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Review

Stability improvement of zeolite catalysts under hydrothermal conditions for their potential applications in biomass valorization and crude oil upgrading

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ABSTRACT

The future applications of zeolite catalysts could target the valorization of abundant biomass resources and the widely distributed heavy oil deposits. However, a major challenge that can limit this possibility is the low stability of the zeolite systems under the hydrothermal conditions. The paper therefore reviewed classified literature on the different methods being considered for improving the stability properties of zeolite catalysts. Zeolite frameworks modification with fluoride ions, phosphorus, rare metals and silanes provides an opportunity for improving the stability during reactions like cracking, alkylation, isomerization, dehydration etc. All of these reactions are commonly encountered during biomass valorization in hydrothermal media and the heavy oil valorization via catalytic cracking and/or aquathermolysis. The paper thus tailored the progress made and identify the directions for further investigations.

Contents

1. Introduction

The refining of petroleum is one of the vital processes through which fuels (liquids and gases) and industrial chemicals are formulated through a series of processes [1–3]. To achieve the refining process, impurities are first removed from the untreated crude oil followed by sequential temperature treatment. The latter produces gases which through distillation process are converted into several liquids fractions desired by the industry [4,5]. Although none of the derived components can be classified as waste, the major demand is for gasoline (i.e. petrol). It has been established that a barrel of processed crude oil can produce between 30 and

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40% of gasoline. However, transportation and related sectors require that 50% of the crude is upgraded into gasoline. Therefore, some of the fractions must be upgraded into gasoline. The upgrading process can be achieved through cracking [6–8], reforming [9,10] or isomerization [11–13], depending on the fraction under consideration. The cracking process involved the splitting of heavy molecules into smaller feeds that meet the gasoline requirements.

In addition to the production of hydrocarbons in the gasoline range, the cracking process can be employed to produce lighter gaseous fractions like olefins of industrial demand. However, the choice of most suitable zeolite catalyst for this application is of great concern for the industry. Modern refineries employ zeolite catalysts [14,15]. They are ordered form of silicoaluminate minerals, comprising of large lattices that described their shapes and structural properties [16,17]. During the cracking process, the hydrocarbon feed (usually alkanes) is contacted with the zeolite catalyst at moderate to low reaction pressure and temperatures that can exceed 500 °C.

The catalytic upgrading of alkanes in the carbon range of C_5 to C_8 via the cracking process have been evaluated using the zeolite catalysts. These model reactions served as representation to the industrial grade naphtha and heavier hydrocarbons cracking process. The overall activity and selectivity properties of the zeolites were found to be dependent on the zeolite acidity and structural properties. The H-Y zeolite was extensively studied and found to be commercially applicable for the fluid catalytic cracking (FCC) process. However, the large cages associated with this zeolite structure limited the production of light olefins like propylene [18]. The high degree of hydride transfer associated with this zeolite can also generate side undesired reactions [19,20]. Among the other studied zeolites, the H-ZSM-5 catalyst is a popular zeolite for the production of both light olefins and gasoline range hydrocarbons, especially due to the possibility of modifying the Si/Al properties without difficulties [21,22].

In addition to heavy oil upgrading [23,24], recent studies have revealed the zeolite catalysts to be suitable for liquid phase biomass upgrading into more valuable compounds like alcohols, aldehydes, ketones, et cetera [25,26]. The reactions which could be cracking and isomerization are usually achieved in hot water/steam at atmospheric pressure to establish good activity and selectivity properties [27,28]. The major challenge of zeolites exploitations for the crude oil and biomass upgrading in hot water is the stability problem. Although reasonable activity could be achieved at the initial stages, the catalytic activity quickly decays due to coking, active sites decay and structural collapse of the zeolites [29,30]. The objective of this paper is therefore to review the progress made on the strategies being adopted to improve the stability of the zeolite catalysts under the hot water/steam conditions for both biomass and heavy oil. Emphasis would be given to the issues such as the incorporation of fluoride, phosphorus and rare earth metals like lanthanum and silane treatment.

2. Stability of zeolites in hot water (i.e. hydrothermal condition)

Both biomass and fossil feedstock can be processed into more useful fuels or as raw materials using hot water as the media and zeolite as catalysts [31]. The liquid state reaction has therefore been predicted to play an outstanding role in future refining processes, especially for the abundant biomass resources [32–34]. The commercial availability coupled with the synthesis feasibility of the zeolite catalysts make their exploitation possible for the hot water application. However, the alteration to their properties under such conditions must be fully addressed. Different works have been published tailoring how the hot water conditions can influence the properties of the zeolite catalysts [35].

Ravenelle and co-workers [31], evaluated the stability of selected zeolites (i.e. H-Y and H-ZSM-5) under such conditions. The zeolites were immersed in water at 150 and 200 °C for period up to 6 h. While the structural deterioration was mechanistically dependent on the collapse of the Si-O-Si bonds via hydrolysis, the overall stability was subject to the framework nature. The H-ZSM-5 catalyst was completely stable at both temperatures due to enhanced resistance to hydrolysis by its frameworks even when the Si/Al ratio was varied. However, degradation with the H-Y zeolite was seriously pronounced and Si/Al ratio dependent. As the zeolite acidity decreases (i.e. Si/Al ratio increases), the degradation by hydrolysis of frameworks was favored. In a related development, Zapata et al. [36], have reported a very poor thermal stability of an H-USY (Si/Al = 30) zeolite after hot water treatment at 200 °C. Their X-ray diffraction data and SEM images have demonstrated a significant loss of the zeolite crystallinity with time. This had been attributed to crystallites dissolution and their subsequent mobility under such conditions. The stability of an MTT zeolite was recently evaluated by Bakare et al. [37]. The catalyst was subjected to hot water treatment at 200 °C using steel autoclaves for period up to 72 h. A significant change to the physicochemical properties was observed. The BET surface area reduced from an initial value of 212 m^2/g to <200 m^2/g, which could be attributed to the leaching of Si-Al frameworks. On the other hand, the zeolite acidity reduced by 0.11 mmol/g. Therefore, the influence of water does not only hydrolyse the Si-O-Si bonds but also the Si-O-Al species in the frameworks.

An important issue the remained debatable is whether the zeolites are more tolerance to hot liquid water than steam under similar conditions. According to Zapata et al. [38], action of steam on H-Y zeolite at temperatures between 100 and 200 °C does not cause any structural alteration to the frameworks. However, the hot water treatment caused a pronounced degradation effect as found with the characterization results. A number of different authors [39–42], have demonstrated MCM-41 as a stable zeolite in steam but not in hot water. According to Ryoo and Jun [39], MCM-41 catalyst can degrade significantly even at temperatures lower than 100 °C. However, Chen and co-workers [40], demonstrated that pure silica-MCM-41 is stable without framework degradation up to 950 °C. Similar findings were corroborated by Kim et al. [42], who reported the same stability properties at temperatures > 850 °C.

The various literature discussed herein have indicated the poor stability of the most zeolite catalysts considered suitable for hot water reactions. Owing to large deposits of heavy oil (Fig. 1) and abundant biomass feedstock (Fig. 2), which could be successfully upgraded into more valuable fuels and chemicals, devising sustainable option for enhancing the stability of the zeolite catalysts is very critical, especially for the future [43]. Modification strategies such as the incorporation of fluoride ions, phosphorus or metals into the zeolite frameworks have recently been investigated by a number of authors while others have focused on silane treatment. Details on these would be covered in the following subsections.

There are numerous literature arguments on the main factors responsible for the zeolite stability under hydrothermal conditions. According to Zhang and co-workers [44], the stability mechanism depends on the zeolite-hot water interaction as regard to the zeolite features like the acidic sites, extra-framework cationic species as well as the silanol defects. Their characterization data however showed that for the H-Y (FAU), H-ZSM-5 (MFI) and H-Beta (BEA) systems studied under hydrothermal conditions at 200 °C, silanol defects plays the key mechanistic role. Hence, the