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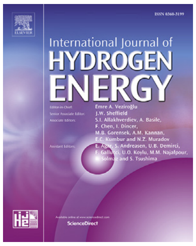

Catalytic steam reforming of n-dodecane over high surface area $Ce_{0.75}Zr_{0.25}O_2$ supported Ru catalysts

Shuang Ji [a], Zhourong Xiao [a], Haocui Zhang [a], Ling Li [a], Guozhu Li [a,b], Li Wang [a,b], Guozhu Liu [a,b,]*

[a] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China*

[b] *Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), Tianjin, 300072, China*

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ABSTRACT

A high surface area (HSA) $Ce_{0.75}Zr_{0.25}O_2$ (CZ) support was synthesized by hydrothermal synthesis method with assistance of surfactant (cetyltrimethyl ammonium bromide, CTAB), and then 2.0 wt% Ru was impregnated on it to obtain a steam reforming catalyst for n-dodecane. The surface area of Ru/HSA-CZ catalyst is 107.6 $m^2\ g^{-1}$, which is ca. three times higher than that prepared through the sol-gel (sg) method (34.3 $m^2\ g^{-1}$, Ru/CZ-sg) and ca. 40% higher than that without CTAB (76.7 $m^2\ g^{-1}$, Ru/CZ-wo). Catalytic steam reforming of n-dodecane, shows the completely conversion of n-dodecane over Ru/HSA-CZ and slightly drops about 6% (650 °C, LHSV = 12 mL/g h, S/C = 4, time on stream = 7 h) while 81% and 70% were observed for the Ru/CZ-wo and Ru/CZ-sg but with twice (or triple) deactivation rates. The possible reason for observed better performance of Ru/HSA-CZ should be attributed to the high metal dispersion of Ru over HSA-CZ, and the favorable Ru-support interaction as evidenced by H_2-Temperature programmed reduction (H_2-TPR), and high redox ability of high surface area $Ce_{0.75}Zr_{0.25}O_2$ support thanks to high Ce^{3+} content. Further steam reforming of n-dodecane over Ru/HSA-CZ at higher LHSV (750 °C, LHSV = 36 mL/g h, S/C = 4) exhibits completed conversion and without significant deactivation.

Introduction

Nowadays fuel cell systems have attracted growing attention as the domestic and distributed power generation technology which is a comprehensive utilization of energy sources and power generations through a non-combustion reaction of hydrogen and oxygen [1–6]. Thus sustainable hydrogen production is one of important issues from natural gas and petroleum oil fractions, various biomass feedstocks through different reactions, such as autothermal reforming, steam reforming, partial oxidation, etc [7]. Among those technologies, catalytic steam reforming of kerosene hydrocarbons with high hydrogen selectivity is becoming a promising route because of its high energy density (about 43 MJ/kg), low cost, relatively easy storage and handling. However, during the steam reforming, carbon and coke deposition from the

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* *Corresponding author*. Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China.

E-mail address: gliu@tju.edu.cn (G. Liu).

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various high-temperature reactions of long-chain hydrocarbons caused serious catalyst deactivation. Therefore, developing a kerosene steaming reforming catalyst with high catalytic activity and stability is still a challenging issue for the on-board applications of fuel cell systems.

Over the past two decades, great efforts have been made to prepare good catalysts for the steam reforming of kerosene. Some researchers found that nickel based catalysts were generally used due to their high activity and low cost, but their serious coke deposition and catalytic instability were the big restrictions in reforming reactions [5,8–11]. Although, some researches have added the second metal to avoid those problems, but it is difficult to solve the problem of carbon deposition as the nickel based catalyst is easy to sinter and poor stability characters, especially in long-chain steam reforming [9,12–15]. In order to better solve those problems many researchers started to use noble metal and it showed good performance for steam and dry reforming reactions. Among the noble metals, Ru based catalysts were reported to have better catalytic activity and stability than Ni based catalysts due to the rapid C–C bonds breaking and strong resistance to carbon [5,15–20]. High amount of Ru over higher surface area support showed complete conversion and no obvious inactivation with long reaction time at 730 °C in steam reforming of kerosene by Fukunaga etc [21]. Analogous trend was also reported by Suzuki etc [16] and Iida etc [6] that Ru based catalyst had more stability in steam reforming of kerosene by reducing coke and deposition. Therefore, Ru based catalysts have been widely used for steam reforming of kerosene and still show great potential for development.

Besides active metal, the supports also play a crucial role in the activity and stability of the catalyst for reforming of hydrocarbon. In recent years, the cerium has been added on Al_2O_3 supports to decrease the rate of carbon deposition on the catalyst surface because the steam adsorption and the mobility of surface oxygen could be enhanced in the steam reforming of long-chain hydrocarbon [22]. On the other hand, in the field of steam reforming of short-chain hydrocarbon or alcohol, CeO_2 as the support also has attracted more and more attention because that Ce^{4+} and Ce^{3+} can coexist to provide oxygen vacancies to eliminate carbon deposition [1,23–27]. Compared with the Al_2O_3, SiO_2 and MgO supports, CeO_2 shows excellent resistance toward carbon formation in steam reforming of liquid hydrocarbon fuel [28]. The addition of ZrO_2 was reported to be favorable for the thermal stability, the oxygen storage capacity and thus the catalytic activity of CeO_2 [29–32]. However, the major limitations for applying CeO_2 or Ce-ZrO_2 supports are their low specific surface area and particles aggregation due to sintering in high-temperature steam reforming [31,33]. Laosiripojana etc [31] applied surfactant-assisted approach to prepare high surface area (HSA) Ce-ZrO_2 support (45 m^2 g^{-1}), and the Ni/$Ce_{0.75}Zr_{0.25}O_2$ (HSA) catalyst which showed the highest activity and stability, compared with the low surface area catalysts (19 m^2 g^{-1}) and catalysts of other Ce/Zr ratio (1:1 or 1:3) due to the redox reactions between the lattice oxygen in methane steam reforming. The high surface area of support was not only beneficial to Ni based catalysts but also for Ru based catalysts. Recently, Carbajal-Ramos etc [34] found that 2 wt%Ru/$Ce_{0.8}Zr_{0.2}O_2$ had bigger specific surface area (108 m^2 g^{-1}) and then appeared higher metal dispersion, better oxygen storage capacity and better catalytic performance of ethanol steam reforming compared with lower surface area support. Through the above researches, it can be seen that the high surface area of Ce-ZrO_2 solid solution as support is favorable to increase catalytic activity and enhance the ability of resistance of carbon deposition for steam reforming [31,32,34–38]. However, as far as we know until now, there is no Ce-ZrO_2 solid solution has been used in steam reforming of long-chain hydrocarbon.

In the present work, the high surface area $Ce_{0.75}Zr_{0.25}O_2$ support was prepared by hydrothermal synthesis method with surfactant (CTAB), and the low surface area support without surfactant and the support by sol-gel method were synthesized for comparison. Furthermore, Ru is selected as the active component and impregnated on these $Ce_{0.75}Zr_{0.25}O_2$ supports respectively for steam reforming of n-dodecane, a model compound of kerosene. The activity and stability of three catalysts were tested under both soft and server conditions. In particular, the effect of the interaction between metal and support were assessed.

Experimental

Materials

Catalyst precursors, $Ce(NO_3)_3 \cdot 6H_2O$ (AR) and $ZrOCl_2 \cdot 8H_2O$ (AR), were purchased from Tianjin Kemiou chemical reagent Co. Ltd. $RuCl_3 \cdot 3H_2O$ (Ru: ≥37%) were purchased from Sino-Platinum metals Co. Ltd. Citric acid (AR), cetyltrimethyl ammonium bromide (99%) and other chemicals were purchased from Shanghai Aladdin biochemical technology Co. Ltd.

Catalyst preparation

Ceria-zirconia solid solution with nominal composition 0.75Ce:0.25Zr:2O were synthesized by two different methods: hydrothermal synthesis method and sol-gel method. For sol-gel method (CZ-sg), at room temperature, 0.1 M of two metal salt solutions: $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were mixed with 0.5 M of citric acid witha certain stoichiometric ratio. The molar ratio of ([Ce] + [Zr])/[citric acid] was kept constant at 0.8. The mixed solution stirred kept at 80 °C until obtained a sol, after that the sol was dried to gel at 120 °C overnight and calcined in air at 500 °C.

In the hydrothermal synthesis method: two kinds of supports were prepared, one was adding surfactant (HSA-CZ): 0.1 M cetyltrimethyl ammonium bromide were added to a 0.1 M aqueous solution containing $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ in the molar ratio of 3/1. The molar ratio of ([Ce] + [Zr])/[cationic surfactant] was kept constant at 0.8. The mixtures were stirred about 15 min and then aqueous ammonia was added dropwise under vigorous stirring until the pH value of the mixed solution was about 11.5. This caused the precipitation of mixed oxide as a pale-yellow solid. The slurry was further stirred for another 2 h and then the mixture was sealed in a Teflon-lined stainless-steel autoclave, heated to 90 °C and sealed at this temperature for 120 h. After

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