasing iron loading of the Fe-CaAl₂O₄-BM system was investigated [Fig. 3(c)]. The iron loading varied between 10, 20, and 30 wt % for the Fe-CaAl₂O₄-BM catalysts. The increases in iron loading are clearly reflected in the post-ball-mill XRD patterns (Fig. S8 in Supplemental Material [30]). The effect of iron loading was evaluated at the optimized reaction conditions of $GHSV = 1.25$ L · g⁻¹ · h⁻¹ at $T_{red} = 700$ °C and $T_{rxn} = 750$ °C. Comparing average methane conversion between the different iron-loaded samples, the 30 wt % Fe-CaAl₂O₄-BM catalyst sustained the highest average methane conversion of 57.55% over 940 min, followed by 20 wt % Fe-CaAl₂O₄-BM at 48.65% over 1020 min, and 10 wt % Fe-CaAl₂O₄-BM at 31.43% over 1195 min. The average instantaneous hydrogen yields for the 10, 20, and 30 wt % Fe samples ranged between 84.5% and 94.3% (Fig. S6(c) in Supplemental Material [30]). In terms of carbon yield, increasing the iron loading positively impacted the overall carbon yield (i.e. g_C/g_{Cat}) while the metal-based carbon yields (i.e., g_C/g_{Fe}) decreased. For carbon productivity, the 10 wt % Fe-CaAl₂O₄-BM, as previously discussed, yielded 28.25g_C/g_{Fe} (2.83g_C/g_{Cat}), the 20 wt % Fe-CaAl₂O₄-BM yielded 19.48g_C/g_{Fe} (3.78g_C/g_{Cat}), and the 30 wt % Fe-CaAl₂O₄-BM yielded 17.86g_C/g_{Fe} (5.06g_C/g_{Cat}). Notably, the range of metal-based carbon yields (i.e., 17.86–28.25g_C/g_{Fe}) lies in the 87th–92nd percentile for productivity of supported monometallic Fe catalysts tested for CDM (Fig. S9 in Supplemental Material [30]). The data utilized to claim that the Fe-CaAl₂O₄-SG carbon yields were in the 87th–92nd percentile for metal-based carbon yields was based on the Fe-only catalyst subset of the 334 tabulated catalysts

from our perspective article on supported metal CDM, or approximately 96 different catalysts monometallic Fe-catalyst based on an exhaustive literature search. The percentiles were abstracted using a Pareto plot, which was generated in OriginLab [7]. Ultimately, the 30 wt % Fe-CaAl₂O₄-BM exhibited the highest sustained methane conversion coupled with modest overall and metal-based carbon yields. Notably, all catalyst samples are observed to partially deactivate during testing. The measured deactivation extents (Θ) for the 10Fe, 20Fe, and 30Fe samples were estimated to be 0.766, 0.641, and 0.365, respectively. The normalized CDM activities based on average CH₄ conversion from 0 to 900 min TOS for the Fe-CaAl₂O₄-BM samples were found to be impacted by iron loading, with the activity decreasing from 129.47 mmol · g_{Fe}⁻¹ · h⁻¹ for the 10Fe sample to between 88.53 and 99.77 mmol · g_{Fe}⁻¹ · h⁻¹ for the 20Fe and 30Fe samples, respectively (Table S2 in Supplemental Material [30]). This decrease in activity corresponds to the decrease in observed carbon yield from 28.3g_C/g_{Fe} to between 19.58 and 17.9g_C/g_{Fe}. Overall, the results indicate that although iron loading increases, the effective iron utilization suffers.

C. Spent catalyst characterization

XRD analysis of the spent products from the ball-mill synthesized 10Fe-MaAl₂O₄-BM samples clearly shows the presence of hexagonal (*P*6₃/*mmc*) graphitic carbon (PDF No. 04-014-0362) (Fig. S10(a) in Supplemental Material [30]). The additional signature of BCC (*Im* $\bar{3}$ *m*) α -Fe (PDF No. 04-014-0360) can be identified. Orthorhombic (*Pnma*) Fe₃C (PDF No. 04-014-3174) cannot be discounted, although the peak signatures may be dampened compared to the residual graphitic carbon and Fe. For the more productive catalysts, like 10Fe-CaAl₂O₄, the graphite and Fe peaks are readily apparent. However, for less reactive catalysts like 10Fe-MgAl₂O₄-BM, the MgAl₂O₄ support diffraction peaks are more prominent, making the XRD pattern identification of residual iron-containing species difficult. Similarly, the presence of graphitic carbon and residual Fe was identified in the spent 20Fe- and 30Fe-MaAl₂O₄-BM samples (Fig. S10(b) in Supplemental Material [30]).

With the observed presence of Fe in the spent samples, it is worth commenting on the fate of Fe in the Fe-CaAl₂O₄-BM catalysts prereduction, during reduction, and during the CDM reaction. Before the catalyst was reduced in hydrogen, it was shown previously that the form of iron oxide in ball-mill synthesized samples is that of Fe₂O₃ supported on CaAl₂O₄. It can be inferred from *ex situ* XRD of post-reduction samples that upon reduction in 80 vol % H₂ balance N₂ at 800 °C that a transformation of Fe₂O₃ to BCC (*Im* $\bar{3}$ *m*) α -Fe (PDF No. 04-014-0360) occurs (Fig. S11 in Supplemental Material [30]). The transition is particularly clear for the (Mg, Ca, Sr)-Al₂O₄-BM supports. Notably,

incomplete reduction of Fe₂O₃ was observed in the case of MgAl₂O₄, as several diffraction peaks associated with Fe₂O₃ are still observed. Reduction of 10Fe-BaAl₂O₄-BM results in diffraction peaks associated with α -Fe, and the diffraction profile did not appear to be appreciably different than what was observed for the ball-milled samples. *In situ* XRD of 30Fe-CaAl₂O₄-BM exposed to 3 vol % H₂ balance Ar indicates that there is a transformation of Fe₂O₃ to BCC α -Fe which occurs between 520 and 680 °C (Fig. S12 in Supplemental Material [30]). Therefore, evidence suggests that the initially present bulk active phase of iron is α -Fe.

Literature on iron-based catalysts for CDM has debated the fate of Fe during the CDM reaction [7]. There has been notable fractionation between those attributing CH₄ activation and carbon diffusion to a ferrite-type structure (i.e., largely BCC α -Fe or FCC γ -Fe) [40–42] or to Fe₃C [43–45] [7]. Recent CDM studies utilizing *in situ* XRD on a SrFe_xAl_{12-x}O₁₉ hexaaluminate have shown that there is a sequential transition from α -Fe → γ -Fe → Fe₃C at 800 and 900 °C under the presence of 10 vol % CH₄ along with the formation of graphite. The study additionally provided computational evidence to suggest that Fe₃C was capable of energetically facile activation of *CH₄ → *CH₃ compared to α -Fe or γ -Fe on select facets [39]. In general, the fate of iron in Fe-based CDM is still an open question, while these recent *in situ* investigations provide convincing evidence that Fe₃C is present, additional *in situ* studies on different Fe catalyst systems would further support these findings.

SEM and TEM were utilized to characterize the morphology of the spent catalyst ball-milled Fe-MaAl₂O₄ catalysts and characteristics of the generated carbon co-product (Fig. S13 in Supplemental Material [30]). SEM indicates that the carbon formed during CDM generally consists of filamentous CNTs of varying diameter and nano-onion-type carbon (Figs. S13(a)–S13(d) in Supplemental Material [30]). It is further apparent from TEM (Figs. S13(e)–S13(h) in Supplemental Material [30]) and STEM-EDS (Figs. S13(i)–S13(l) in Supplemental Material [30]) that the carbon nanotubes are most likely formed by a tip-growth CNT mechanism, as there is a lack of evidence of tipless CNTs, which would constitute a base-growth mode. For example, one can see several of these features for the 10Fe-CaAl₂O₄-BM sample, showing the encapsulation of iron in Fig. 4(a) and the filamentous nature of the carbon from SEM in Fig. 4(b). From TEM, it is also apparent that the CNTs are predominately multiwalled carbon nanotubes (MWCNTs), as in the case of the spent 10Fe-BaAl₂O₄-BM sample, with CNT diameters ranging between 29.68 and 258 nm (Table S5 in Supplemental Material [30]). Generally, across all imaged samples, there is a notable presence of encapsulated iron along the CNT growth axis, which is a result of iron particle fragmentation during the CNT growth (Figs. S13(e)–S13(h) in Supplemental Material [30]). The consistent presence of

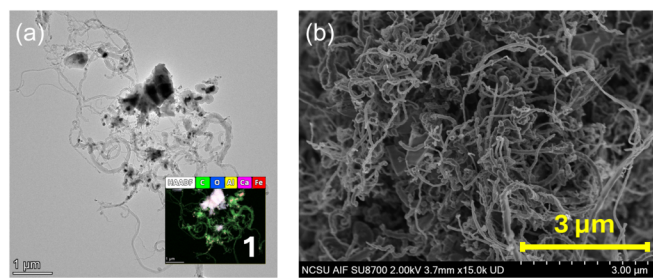


FIG. 4. Electron microscopy images of 10Fe-CaAl₂O₄ (a) TEM images and (b) STEM-EDS (c) SEM images after reaction. Note: reaction conditions were $T_{red} = 800^\circ\text{C}$, $T_{rxn} = 800^\circ\text{C}$, and $GHSV = 5 \text{ L} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$.

fragmentation is a likely explanation for the gradual deactivation of the Fe-CaAl₂O₄-BM catalysts even at higher iron loadings. As CDM progresses, active iron catalyst particles break apart or fragment into smaller pieces and remain lodged inside the CNT. Ultimately, the effective active metallic surface area for the catalyst will steadily attenuate, resulting in a decrease in catalytic activity and irreversible deactivation.

Raman spectroscopy was utilized to probe the vibrational modes of the formed carbon product. Three dominant peaks were identified in the 1000–3000 cm⁻¹ region, which are attributable to the I_D, I_G, and 2D vibrational modes of graphitic carbon. For all samples, vibrational modes for I_D ranged between 1347.82 and 1352.22, for I_G between 1580.15 and 1584.54, and for the 2D between 2691.69 and 2700.48 cm⁻¹, respectively (Fig. S14 in Supplemental Material [30]). An increase in the intensity of the I_D vibrational mode indicates the formation of more disordered carbon in the form of multiwalled carbon nanotubes or amorphous carbon, whereas the I_G vibrational mode typically indicates the ordered graphite on the catalyst surface. The ratio of I_D/I_G gives a proxy for the quality of the carbon, with a low peak ratio indicating a higher level of less defective graphitic structure. The I_D/I_G ratios for 10Fe-MAI₂O₄-BM with ($M = \text{Mg, Ca, Sr, Ba}$) ranged between 0.400 and 0.500, respectively (Table S6 in Supplemental Material [30]). Per the literature of previously tested catalysts for CDM, most I_D/I_G ratios typically range between 0.7 and 2.3 for MWCNT-type carbon and < 0.5 for more graphitic carbon [46–55]. This indicates that the carbon produced via Fe-MAI₂O₄-BM with ($M = \text{Mg, Ca, Sr, Ba}$) is more graphitic and noticeably more so than many other catalysts previously characterized. The TGA O₂-TPO profiles of the spent product under 10 vol % O₂ were also obtained (Fig. S15 in Supplemental Material [30]). In general, the maximum weight loss occurs in the range of 575–724 °C. These features are consistent with similar O₂-TPO experiments of MWCNTs formed on various catalyst systems, which showed overall weight loss in the region between 345 and 771 °C range,

and inflection points observed in the range between 488 and 728 °C [27,49–52,55–58].

IV. CONCLUSIONS

CDM is an alternative hydrogen production technology compared to established technologies like SMR and CG. Compared to SMR or CG, CDM has the potential to lower CO_x emissions while concurrently yielding potentially valuable carbon byproducts. In this study, iron supported on various alumina-based supports with a general formula of Fe-MAI₂O₄ with ($M = \text{Mg, Ca, Sr, Ba}$) were evaluated for their CDM performance in the range of 750–800 °C. Two low-complexity synthesis methods were screened, which included preparation of the 10Fe-MAI₂O₄ catalyst via *ball-milling* or through a one-pot modified Pechini (*sol-gel*) method. Several operating conditions (i.e., pre-reduction temperatures, reaction temperatures, GHSV, and iron loading) were varied in efforts to determine an efficient catalyst and operating conditions for CDM.

When a ball-milling synthesis route was utilized, XRD confirmed the correct support phase of MAI₂O₄ with ($M = \text{Mg, Ca, Sr, Ba}$) was synthesized. Iron deposition via ball milling yields dispersed Fe₂O₃-type iron on the MAI₂O₄ supports as confirmed via characteristic Raman vibrations of the A_{1g} and E_{1g} modes of Fe₂O₃. Conversely, sol gel synthesized 10Fe-MAI₂O₄ catalyst generated iron that was less reducible. Evidence of decreased reducibility from the sol-gel synthesized samples is reflected in the maximum hydrogen consumption intensity shifting toward significantly higher temperatures in H₂-TPR and in the observed shift of the characteristic Raman vibrations shifted toward higher wave numbers characteristic of iron in spinel phases.

In terms of CDM performance, this work concludes that lower reduction and reaction temperatures in addition to lower GHSV increase overall stability and productivity during CDM. In particular, the (10, 20, 30)Fe-CaAl₂O₄-BM catalysts tested at optimized reaction conditions of $GHSV = 1.25 \text{ L} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $T_{red} = 700^\circ\text{C}$, and $T_{rxn} = 750^\circ\text{C}$ emerged as highly productive, exhibiting a competitive carbon yield ranging between 17.86g_C/g_{Fe} (5.06g_C/g_{Cat}) and 28.25g_C/g_{Fe} (2.83g_C/g_{Cat}). This carbon productivity places the catalysts between the 87th and 92nd percentiles among previously reported supported monometallic Fe catalysts for CDM. TEM and SEM of the spent product indicate that the carbon product forms primarily via a tip-growth mechanism, with both nano-onions and filamentous carbon being generated. Raman spectroscopy of the spent product determined most of the carbon formed on the Fe-MAI₂O₄-BM catalysts was graphitic in nature, as peak ratio values (I_D/I_G) ranged between 0.400 and 0.500. Overall, *ball milling* appears to be an effective low-complexity strategy to prepare dispersed iron for CDM.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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