



Full Length Article

Autothermal reforming of heavy-hydrocarbon fuels by morphology controlled perovskite catalysts using carbon templates



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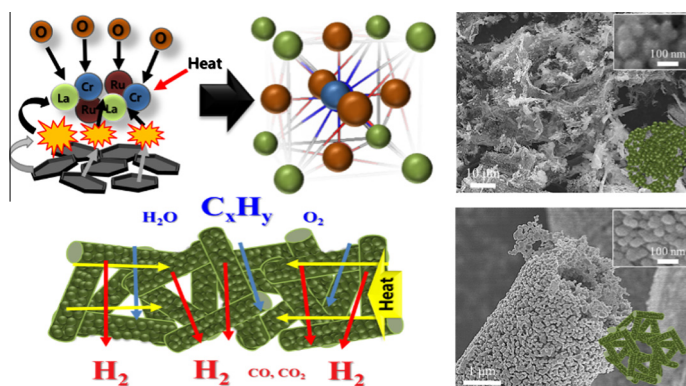
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GRAPHICAL ABSTRACT

The synthesis of morphology-controlled perovskite catalysts using activated carbon templates was introduced for the applications to the heavy-hydrocarbon autothermal reforming. The effect of the carbon templates was investigated to determine how carbon templates influence to the formation of the perovskites. Hollow fiber and porous grain perovskites provided higher specific surface areas than the non-templated perovskite, which showed better activity and durability on the H₂ production from heavy-hydrocarbon.



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ABSTRACT

A novel synthesis of morphology-controlled perovskite networked with LaCr_{0.8}Ru_{0.2}O₃ nanoparticles was introduced using activated carbons as sacrificial templates. These catalysts were used for the hydrogen production by heavy-hydrocarbon autothermal reforming. To investigate the effect of the carbon templates, morphology-controlled perovskites using activated carbons and a non-templated catalyst were prepared to determine how carbon templates influence the chemical structure of the perovskite. The carbon templates produced a crystalline structure with the well incorporation of Ru under mild

Abbreviations: AC, activated carbon; ACF, activated carbon fiber; ATR, autothermal reforming; BET, Brunauer-Emmett-Teller; DBT, dibenzothiophene; GDC, gadolinium doped ceria; GHSV, gas hour space velocity; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TPR, temperature-programmed reduction; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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calcination conditions. The morphology of the hollow fibers provided a higher specific surface area than that of the porous grain catalyst with a similar average particle size (~80 nm). It was found that the hollow fibers showed a unique pore structure with large macropores from 1 to 100 μm, which might offer a higher surface area and enhanced mass transfer of the reactants. This provided a higher activation energy for H₂ production than the porous grain and non-templated catalysts during the autothermal reforming of heavy hydrocarbons. As a result, the fibrous feature and well-defined chemical structure were crucial factors when cracking the hydrocarbon chain. The hollow fiber catalyst showed high reforming efficiency for H₂ production (>65 mol%) from heavy-hydrocarbon fuels during long-term experiments, featuring substantial durability with low carbon deposition and no structural changes.

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1. Introduction

Hydrogen is considered an efficient and environmentally friendly energy carrier for use in fuel cells in a hydrogen economy [1–3]. Hydrogen can be obtained directly from heavy-hydrocarbons (diesel, gasoline, etc.) using an autothermal reforming process by co-feeding oxygen, steam, and fuels, thus combining the advantages of steam reforming and partial oxidation, such as high hydrogen concentration and rapid response, respectively [4–7]. The requirements for reforming catalysts are the activity to produce consistently high hydrogen yields and conversions of the fuels, and a high selectivity for converting fuels to carbon oxides. Moreover, the catalysts should have a tolerance for sulfur and resistance to coke formation, because they generally consist of conventional metals such as Ni or Pt, which are rapidly deactivated by coking and sulfur poisoning [8–12]. These factors need to be considered when designing a highly active and stable catalyst for heavy-hydrocarbon autothermal reforming.

Perovskite materials, which are mixed-valence oxides with the unit formula of ABO₃, where A and B are cations with coordination numbers 12 and 6, respectively, have been studied in several fields such as catalysis, energy, and environmental applications [13–15]. Catalysts featuring perovskite oxide systems have been investigated for the reforming reaction due to their successful extraction of hydrogen from heavy-hydrocarbons, and their stability under redox conditions, hydrogen rich environments, and thermal sintering due to the high temperature required in the process. Furthermore, resistance to coke formation, and in particular tolerance to sulfur poisoning, of perovskite catalysts comes from a low binding energy, which makes them suitable for heavy-hydrocarbon reforming [16–21].

Recently, methods for the preparation of bi-dimensional perovskite with unique architectures and morphology have emerged in the form of nanoparticle, fibrous, porous, scaffold, and skeletal structures for catalysis, fuel cell, and other applications [22–25]. It is challenging, but desirable, to develop an ideal catalyst with an efficient fibrous morphology having beneficial features by constructing (1) an efficient mass flow network with a multi-scaled hierarchical porosity, which suffers minimal gas diffusion and concomitantly provides a low-pressure drop in the reactor, (2) a high geometric surface area with large cavities, while also being lightweight for improved overall reaction performance, (3) better heat transfer and lower excess air levels, allowing a higher thermal efficiency, and (4) suitable catalyst structures with the flexibility to fit almost any required geometry [26,27].

To achieve such unique architectures, templates such as polymers, biomolecules, and carbon have been used not only to manipulate their structure, crystallinity, size, and shape, but also their crystal growth and the configuration of the catalysts, because the templates can also act as dispersion agents and steric stabilizers [16–29]. Using a carbon template is a simple method that can generate many unique metal oxide morphologies through fewer steps and in greater yield [30–32]. Especially, carbon templates exhibit

dominant characteristics such as a high specific surface area, high adsorption capacity, and uniform pores with microstructure. Carbon impregnated with the catalyst precursors prevents their migration to these pore mouths. As our previous study has focused mainly on the different doping series to enhance the catalytic activity, it was partially mentioned that the thermal degradation of the carbon provides a mild reduction by in-situ carbon monoxide generation, and improves the textural properties of the final catalyst [6].

Here, we made an attention to the different morphologies and pore structure of hollow fibrous and porous grain perovskites that were composed of a Ru-doped LaCrO₃ perovskite nanoparticle network. These were prepared through a novel process by employing either activated carbon fiber (ACF) or activated carbon (AC) as sacrificial templates, respectively. The unique porous structures are also examined through the Brunauer-Emmett-Teller (BET) and Mercury intrusion porosimetry. The effect of the carbon templates to the structure and physical properties of the catalysts was also compared to a non-templated perovskite, and was investigated through characterization tools of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and hydrogen temperature-programmed reduction (H₂-TPR). Then, the production of H₂ by autothermal reforming (ATR) of heavy-hydrocarbon fuel was compared between the LaCr_{0.8}Ru_{0.2}O₃ hollow fiber, porous grain, and non-templated perovskite catalysts.

2. Experimental

2.1. Chemicals and preparation of catalysts

Two different carbons, activated carbon fiber (ACF, OG-20A, Osaka Gas Co. Ltd.) and activated carbon (AC, MFCD00133992, Yakuri) were prepared as templates. The perovskite precursors, lanthanum(III) nitrate nonahydrate (La(NO₃)₃·9H₂O, 99%, Aldrich), chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99%, Yakuri), and ruthenium(III) nitrosyl nitrate (HN₄O₁₀Ru, 99%, Aldrich) were purchased and used as received.

The procedure for the synthesis of LaCr_{0.8}Ru_{0.2}O₃ whose morphology was controlled by carbon templates is illustrated in Scheme 1. Morphology-controlled perovskite catalysts were prepared using an aqueous impregnation synthesis, which is a rapid and convenient method that yields high-surface-area oxides. ACF (for hollow fiber) and AC (for porous grain) templates were sequentially treated with aqueous HNO₃ (6 M, Duksan) and H₂SO₄ (6 M, Duksan) to generate a negatively charged surface. Then, the treated carbons were soaked in deionized water with a mixed aqueous solution of La^{III}/Cr^{III}/Ru^{III} ions for 24 h. The impregnated carbon templates were calcined by mild heat treatment at 1027 K for 6 h with sufficient airflow to form perovskite catalysts by the removal of the carbon content via combustion. For comparison, LaCrO₃ was synthesized by the introduced method and a non-template LaCr_{0.8}Ru_{0.2}O₃ was prepared in the absence of a carbon

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