



## Hydrocracking catalysts based on hierarchical zeolites: A recent progress



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### ABSTRACT

Consequent to the foreseeable depletion of the light crude oil reserves, the heavier hydrocarbon chains would be the focus of the global energy industry. The hydrocracking of vacuum gas oil (VGO) and demetallized oil (DMO) components of the heavy oil presents a promising factor for the global energy future. Catalytically, the hierarchical zeolites are prospective reaction systems been considered. In addition to new routes for the catalyst synthesis, the paper encompassed technological challenges, mechanisms involved, role of catalyst modification, diffusional characteristics and the deactivation parameters associated with the overall process. Areas requiring further investigations were also discussed.

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### Introduction

Although there are many challenges associated with the exploitation and utilization of crude oil, especially due to the posed environmental pollution and unsustainable nature [1–5], the crude oil will continue to supply the planet with fuels and chemicals for more decades to come. The increasing global population coupled to the advancement in technology implied an escalation in fuel consumption over the years [6–10]. The trend is also projected to rise for the future. Both light and heavy crude oil deposits are distributed in different parts of the world in huge quantities (see Figs. 1 and 2) [11,12]. Therefore, exploration of more valorization options for meeting global energy sustainability requirements are inevitable. Fuels such as gasoline, diesel and jet fuels are the key desirable commodities required for daily global transportation. Their extraction from the crude oil feedstock is the primary objective of the oil refineries and therefore efforts to are always underway to device new technologies for their efficient production at affordable prices and with less-environmental difficulties [13–17].

Recently, the application of the hydrocracking process to valorize crude oil fractions into these fuels (especially the diesel) is attracting industrial attention. The process is employed by modern refineries to upgrade heavy oil fractions into fuels suitable for transportation and/or as petrochemical plant feedstock [18,19]. At the industrial scale, the hydrocracking process is affected by the process design, the choice of catalyst and the selected reaction parameters. The process is commonly achieved in two steps. Initially, polyaromatics are upgraded into saturates through the elimination of N- and S-species in the form of NH<sub>3</sub> and H<sub>2</sub>S gases [20,21]. This is required to ensure catalyst efficient performance and inhibits its rapid deactivation by the catalyst poisons. The second step of the hydrocracking method proceeds with the degradation (i.e. cracking) of high molecular weight hydrocarbons using a bifunctional catalyst (i.e. catalyst possessing both acid and metal functions). Therefore, the achievable yields of the required products are subject to the suitable choice of the reaction feed in addition to catalytic activity-selectivity properties and the upgrading parameters adopted [22–24]. An overall mechanism of the heteroatom-removal process during the hydrocracking is illustrated in Scheme 1. In addition to aromatic ring saturation, mechanistic processes such as ring opening, isomerization and the regular C–C, C–S, C–N and C–O cleavages have been encountered.

Hydrocracking is achieved in the refinery operation unit called hydrocracker and a variety of feed stock could be upgraded depending on the cracker configuration. The common process feeds employed are vacuum gas oil (VGO) [25,26], atmospheric gas

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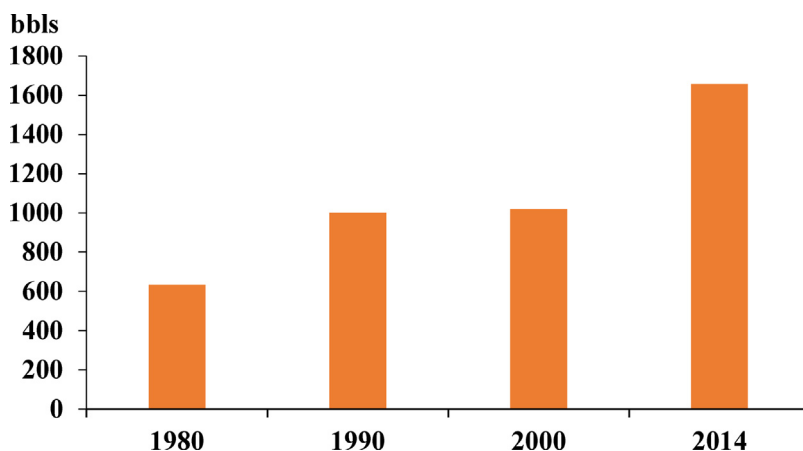


Fig. 1. Global trend of crude oil reserves over the years (1980–2014).

Data source: Ref. [11].

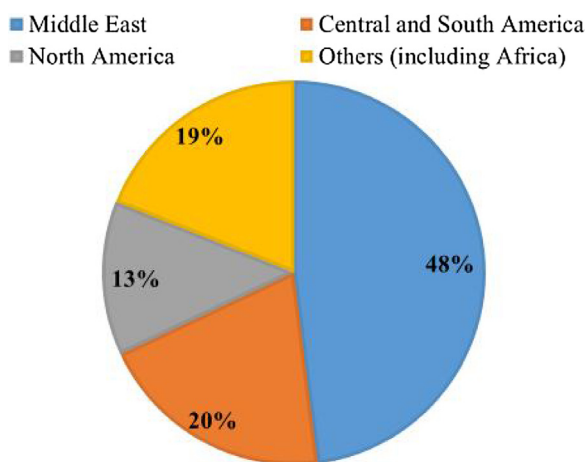


Fig. 2. Share of global crude oil reserves among the global countries.

Data source: Ref. [12].

oil (AGO) and de-asphalted oil [27,28] and de-metallized oil (DMO) [29,30]. Other suitable feeds include the thermally cracked products and the heavy cycle oil (HCO) [31–33]. Fig. 3 represents a typical hydrocracking unit for a feed upgrading. The unit could be a two-stage as described above or a single operation unit. In the latter case, a mono-phase (i.e. single phase) bifunctional catalyst bed is employed. A major drawback commonly encountered with this cracking method is the full exposure of the catalyst system to the evolved  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases generated during the upgrading process. However, as discussed earlier the two-step operation method could limit the chance of catalyst deactivation over time. The process parameters are usually limited to  $\text{H}_2$  pressure in the range of 75–160 bar,  $2.5 \text{ h}^{-1}$  space velocity and very high hydrogen/oil ratio (could be up to 800). Reaction temperatures could be ranged between 300 and  $500 \text{ }^\circ\text{C}$  [34,35]. However, severe reaction conditions have a negative effect of rapid catalyst deactivation.

Fundamentally, the choice of an appropriate catalyst system is most important parameter for a successful operation. Although different zeolite catalysts have been evaluated, the low yield of desired reaction products, poor catalyst stability and associated high process energy requirements attributed to the search for better catalyst design options. Recently, hierarchical (i.e. mesoporous) zeolite catalysts have been documented to show improved activity-stability properties in related reactions [36–40]. This trigger their consideration for the hydrocracking process. The

paper therefore tailored a review of recent literature on the role of the mesoporous zeolites as hydrocracking catalysts. Importance was placed on the catalyst design, selectivity and activity-stability properties. Factors responsible for catalyst deactivation by coke deposition and poor thermal stability and process mechanism(s) were simultaneously discussed. Important paths for the hierarchical zeolites preparations were covered and areas requiring further investigations have also been identified and discussed.

#### Mesoporosity role in catalyst support for hydrocracking

The hierarchical (i.e. mesoporous) catalysts represent a category of catalytic systems with pores having diameter in the range of 2–50 nm unlike the bulk (i.e. microporous) materials with diameters  $< 2 \text{ nm}$ . The mesoporous catalysts are characterized by certain features that prompted their industrial consideration for refining catalysis [41,42]. They possessed optimal textural properties, uniform pore distribution and enhanced-stability characteristics [43]. Of great catalytic importance is their porosity network that is susceptible to unrestricted diffusion of reactants and the resulting products [44,45].

The VGO, HCO and AGO are characterized by very high viscosity due to their compositions of high boiling compounds as well as amounts of heterocyclic compounds containing metallic (i.e. V, Fe, Ni) and S- and N-species [46,47]. They can also possess large quantities of free-carbon species [48,49]. Consequent to this complex compositions, the hydrocracking catalyst systems could easily be deactivated with an overall reduction in the process efficiency. There are several factors that can be attached to the lost catalyst in this regard. These include the accumulation of the coke precursors on both the external and internal configuration of the catalysts, the rapid deposition of metallic poisons and complete pore blockage. When this takes place, the catalyst pore-size became narrowed thereby restricting the accessibility by both products and reactant species. Therefore, the catalytic activity and selectivity properties drastically reduced. By implication, catalyst pore-structure is an essential factor that can evaluate the conversion, selectivity and stability properties of the catalysts during hydrocracking reaction [50]. As shown in Fig. 4, the degree of treatment is an important parameter in creating the mesopores in the zeolite of interest. Enough catalyst synthesis and post-synthesis treatment times are necessary to develop a more hierarchical system with reduced-diffusional difficulties [50].

As the hydrocracking catalysts are commonly bifunctional, the catalytic design targets the production of mesoporous support materials that allow active and synergic metal-support interaction

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