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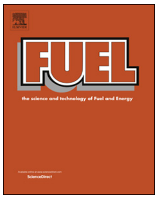

Full Length Article

Impact of acidity in ZrO_2-TiO_2-Al_2O_3 composite oxides on the catalytic activity and coking behaviors during *n*-decane cracking

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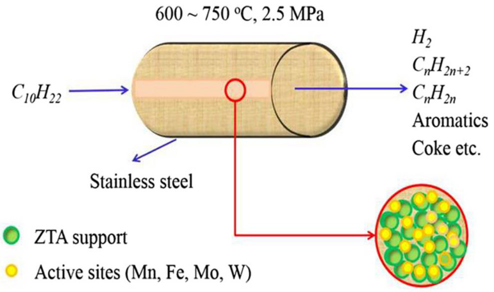
GRAPHICAL ABSTRACT



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ABSTRACT

Mn, Fe, Mo or W as a promotor was introduced into ZrO_2-TiO_2-Al_2O_3 (ZTA) composite oxides by impregnation method, in order to examine the influence of these promotors on catalytic activity and coking behaviors during *n*-decane cracking. The as-prepared catalysts were characterized by several different techniques: N_2 adsorption–desorption, X-ray diffraction (XRD), temperature programmed desorption of ammonia (NH_3-TPD), in situ infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). The characterization results revealed that the incorporation of these metal oxides enhanced the total amount of acid sites and gave rise to the formation of much stronger acid sites, especially Mo. Moreover, Mo-promoted ZTA catalyst was found to be the most efficient one for *n*-decane cracking (conversion 88.4%, heat sink 3.79 MJ/kg at 750 °C) due to an optimum balance between the number of strong acid sites (0.24 mmol NH_3/g) and the total amount of acid sites (0.59 mmol NH_3/g). Besides, the temperature programmed oxidation (TPO) results showed that Mo-modified ZTA catalyst exhibited more desirable anti-coke capacity in comparison to the others owing to its appropriate acid property.

1. Introduction

One of the major challenges associating with hypersonic flight is the "thermal barrier", which may result in serious damage to the aircraft engine and fuel supply system [1–3]. Regenerative cooling technology with the use of endothermic hydrocarbon fuels (EHF) as an ideal coolant and propellant is considered as an effective method. EHF can not only reduce the heat load derived from the physical absorption heat, but also improve the propulsion efficiency due to the formation of low-carbon hydrocarbons in cracking reactions when it flow through channels on the surface of engine [4–6]. Particularly, EHF catalytic cracking requires lower temperature and presents better selectivity of preferred products (low-carbon alkenes) than thermal cracking. Therefore, EHF catalytic cracking is becoming a research hotpot in

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recent years [7–9].

Nowadays, composite oxides, zeolites and noble metals are the most commonly used catalysts in EHF cracking [10–12]. Composite oxides catalysts present much better high-temperature stability than zeolites, and more desirable resistance to coke deposition compared with noble metal catalysts, have been widely used in EHF cracking. In our previous studies [13–15], composite oxides catalysts CeO_2-Al_2O_3, ZrO_2-TiO_2-Al_2O_3 with different mass ratio and $Zr_xTi_{0.9-x}Al_{0.1}O_2$ with different ZrO_2:TiO_2 ratios were used for the cracking of RP-3 jet fuel, and these catalysts exhibited better activity and high-temperature stability.

As we all know, EHF catalytic cracking reactions generally proceed according to carbenium-ion chain mechanism. On the base of the mechanism in catalytic cracking, there is a close correlation between catalytic activity and the acidity of cracking catalysts. Fonseca et al. [16] researched *n*-decane cracking over H-Y zeolite, and found that the strong acid sites were associated to the formation of carbenium ions, while the other acid sites contributed to the bi-molecular process. Liu et al. [17] stated that naphtha cracking over P/HZSM-5 catalyst with high activity and long-term stability due to the reduction of Brösted acid sites. Cumming and Wojciechowshi [18] made a literature review about carbenium-ion chain mechanism of catalytic cracking, they proposed that a higher density of acid sites on the catalysts surface would increase coke deposition and catalyst deactivation deriving from more interionic reactions. Moreover, our previous works [13–15] found that increase the surface acidity and the ratio of strong acid sites while decrease of acid density of the catalyst is an effective method to improve low-carbon alkenes selectivity and reduce coke deposition. It can be seen from above studies, the acid property (such as the amount, nature, density, and strength distribution) has a crucial impact on catalytic activity and the formation of coke deposition.

In order to improve acidic properties of catalysts, introducing another metal is considered as an alternative and attractive route. It is reported that Fe, Mn, Mo, W are effective acidic additive to adjust the surface acidity of catalysts [19–24]. Foo et al. [19] studied high temperature selective catalytic reduction (SCR) reaction by using the Fe modified WO_3-ZrO_2 catalysts. They found that the introduction of Fe increased the strength of Brösted acid sites and formed new Fe^{3+} Lewis acid sites. With respect to the research on synthesis of ε-caprolactam, Mn/SiO_2-Al_2O_3 catalyst exhibited stronger acid centers compared with SiO_2-Al_2O_3 [20]. With regarding to WO_x/ZrO_2 catalysts, it is reported that only small amount of WO_x (1 wt%) would result in remarkable increase of the acid strength of the catalysts [21,22]. Almeida et al. [23] found that adding MoO_3 increased the acidity and catalytic activity during the esterification of fatty acids with methanol. Shao et al. [24] also found that modified by molybdenum oxide species enhanced both Brönsted acid and Lewis acid sites. Likewise, Fe and W promoted catalysts were dominated with Lewis acid sites, while both Lewis and Brösted acid sites were prevailed on Mn/Mo-modified samples [24,25]. Nevertheless, how does the acid property of catalysts affect the catalytic activity during EHF cracking reactions, and what is the difference among these additives, are still not fully understood. Therefore, it is necessary to systematically study the effect of catalyst acidity on the catalytic activity, selectivity and coke deposition in cracking reactions.

In this work, we aim to search for suitable catalysts and study their catalytic performances for *n*-decane cracking. Several types of metal oxides with diverse acid properties, MnO_2, Fe_2O_3, MoO_3 and WO_3, were selected as the additives. A series of catalysts coatings with M_xO_y/ZrO_2-TiO_2-Al_2O_3 (M = Mn, Fe, Mo, W) were prepared and used to study the catalytic activity for *n*-decane cracking. By introduction of these additives, the surface acidic property of ZrO_2-TiO_2-Al_2O_3 composite oxides could be tuned, along with their textural characteristics. Thus, different catalytic performances are observed over each catalyst. This work can provide some useful information of catalysts design and additives screening for solid acid catalysts applied to EHF cracking.

2. Experimental section

2.1. Catalysts preparation

ZrO_2-TiO_2-Al_2O_3 composite oxides (the mass ratio of ZrO_2:TiO_2:Al_2O_3 = 1:1:3) were synthesized by classical co-precipitation method, and the preparation process was similar to our early work [13]. The catalyst powders were prepared by incipient wetness impregnation method, which consists in soaking the prepared support in the aqueous solution of $Mn(CH_2COO)_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ (MnO_2, Fe_2O_3, MoO_3 and WO_3 are all 7.0 wt%), respectively. After evaporation of the wet samples, the obtained powders were dried at 120 °C, and then calcined at 600 °C under ambient atmosphere for 3 h.

The ZrO_2-TiO_2-Al_2O_3 support and synthetic catalysts powders were subsequently ball-milled with deionized water to form homogeneous slurry, and then coated on the inner wall of stainless-steel microchannels (SS304 Φ3 × 0.5 mm, 800 mm length) by washcoating method (a preparation method of catalyst coating, catalyst slurry was sucked into inner wall of a stainless steel tube by vacuum, and controlled loads and uniformity by adjusting the vacuum pressure and slurry viscosity), leading to the formation of a uniform wall-coated layer. Finally, the monolithic catalysts accompany with the collected slurry were dried overnight at 120 °C and calcined at 600 °C for 2 h, labeled as ZTA, Mn-ZTA, Fe-ZTA, Mo-ZTA and W-ZTA, respectively. The catalyst loading of all catalysts was 0.2 ± 0.01 g/800 mm.

2.2. Catalytic activity evaluation

The experimental apparatus for *n*-decane cracking under high temperature and high pressure conditions is shown in Fig. 1. It is

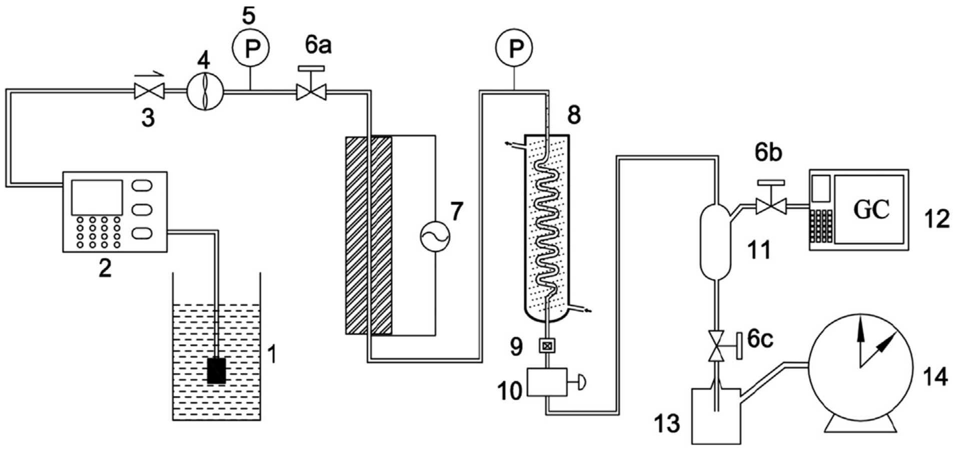

Fig. 1. The experimental apparatus for the cracking of *n*-decane (1) fuel tank (2) high pressure pump (3) check valve (4) mass flowmeter (5) manometer (6) off valve (7) electrical heater (8) water condenser (9) filter (10) back pressure controller (11) gas-liquid separator (12) gas chromatography (13) conical flask (14) gas flowmeter.

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