



Cracking of n-dodecane during supercritical state on HZSM-5 membranes

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ABSTRACT

In the new generation of aircraft, jet fuel will serve as both an energy source and a heat sink for cooling through endothermic fuel reactions. Catalytic cracking of hydrocarbon fuel has proved to be potential for endothermic reaction. For this application, we have prepared ZSM-5 membranes as catalyst on the surface of stainless steel by secondary growth method. An optimized activation procedure of ZSM-5 membrane for catalytic cracking reaction is established by combining the results of catalytic reaction with thermal analysis (TGA and DSC). Taking n-dodecane as a model compound, the influence of silica alumina ratio ($SAR = nSiO_2/Al_2O_3$) of initial gel on the activity of hydrocarbon cracking reaction were studied. The results also demonstrate that the conversion of catalytic cracking reaction is much higher than that of pyrolysis during supercritical state. In addition, hydrogen molar ratio in gas production decreases with increasing the reaction temperature. Besides that, the optimum temperature for coke removal and the reduction of zeolite catalysts is between 550 °C and 600 °C.

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1. Introduction

In aeronautics research, when flight speed increases to higher Mach numbers, the temperature of the ram air taken on board of the vehicle becomes too high to cool the structure [1]. Therefore, it is necessary to prevent the vehicle from burnout by cooling the vehicle structure. However, there are no extra spaces to take coolant in the aircraft except fuel. In this case, endothermic fuels become the effective strategy to remove the waste heat from aircraft subsystems. But, when the vehicles cruising in the speed of hypersonic regime (above Mach 6), sensible heating of the fuel is not enough to cool the vehicle and endothermic reactions like thermal cracking and catalytic cracking are needed [2,3].

Actually, the heated fuel decomposes into small molecules like short alkane and olefin in the heat exchanger process that were carried out in micro channels of the propulsion in which the heat transfers from the vehicle structure to the fuel [4]. These chemical reactions require not only as many conversion rates as possible, but also the higher selectivity of products which is needed in the applications and the lower selectivity of products which do not need. For example, the formation of olefin can provide more absorbed heat than alkanes; hydrogen is useful in the ignition of scramjet propulsion system; but the deposition of coke is very harmful to the propulsion system which can barricade the heat transfer and even

block the channels of the propulsion. It has been recognized that zeolites can accelerate the cracking and dehydrogenation reactions of hydrocarbon fuels, suppress the formation of alkanes, and increase the heat sink capacity significantly [5,6].

Several papers have investigated various zeolites, like mesoporous and microporous zeolites, to cover the technology of different cracking properties by shape selectivity [7–9]. Corma et al. [7] have compared USY, Beta and ZSM-5 zeolites for cracking of n-alkanes, which implied that ZSM-5 is the optimal catalyst in many conditions, such as: the selectivity to hydrogen transfer; the olefin to paraffin ratio of the production; low selectivity to aromatics; the ratio of protolytic cracking to hydride transfer. Zhao et al. [10] also found that HZSM-5 is the better choice due to the acid strength and the stability in the catalytic tests over H-SAPO-34, HZSM-5 and H-mordenite zeolite.

ZSM-5 has a SiO_2/Al_2O_3 ratio (SAR) of 20 and upward to any finite number. Framework aluminum atoms result in acidity which can crack hydrocarbon followed the carbonium ion mechanism. But resulting from the property of carbonium ion, the productions contain more propylene and butylene than ethene, and also the yield rate of alkene is low. Consequently, a higher SAR zeolite has been introduced to reduce the density of acid sites which can reduce the hydrogen transfer reaction and enhance the selectivity of alkenes, as witnessed by several papers [11,12].

Zeolites mixed with binder material in various forms such as pressed pellets, cylindrical extrudates and granules have been used as catalysts in the conventional industry [13]. But these zeolites are difficult to adapt applications of hypersonic aircraft. One strategy to solve this problem would be introducing zeolite membranes as catalyst which can improve the accessibility of the catalyst to the reactant, reduce the diffusion path as well, increase the catalyst activity at the same time, and enhance heat transfer by reducing the thickness of the zeolite layer.

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In recent years, it has been recognized that structured zeolite, like thin zeolite membranes, which prepared by secondary growth method (or seeding method), may have superior properties compared to conventional catalysts [14,15]. Compared with the in situ hydrothermal synthesis method, secondary growth method approach offers certain advantages such as easier operation, higher controllability in crystal orientation, microstructure and film thickness, and leading to much better reproducibility. Therefore, it will be very promising to extend the application field of zeolite membranes, which employed secondary growth method, into catalytic cracking of endothermal fuel during supercritical state.

In this work, ZSM-5 membranes on nonporous stainless steel supports (chips and packings) were synthesized by secondary growth method with a systematic variation of the SAR of initial gel from 50 to 1500. The seeds and membranes were characterized by XRD, TEM and SEM respectively. The zeolite powder that was deposited in the process of hydrothermal treatment, was characterized by TGA and DSC. The catalysis properties of the membranes were investigated by cracking n-dodecane as one of typical endothermic hydrocarbon fuels in a fixed-bed reactor at 450–500 °C, 4 MPa.

2. Experimental

2.1. Zeolite membrane synthesis

There are two kinds of stainless steel support for growth of membranes, rectangular (10 mm × 10 mm × 1 mm) pieces of AISI 304 stainless steel foil for characterization and triangular spiral stainless steel packings for fixed-bed cracking reaction.

A membrane growth process is described as follows and a schematic is shown in Fig. 1. First of all, the supports were thoroughly cleaned with 2 M KOH solution under sonication at room temperature for 1 h. After rinsing with double distilled water (DDW), the supports were immersed in a concentrated HCl solution with ultrasound treatment at room temperature for 10 min. Finally, to remove the Cl⁻ introduced during the previous treatment, an additional washing with distilled water for many times until the solution has a neutral pH value.

Colloidal crystals of silicalite-1 used as seeds were synthesized in a clear homogeneous solution with molar composition 9TPAOH:25SiO₂:1450H₂O:100EtOH, according to the literature procedure [16].

The synthesis solution was prepared by mixing tetrapropylammonium hydroxide (TPAOH; 40% water solution, Alfa Aesar) as structure directing agent, DDW, ethanol (EtOH; 99.8%, Carmel, Tianjin, China) and tetraethyl orthosilicate (TEOS; 98%, Carmel, Tianjin, China) as silicon source. After 24 h electromagnetic stirring, the clear solution was loaded in a Teflon lined autoclave and put in a preheated electric oven without agitation at temperatures of 98 °C for 24 h.

After the hydrothermal crystallization, the seed sol was obtained. The supports were immersed in the silicalite-1 seed sol under ultrasound treatment for 2 min. Subsequently, the seeded supports were dried at room temperature and calcined in air at 450 °C for 3 h with a heating and cooling rate of 1 °C/min.

The precursor solutions for the secondary growth of zeolite were prepared from aluminum nitrate (Al(NO₃)₃·9H₂O, 98%, Carmel, Tianjin, China) as alumina source. The molar ratio of the resulting a clear secondary growth solution was 4TPAOH:25TEOS:2750H₂O:xAl(NO₃)₃. The x in the formula can be adjusted by different SAR of initial gel. The secondary growth solution was prepared by dissolving Al(NO₃)₃ in TPAOH and DDW followed by drop-wise additional of TEOS under vigorous stirring. The clear solution was aged at room temperature for 24 h under stirring before use.

The seeded steel chips were mounted in Teflon holders vertically in order to avoid sedimentation of crystals onto the support surface during the subsequent hydrothermal treatment. For secondary growth of zeolite on the packings, 3 g seeded packings were mounted in the Teflon lined autoclave for each reaction with 25 g of secondary growth gel at 185 °C for 24 h.

After synthesis of the films by the method described above, the ZSM-5 coated substrates were calcined in order to remove the template from the zeolite pores. Calcination was performed at 450 °C for 2 h with a heating and cooling rate of 1 °C/min. The detailed treatment of different activation methods were given in Table 1 from which HZSM-5 can be obtained.

2.2. Characterization methods

The average crystal size in seed sol was determined by dynamic light scattering (DLS; Brookhaven BI-200SM, America) and transmission electron microscopy (TEM; JEOL JEM-100CXII, Japan). The

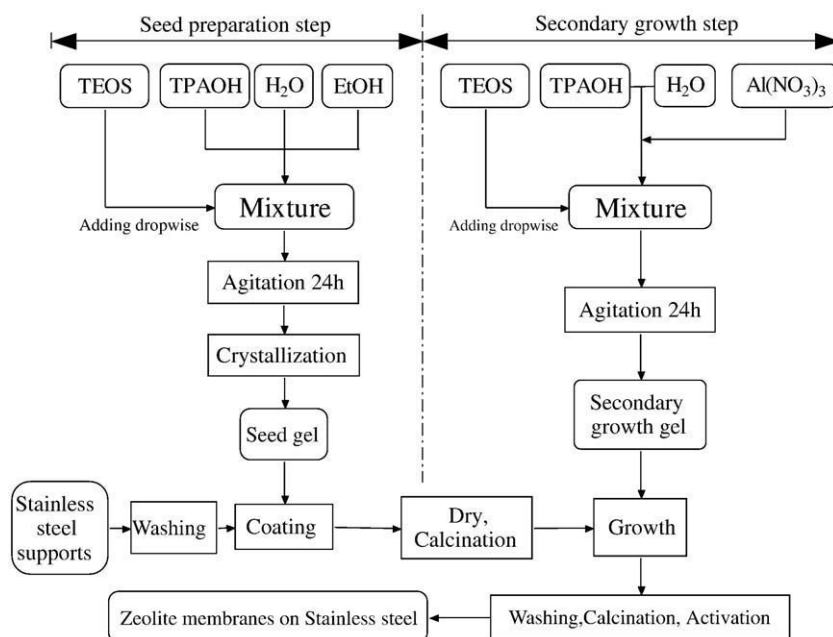


Fig. 1. Schematic illustration of zeolite synthesis by secondary growth method.

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