Applied Catalysis A: General 423–424 (2012) 108–113

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

ZSM-5 crystals grown on the wall of a long tubular reactor as a structured catalyst for cracking of endothermic fuels

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ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form 16 January 2012
Accepted 16 February 2012
Available online 24 February 2012

Key words:
Ni-based alloy
ZSM-5
Structured catalysts
Catalytic cracking
Endothermic fuels

ABSTRACT

In situ growth of ZSM-5 crystals on the surface of Ni-based alloy supports by hydrothermal synthesis and their mechanical, structural stability were investigated. ZSM-5 crystals grown on the wall of a long (750 mm) tubular reactor with a small inner diameter (1 mm) was evaluated as a structured catalyst for cracking of *n*-heptane as a model endothermic fuel. The results have shown that the adhesion strength between ZSM-5 crystals and the support was strong enough to resist a heating/fast-cooling cycle (the sample was immersed into water immediately after being heated to be 750 °C). The crystalline structure of ZSM-5 crystals was also stable against the heating/fast-cooling cycle. The structured catalyst was shown to be catalytically active for cracking of *n*-heptane (LHSV = 200 h^{-1}) at 700 °C. The formation rates of gaseous cracking products were 9.8 ml min^{-1} and 29.3 ml min^{-1} for the bare tubular reactor and the tubular reactor with ZSM-5 crystals grown on the wall, respectively. These structured catalysts show high promise for cracking of endothermic fuels at high temperatures.

1. Introduction

As the flight speed of an aircraft increases, aerodynamic heating becomes increasingly severe and critical demands are placed on the structural and thermal capabilities of the engines and airframe. Since the air taken on board for the vehicles at supersonic or hypersonic speeds is too hot to cool the engines and airframe, it becomes more necessary to use endothermic fuels as the primary coolant [1].

Endothermic fuels are fuels which have the capacity to absorb large quantities of physical and chemical heat. The capacity to absorb physical heat (sensible and latent heat) and the capacity to absorb a heat of reaction are referred to as the fuel's physical and chemical heat sink, respectively. Although several types of endothermic reactions have been studied as possible sources for the fuel's chemical heat sink, cracking of paraffinic hydrocarbons over zeolite catalysts is considered to be a most promising route because it can provide a high chemical heat sink and yield products with superior combustion characteristics [2].

In addition to the requisite high activity and selectivity characteristics of the catalysts itself, the arrangement of the catalyst in the cooling system is also crucial especially for aircraft applications where both size and weight are important. It has been reported that the tubular reactor coated with zeolite catalysts on the wall had many advantages over the conventional packed-bed tubular reactor, such as low pressure drop and high rates of both heat and mass transfer [3].

SAPO-5 and ZSM-5 crystals coated on stainless steel tubes by the wash-coating method have been applied for cracking of Norpar 12 [3], JP-7 [4,5], JP-8 + 100 [4,5], JP-10 [4,5] and *n*-dodecane [6]. The wash-coating technique, however, has to use inorganic binders to improve the adhesion strength between zeolite crystals and the support, which has the risk of blocking zeolite pores and thus leads to reduced effectiveness of the catalyst. The hydrothermal synthesis is another common method to grow zeolite crystals on the support, especially the in situ hydrothermal synthesis has many merits for growing zeolite crystals firmly on the support since it does not require a binder and a chemical bonding can be formed between the crystals and the support surface.

The growth of ZSM-5 crystals on the support (to fabricate structured catalysts) by the hydrothermal synthesis [7–12] and their applications for selective catalytic reduction of nitrogen oxides (SCR-NO_x) [13], methanol to olefins [14], xylene isomerization [15], N_2O decomposition and benzene hydroxylation to phenol [16] have been reported. However, studies on applying these structured catalysts for cracking of paraffin hydrocarbons are quite few [17,18].

Since metals or alloys have higher mechanical strength, higher thermal conductivity and easier processing characteristics than ceramics, they are the most appropriate supports for growing zeolite crystals to fabricate structured catalysts. The great difference in the properties between metals or alloys and zeolite crystals, however, makes it more difficult to attach zeolite crystals onto

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doi:10.1016/j.apcata.2012.02.020