Catalysis Today 136 (2008) 258–265

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Rhodium supported on thermally enhanced zeolite as catalysts for fuel reformation of jet fuels

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ARTICLE INFO

Article history:
Available online 12 May 2008

Keywords:
Jet Fuel
JP8
Fuel reforming
Rhodium
Hydrogen
Fuel processing
Zeolite

ABSTRACT

Autothermal reformation of military jet fuel (1096 ppmw sulfur) was investigated with rhodium supported on thermally stabilized Y zeolite catalysts. The zeolite catalysts were thermally stabilized by ion exchanging with nitrate solutions of rare-earth metals (La, Ce, Sm, Gd, Dy and Er). Surface area analyses indicated that the exchanged zeolite could maintain its porous structure as high as 950 °C instead of 800 °C for a commercial NaY zeolite. The structure of the exchanged zeolite was characterized by X-ray diffraction (XRD). Rh-SmNaY zeolite reforming catalysts were prepared by incipient wetness and organometallic synthesis. The JP8 reforming experiments were performed in a short contact time adiabatic reactor with a monolithic catalyst with the addition of air and steam at a temperature below 920 °C. The effects of steam and fuel-to-air ratio (C/O ratio) were studied. Hydrogen and carbon monoxide were produced as the main products. Durability tests were performed with Rh/SmNaY-zeolite catalysts. This work shows that zeolite based catalysts can convert transportation fuels such as high sulfur jet fuel (over 1000 ppmw S) to syngas for solid oxide fuel cell applications.

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1. Introduction

Fuel cells can provide portable power for battery chargers and auxiliary power without engine idling; however, one of the key challenges is the hydrogen source. Previously, there were literature studies focusing on hydrogen generation by catalytic partial oxidation and autothermal reforming of alkanes, diesel and jet fuel with a standard noble metal supported on high surface area alumina [1–5]. Low C/O ratio, presence of water and the use of Rh instead of Pt can improve the selectivity of syngas (H_2 and CO) formation [1–3]. In one patent catalytic partial oxidation of jet fuel was described [4]. The reaction uses no water and uses oxygen in air as the oxidant. The reaction occurs at temperature greater than 1050 °C. This high temperature limits the choice of construction materials, and the heat management becomes a challenging problem. In another patent, sulfur tolerant catalysts for steam reformation of diesel and jet fuel are described [5] The process uses water as the oxidant, and it needs 3–4 portions of water for each portion of fuel as inputs.

Despite the success of making hydrogen from sulfur containing jet fuel, there is a critical need to develop new catalysts for better coke resistance and for higher sulfur tolerance. Some investigators developed novel perovskite-based, ceria-based and mixed oxide catalysts to reform surrogates of jet fuel and gasoline [6–9]. Varma and co-workers have investigated cerium- and nickel-substituted $LaFeO_3$ perovskite catalysts to reform a JP8 surrogate [6]. JP8 is a kerosene-based jet fuel for the US Army and Air Force. Their results suggested that the nickel-rich catalyst exhibited significant coking, but the addition of cerium greatly enhanced coking resistance of the catalysts. Qi et al. proposed that partially substituting La with Ce at the A-site of $LaNiO_3$ would improve oxygen mobility, thermal stability and catalyst durability [7]. Shekhawat et al. developed Rh-Ce-Zr mixed oxide catalysts for the reformation of *n*-tetradecane with 1-methylnaphthalene or dibenzothiophene [8]. In a recent patent, Krumpelt et al. described sulfur tolerant catalysts for autothermal reformation of gasoline and diesel [9]. At their selected federates of water, air and blended gasoline surrogate, the total syngas ($H_2 + CO$) concentration (water-free, He-free) was between 73% and 81%.

Zeolite is a common fluid catalytic cracking (FCC) catalyst for hydrocarbons. Y zeolite is the main component with ZSM-5 as an additive. The typical reaction involves hydrocarbon molecules diffusing through the matrix pores into the zeolite crystal. Only certain molecules with certain molecular diameters can penetrate the zeolite structure. A typical temperature range for FCC reaction is from 480 to 550 °C with a contact time of 1–4 s [10]. Zeolite is useful to remove aromatics from diesel fuel by ring-contraction and ring-opening of aromatics such as tetralin [11]. There are

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0920-5861/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.cattod.2008.03.027

several reviews on the mechanism of catalytic cracking over solid-acid catalysts [10,12,13]. Protolytic cracking mechanism, bimolecular cracking mechanism and other mechanisms were discussed in detail in these reviews.

It is a common practice of refineries to add rare-earth elements to the zeolite to form ultra-stable Y zeolite (USY). During the regeneration cycles in a FCC unit, additions of rare-earth cations prevent dealumination and improve thermal stability [14]. Several investigators recently studied the role of rare-earth ions for hydrocarbon cracking over Y zeolite [15–17]. A recent study has identified that the role of rare-earth cations in Y zeolite for hydrocarbon cracking is to ensure the retention of high Bronsted acid site density under hydrothermal conditions [15]. These investigators proposed that the zeolite elasticity was increased to lower the composite activation barriers for hydride transfer and β-scission reactions. de la Puente et al. suggested that the hydrogen transfer properties in conversion of cyclohexene increased with the Bronsted acidity and the ionic radius of various rare-earth elements [16]. Liu et al. proposed that the modification of rare-earth directs more hydrocarbons into the pores of Y zeolite to be converted and reduces the possibility of naphtha olefin forming through surface cracking reactions [17].

The main objective of this work is to investigate the usefulness of zeolite as a high surface area support in reforming catalysts. This new class of zeolite reforming catalysts will be evaluated by converting high sulfur transportation fuel (1000 ppmw S or above) to hydrogen with a relative small steam-to-carbon ratio (1 or less). One recent study shows that zeolite catalyst converts methane into hydrogen for fuel cell applications [18] while another study used zeolite as a FCC prereformer to crack the fuel into smaller hydrocarbons [19]. However, zeolite has not been studied as a reforming catalyst for hydrogen generation from transportation fuels. This paper will first discuss the catalyst synthesis and characterization. Then hydrogen generation with millisecond contact time will be demonstrated.

2. Experimental

2.1. Material synthesis

A commercial NaY zeolite (Zeolyst, CBV 100, Si/Al ratio = 5.1) was first exchanged with a 2 M ammonia nitrate solution. The suspension was then centrifuged and washed with de-ionized water 3 times. The exchange-centrifuge-washing process was then repeated twice. The solid (NH_4-NaY zeolite) was dried in a vacuum furnace at 60 °C for 5 h and 120 °C for 1 h. The dried solid was then exchanged with 0.1, 0.2 or 0.4 M nitrate solutions of rare-earth elements (RE = La, Ce, Sm, Gd, Dy or Er) for 68 h. The centrifuge-washing sequence was repeated 3 times. The solid (RE-NaY zeolite) was dried in a vacuum furnace at 60 °C for 5 h and 120 °C for 1 h. Finally, the solid was heated treated in a tube furnace with flowing air at 600 °C.

Four Rh-based catalysts were prepared in this work (Table 1). A standard Rh-alumina foam catalyst (Catalyst 1) was prepared by incipient wetness. The alumina monolith foam (Vesuvius, 80 ppi, 1 in. diameter, 0.5 in. thickness) was wash-coated with 5 wt% γ-alumina to roughen the catalyst surface and to increase its surface area. Then the foam was calcined in a box furnace at 700 °C for 15 h. An aqueous $Rh(NO_3)_3$ solution was added dropwise to the foam, and the resultant foam was calcined in the box furnace at 700 °C for 15 h.

The Rh-SmNaY zeolite foam catalyst (Catalyst 3) was also prepared by incipient wetness similar to the preparation of standard Rh-alumina foam catalyst (Catalyst 1). The monolith foam was coated with 5 wt% SmNaY zeolite without any γ-alumina coating. The incipient wetness procedure would deposit Rh particles on the surface of the zeolite-coated foam. The SmNaY zeolite was obtained from previously described ion-exchanged method with 0.4 M $Sm(NO_3)_3$. A control catalyst (Catalyst 2) was prepared with NaY zeolite without any rare-earth thermal stabilizer.

The ship-in-the-bottle procedure of synthesizing Rh nanoclusters inside the supercages of NaY zeolite was investigated by Weber and Gates [20]. In this study the same organometallic approach was applied to insert the Rh nanoclusters inside the supercages of rare-earth exchanged NaY zeolite. The SmNaY zeolite was first calcined with flowing air at 300 °C for 12 h and then was degassed in a vacuum furnace at 250 °C for 12 h. The zeolite was then transferred into an argon-filled glove box. The zeolite was added to an air-tight flask with a mixture of desirable amount of $Rh(CO)_2(acac)$ in pentane. The slurry was stirred at room temperature for 3 days. The solid was separated by vacuum filtration, and it was transferred to an air-tight quartz tube reactor. The resulting solids were carboxylated in 5% CO (balanced Ar) at 125 °C for 8 h and then decarboxylated in pure He at 200 °C for 12 h. Elemental analyses of Rh-SmNaY powder were performed by Galbraith Laboratories, Knoxville, TN. The loadings of Rh and Sm in Rh-SmNaY powder were determined to be 2.07 and 4.44 wt%, respectively. Next the Rh-SmNaY powder was mixed with an alumina binder to form a slurry, and then the slurry was coated onto a ceramic alumina monolith foam. The finished catalyst foam was labeled as Catalyst 4. The Rh loading of this catalyst foam was 0.0508 wt%.

2.2. Material characterization

The thermal stability of these exchanged zeolite samples was examined by measuring the specific surface area with BET analysis (Micromeritics, ASAP 2000) after sample annealing. Each annealing was performed in a tube furnace with flowing air at an evaluated temperature for 3 h.

X-ray diffraction (XRD) experiments were performed with a Rigaku Ultima III diffractometer using a Cu Kα radiation source working at 40 kV and 44 mA. The XRD patterns of Sm, Dy or Er-loaded zeolite were measured in Bragg-Brentano (BB) configuration to identify any impurities or secondary phase, as well as in parallel beam (PB) configuration to determine the lattice constant or unit cell parameter. The XRD patterns were generated by measuring 2θ from 4° to 80° with a step size of 0.02° and measuring time of 12 s per step (BB) or 24 s per step (PB).

2.3. Fuel characterization

Sulfur analysis of a military jet fuel (JP8) sample was performed with an Agilent gas chromatography (GC) with an Ionics/Sievers

Table 1
Preparation of reformation catalysts in this study

Catalyst no.	Materials	Weight of finished catalyst foam (g)	Coating (wt%)	Rh loading (wt%)
1	Rh/γ-alumina	6.505	3.51 (alumina)	2.50
2	Rh/NaY zeolite/γ-alumina	6.432	2.55 (NaY zeolite)	1.97
3	Rh/Sm-NaY zeolite/γ-alumina	6.518	3.41 (Sm-NaY)	2.13
4	Rh/Sm-NaY zeolite/γ-alumina	6.410	2.40 (Sm-NaY)	0.0508