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REVIEW

The catalytic naphtha reforming process: hydrodesulfurization, catalysts and zeoforming

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Abstract

High-octane gasoline production by catalytic naphtha reforming is a major process in the petroleum industry. Sulfur components involved in the reforming process are causing pollutions and catalyst poisoning. Hydrodesulfurization has been developed to remove sulfur species from naphtha. Bimetallic and trimetallic catalysts are used to improve the naphtha reforming. Another solution to produce gasoline is the zeoforming process, which involves zeolites. This article reviews the naphta reforming reaction.

Keywords Naphtha reforming · Hydrodesulfurization · Zeoforming · Gasoline

Introduction

The most important part of modern processing plants and the core producer of high-octane gasoline (~ 40% of the world production) and aromatic hydrocarbons are the units of catalytic naphtha reforming. Sulfur and sulfur-containing compounds, e.g., hydrogen sulfide (H_2S), mercaptans, organic sulfides and disulfides are present in crude oil and remain to various degrees in the products obtained from the refining of these crude oils. The presence of sulfur in naphtha invariably has a negative, and typically immediate, effect on the performance of catalysts. In addition, sulfur compounds in transportation fuels are becoming an important global concern, as they pose serious threats to the environment and air quality. In order to prevent atmospheric toxic waste and to avoid the reforming catalyst consequent poisoning, the hydrodesulfurization (HDS) processes are used to convert sulfur compound to H_2S (hydrogen sulfide), which is removed by washing, and hydrocarbons. Bifunctional metal–acid catalysts are applied in the hydrodesulfurization process in order to minimize sulfur compounds.

The metal function is provided by platinum (Pt), which is supported over the acid function, chlorinated gamma alumina (γ-Al_2O_3). The addition of metals [such as Ge (McCallister and O'Neal 1971), Sn (Rausch 1973) and Re (Hansel 1949)] can improve Pt catalytic properties which modifies the catalyst selectivity, activity and stability (Carvalho et al. 2004a, b). The application of other trimetallic catalysts such as Ni–Mo–W/Al_2O_3 and Ni–Mo–W/SBA-15 was also patented. Mendoza-Nieto et al. (2013) used Ni–Mo–W catalysts supported on SBA-15 for deep hydrodesulfurization. They reported that the best catalytic activity in hydrodesulfurization was belonging to trimetallic Ni–Mo–W/SBA-15 catalyst. Other researchers used zeolite as catalyst to remove sulfur from naphtha. Salem and Hamid (1997) found that for equal cracked and virgin naphtha mixture at 80 °C, the sulfur amount was decreased around 65% and 30% by using activated carbon and Zeolite, respectively. Likewise, the previous research (Kulprathipanja et al. 1998) found that molybdenum (Mo)- and nickel (Ni)-exchanged zeolite Y and X can be used for removing of sulfur from hydrocarbons stream. Usual processes of adsorption have an adsorption cycle whereby the contaminant is adsorbed from the feed, followed by desorption cycle whereby the contaminant is removed from the adsorbent. Therefore, zeolites have an

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advantage of removing sulfur on conventional catalysts (such as Pt/Al_2O_3) for naphtha reforming process.

Yet, sulfur components in naphtha are the problems of catalyst deactivation and high-octane gasoline production. Consequently, the advantages of zeolite as a catalyst with non-noble metals for reforming of naphtha (zeoforming process) are its environmental-friendliness as well as being strong against sulfur. Therefore, it would be beneficial for those interested in high-octane gasoline production research to get an idea about the current status of this industry, including nature of sulfur impurities in naphtha, hydrodesulfurization of sulfur-containing heterocyclic compounds, the effect of additional metal on catalytic naphtha reforming process, advantages of zeolite and zeoforming process for naphtha reforming, catalyst deactivation and reactor setup. The aim of this paper is to provide an overview of literatures on sulfur component in naphtha, hydrodesulfurization, bi- and trimetallic catalysts, zeoforming technology and make through a comparative analysis.

This article reviews the naphtha reforming reaction. As shown in Fig. 1, the "Sulfur compounds in transportation fuels" section presents an introduction and the background of study on naphtha reforming process. The "Hydrodesulfurization" section provides information regarding the sulfur compounds in transportation fuels. The "Reforming catalysts" section describes the hydrodesulfurization for removal of sulfur and thermodynamics of hydrodesulfurization. In the "Catalyst deactivation" section, discussion about catalysts used for naphtha reforming process such as bimetallic, trimetallic and zeolites as well as zeforming process for high-octane gasoline production are provided. The "Choice of reactor" section presents different mechanism of catalyst deactivation. The "Recommendations" section describes the reactor-scale setup for naphtha reforming process. Finally, the "Conclusion" section discusses the recommendation for future work and conclusion of this review.

Sulfur compounds in transportation fuels

Sulfur compounds in transportation fuels, such as diesel and gasoline, are becoming an important global concern, as they pose serious threats to the environment and air quality (Stanislaus et al. 2010). The Environmental Protection

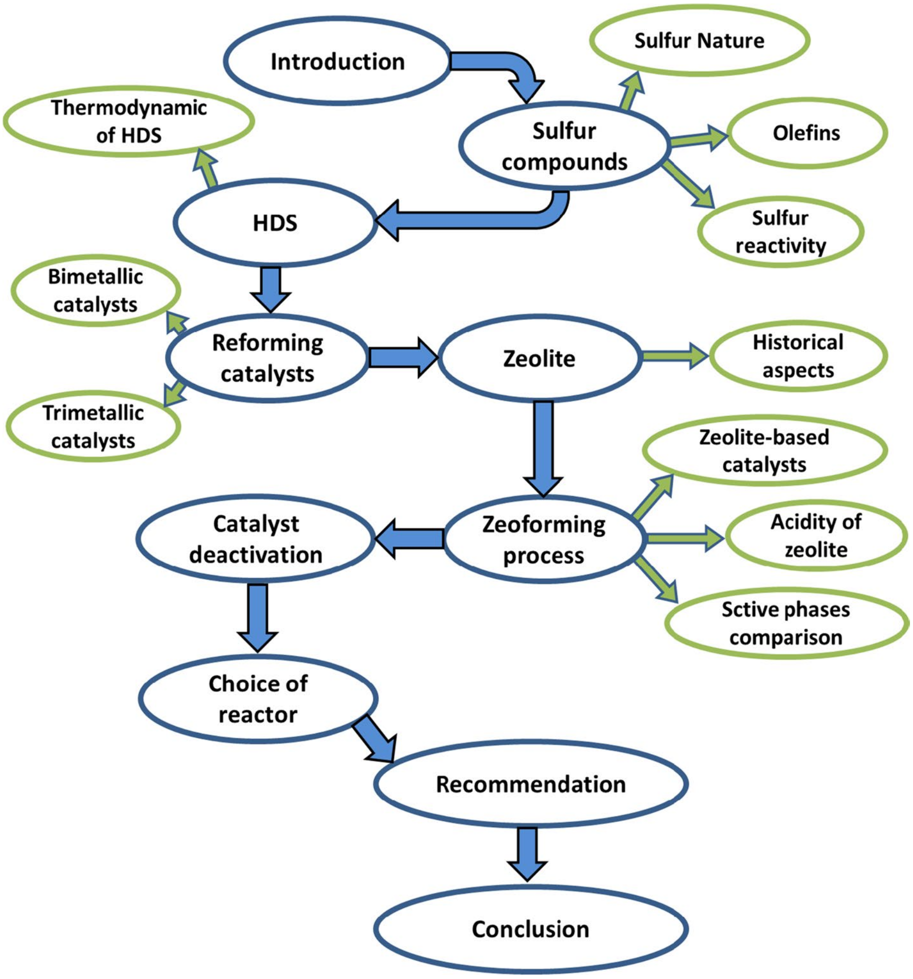

Fig. 1 Content of this article. *HDS* hydrodesulfurization

Agency (EPA) regulations regarding air quality policy in the USA require that the sulfur content in federal gasoline cannot exceed 10 ppmw by January 1, 2017, while ultralow-sulfur diesel (ULSD) must contain less than 15 ppmw of sulfur (Lee and Valla 2017). Another importance of deep desulfurization is motivated by the extensive use of liquid hydrocarbon fuels for the application of fuel cell. Gasoline and diesel are readily available, are easily storable and contain high amount of energy density, making them favorable sources of hydrogen gas for fuel cell systems (Pieterse et al. 2011). However, the operation of fuel cells is restricted even by present strict sulfur regulations. In fact, fuels used in solid oxide fuel cell (SOFC) and proton exchange membrane fuel cell (PEMFC) should be kept below 5 and 0.1 ppmw of sulfur, respectively (Duarte et al. 2011).

Gasoline, diesel and jet fuels are three main kinds of transportation fuels which are vary in property, structure and composition. The common types of sulfur compounds in liquid fuel are:

1. Gasoline range: naphtha, fluid catalytic cracking (FCC) naphtha,
    - sulfides (R_2S); mercaptanes (RSH); and disulfides (RSSR);
    - thiophene and its alkylated derivatives;
    - benzothiophene.
2. Diesel fuel range: middle distillate, light cycle oil (LCO),
    - alkylated benzothiophenes;
    - dibenzothiophene (DBT) and its alkylated derivatives.
3. Jet fuel range: heavy naphtha, middle distillate,
    - benzothiophene (BT) and its alkylated derivatives.
4. Boiler fuels feeds: heavy oils and distillation resides,
    - ≥ 3-ring polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT);
    - phenanthro[4,5-b,c,d]thiophene (PT) and their alkylated derivatives.

Tables 1 and 2 show the US highway diesel pool volume fraction and the corresponding US highway diesel blend stocks sulfur levels, respectively. Among the diesel

Table 1 Volume fraction of US highway diesel pool from each feedstock component (Reproduced with permission from Song and Ma 2003)

Diesel blend stock	Percentage of US highway diesel fuel pool per blend stock boiling fraction				
	Naphtha	Light distillate	Heavy distillate	Light gas oil	All boiling fractions combined
Straight-run	0.1	6.4	4.9	1.0	12.4
Hydrotreated straight-run	0.3	8.1	41.2	2.3	51.9
Cracked stock	–	0.1	0.8	2.2	3.1
Hydrotreated cracked stock	–	2.1	15.6	1.7	19.4
Coker gas oil	–	–	1.0	–	1.0
Hydrotreated coker gas oil	0.1	2.1	3.7	2.3	8.2
Hydrocrackate	–	1.3	2.7	–	4.0

US: United States

Table 2 Corresponding US highway diesel blend stocks sulfur levels

Diesel blend stock	Sulfur content (ppmw) by boiling fraction				
	Naphtha	Light distillate	Heavy distillate	Light gas oil	All boiling fractions combined
Straight-run	827	1770	2269	4980	2218
Hydrotreated straight-run	362	119	394	548	358
Cracked stock	–	2219	2892	6347[a]	5322
Hydrotreated cracked stock	18	37	939	1306[a]	874
Coker gas oil	540	1800	3419	–	3419
Hydrotreated coker gas oil	8	25	310	400	258
Hydrocrackate	–	12	120	–	85

US: United States

[a] Indicating properties that were not reported in the refiner survey. These values were calculated by EPA using the reported sulfur contents of like boiling fractions in other diesel blendstocks by assuming the same relative sulfur levels between boiling fractions

blend stocks, the light cycle oil from fluid catalytic cracking contains highest amount of sulfur and aromatics, and the light cycle oil also tends to have the highest contents of refractory sulfur compounds, especially 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Nature of the sulfur impurities

Thiophene, alkylthiophenes, thiols, sulfides, thiophenols, benzothiophene and tetrahydrothiophene are the main sulfur components of fluid catalytic cracking gasoline (Myrstad et al. 2000; Krumpelt et al. 2005; Zinnen 1999). Alkylthiophenes contain three- and four-carbon-atom-substituted thiophenes (C3- and C4-thiophenes) which are typically in the boiling range of gasoline, but it is hard to express whether these are polymethylated or longer-chain-substituted thiophenes. Yin et al. (2002a, b) found that thiophene sulfur represents a large fraction of the total sulfur content in fluid catalytic cracking gasoline (> 60 wt%). By using gas chromatography, they detected more than 20 different kinds of thiophenes among which a certain number (di- and trimethyl-, ethyl-, ethylmethyl-, di- and triethyl-, iso-propyl-, tertiobutyl-) could be identified by GC/MS analysis (Table 3).

Table 3 Gas chromatographic analysis of thiophene derivatives in fluid catalytic cracking naphtha. (Reproduced with permission from Yin et al. 2002)

Compounds	Percent ratio of total thiophenes (sulfur %)	Sulfur content in naphtha (μg/g)
Thiophene	6.3	69.2
2-Methylthiophene	10.0	109.8
3-Methylthiophene	13.8	152.6
Dimethylthiophenes	35.4	389.8
Unknown thiophene	4.0	43.9
Iso-propylthiophene	2.4	26.4
Methyl ethylthiophene	4.2	46.1
Trimethylthiophene	5.6	61.5
Unknown thiophene	1.6	17.6
Trimethylthiophene	4.1	45.0
Four-carbon alkylthiophene	10.5	116.4
Unknown thiophene	2.1	23.0

Olefins

The unsaturated aliphatic hydrocarbons (olefins or alkenes), like paraffins, are either branched structures or straight chains, but contain one or more double bonds. They are a class of chemicals that includes ethylene, propylene and 1,3-butadiene. Ethylene, also called ethene, is an industrial petrochemical and natural product. Ethylene is a basic building block for the chemistry industry and is the largest volume organic chemical produced in the USA and globally. Many countries now require automotive gasoline fuels to have a sulfur content that satisfies a strict standard, such as 15 ppmw of sulfur or less. One of the difficulties in meeting such a standard can be related to incorporating cracked naphtha fractions into gasoline. Cracked naphtha fractions can potentially be beneficial for the octane rating of a gasoline due to the presence of olefins in such fractions. However, conventional desulfurization methods for removing sulfur from naphtha fractions by hydrodesulfurization can tend to also saturate olefins, thus mitigating the benefit of using a cracked naphtha fraction.

In numerous aspects, to produce naphtha boiling range fractions suitable for incorporation into a naphtha fuel product systems and methods are provided. The amount of sulfur might be decreased and octane number increased by the fractions of naphtha boiling range produced according to methods described herein. For instance, the feed of naphtha boiling range can be separated to form a lower boiling and higher boiling portions. The lower boiling portion, containing a substantial amount of olefins, can be exposed to an acidic catalyst, such as a zeolite, without the need for providing added hydrogen in the reaction environment. This can allow for sulfur removal while reducing or minimizing the amount of olefin saturation. Additionally, during the exposure of the lower boiling portion to the acidic catalyst, a stream of light olefins (such as C_2–C_4 olefins) can be introduced into the reaction environment. Adding such light olefins can enhance the C^{5+} yield and/or improve the removal of sulfur from sulfur species such as thiophene and methylthiophene compounds in the naphtha feed (Harandi et al. 2017).

Selecting a suitable fractionation temperature can assist with making a desired naphtha boiling range product based in part on the nature of the distribution of olefins and/or sulfur within the various compounds in a naphtha boiling range feed. In a naphtha boiling range feed, a substantial portion of the olefins present in the feed can correspond to olefinic compounds having a boiling point of about 225 °F (~ 107 °C) or less, or about 210 °F (~ 99 °C) or less, or about 205 °F (~ 96 °C) or less, or about 200 °F (~ 93 °C) or less, or about 190 °F (~ 88 °C) or less, or about 180 °F (~ 82 °C) or less. The amount of olefinic compounds having such a boiling point can correspond to about 20–80% of the total weight of olefinic compounds in a naphtha feed. For example, a naphtha boiling range feed can be separated to form a lower boiling portion and higher boiling portion at a fractionation temperature of about 300 °F (~ 149 °C) or less, 270 °F (~ 132 °C) or less, or about 250 °F (~ 121 °C) or less, or about 240 °F (~ 116 °C) or less, or about 225 °F (~ 107 °C) or less, or about 210 °F (~ 99 °C) or less and/or at least about 160 °F (~ 71 °C), or at least about 170 °F (~ 77 °C), or at least about 180 °F (~ 82 °C). After such a fractionation, the weight of olefins in the lower boiling portion can correspond to about 20% to about 80% of the weight of olefins present in the feed prior to fractionation, such as about 20% to about 40%, or about 20% to about 50%, or about 20% to about 60%, or about 20% to about 70%, or about 20% to about 80%, or about 30% to about 40%, or about 30% to about 50%, or about 30% to about 60%, or about 30% to about 70%, or about 30% to about 80%, or about 40% to about 50%, or about 40% to about 60%, or about 40% to about 70%, or about 40% to about 80%, or about 50% to about 60%, or about 50% to about 70%, or about 50% to about 80%, or about 60% to about 80%.

Reactivity of sulfur compounds

The types of sulfur compounds can make the desulfurization easy or difficult. Previous researches have dealt with the transformation of thiophene on fluid catalytic cracking-type catalysts. However, thiophene itself is rather unreactive under the conditions of fluid catalytic cracking and the mechanism of its decomposition on pure acidic materials is still not well understood. In fact, most of the recent relevant studies deal with other sulfur compounds like alkylthiophenes, tetrahydrothiophene and benzothiophene (Leflaive et al. 2002; Corma et al. 2001; Brunet et al. 2005). As predictable, the higher boiling compounds are desulfurized more difficult than the low boiling ones. The reactivity of sulfur compounds increases in the order alkylbenzothiophenes > benzothiophenes > thiophenes > sulfides > disulfides > mercaptans. Within a group, the reactivity increases with decreased molecular size and varies depending on whether the alkyl group is an aliphatic or aromatic group. Among thiophene derivatives, the thiophenes are more reactive than alkylthiophenes, probably due to steric effects (Antos and Aitani 2004). Zeelani et al. (2016) mentioned that the reactivity of sulfur compounds for oxidation increases with increase in electron density on sulfur atom. The reactivity of refractory sulfur compounds decreases in the order of 4,6-DMDBT > 4-MDBT > DBT. The order of reactivity in hydrodesulfurization of sulfur compounds is reverse of the above pattern. Lü et al. (2014) studied Oxidative desulfurization of model diesel. As shown in Fig. 2, the reactivity of catalytic oxidation of sulfur-containing compounds can be listed as dibenzothiophene (DBT) > 4-methyldibenzothiophene (4-MDBT) > 4,6-dimethyldibenzothiophene (4,6-DMDBT) > benzothiophene (BT). The reactivity of those sulfur compounds was influenced mainly by two factors, that is, electron density on the sulfur atom and steric hindrance of sulfur compounds. The lowest electron density on the sulfur atom of BT (5.696) leads to a lowest reactivity (Otsuki et al. 2000). The electron density differences of DBT, 4-MDBT and 4,6-DMDBT (5.758, 5.759 and 5.760 for DBT, 4-MDBT and 4,6-DMDBT, respectively) are so small that they can be ignored (Otsuki et al. 2000; Shiraishi et al. 2002). Therefore, reactivity was mainly affected by the steric hindrance of the methyl groups, which became an obstacle for the approach of the sulfur atom to the catalytic active species in IL. It indicated that the reaction rates of these sulfur-containing compounds are sensitive to the electron density on sulfur atoms and the steric hindrance of the substituted groups of sulfur-containing compounds (Lü et al. 2013).

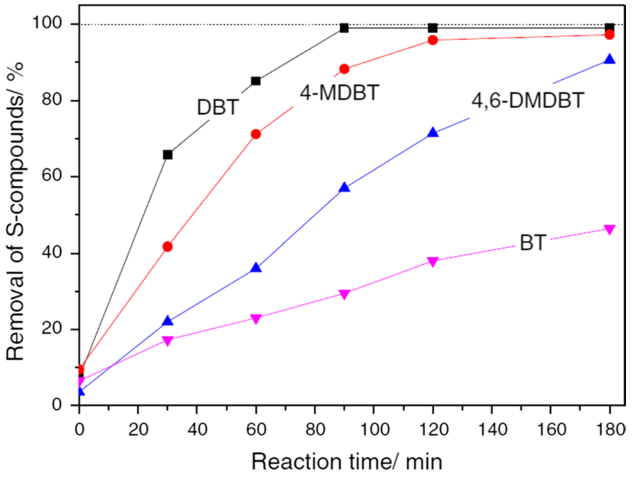

Fig. 2 Removal of sulfur-containing compounds versus reaction time. (Reproduced with permission from Lü et al. 2014)

Hydrodesulfurization

The requirement of clean burning fuel production has increased the importance of hydrodesulfurization (HDS) in petroleum industries. The previous studies are worked on the effects of bimetallic NiMo, CoMo or NiW catalysts supported on alumina, on the development of process, on low-pressure reaction studies of thiophene having relatively high reactivity and on catalyst characterization by physical methods. Most of the studies have focused on NiMo, CoMo or NiW sulfide catalysts supported on alumina. Almost all the reviews have concentrated on alumina-supported CoMo, NiMo and NiW sulfide catalysts in order to reduce sulfur, nitrogen and aromatics while enhancing cetane number, density and smoke point by hydrotreating process. Even reviews that are not limited to the above catalytic systems basically deal with studies of simple compounds such as thiophene (Vasudevan and Fierro 1996).

Significant research efforts have been dedicated toward catalyst development for HDS in order to minimize the sulfur in fuels to less than 0.05 wt%. The nitrogen and aromatics might also decrease in future. As a result of the steric hindrance of the alkyl substituents to which the sulfur atom is bound, the removing of sulfur compounds that remain in diesel fuels after HDS is refractory and difficult. It would be beneficial for those interested in development of suitable catalysts to get the low sulfur level. Assessments of catalyst activity for dibenzothiophene or thiophene model compounds and various components present in the feedstock were the investigation of previous researches.

Thermodynamics of hydrodesulfurization

If hydrogen presented in stoichiometric quantity in the hydrogen reaction with sulfides, thiophene, thiols and disulfides in order to produce saturated hydrocarbons and H_2S in the conventional temperature range in technical processes (300–500 °C) there is no thermodynamic limitation. The thermodynamic data of dibenzothiophene are shown in Table 4. These data show that the hydrodesulfurization reaction to produce biphenyl ($C_{12}H_{10}$) and H_2S is thermodynamically favored in the industrial-scale temperature range. HDS and supplementary hydrogenation reactions which occur during the process are highly exothermic.

Reforming catalysts

The metal function of Pt and acid function of AlCl3 were used as bifunction catalyst for naphtha reforming process (Hamoule et al. 2011; Rashidzadeh et al. 1999). The hydrogenation and dehydrogenation reactions are controlled by metal function and isomerization and cyclization reactions with acid ones. Sufficient equilibrium between these functions is required in order to attain the best catalytic activity in naphtha reforming process. The essential concern to improve the naphtha reforming process efficiency is decreasing the deactivation of catalyst and increasing the activity and selectivity of catalysts. The strength of support acid site amount can be altered by adding component to the acid function. Adding second or third metal component to Pt modifies the metal function. The next part provided an overview of literatures on the effect of bimetallic, trimetallic and support for naphtha reforming process and make through a comparative analysis.

Table 4 Thermodynamics of reactions involved during HDS. (Reproduced with permission from Vrinat 1983)

Compound	Reaction	ΔH_{300K} (kcal mol^{-1})
Methane thiol	$CH_4S + H_2 \rightarrow CH_4 + H_2S$	− 19
Dimethyl sulfide	$C_2H_6S + 2H_2 \rightarrow 2CH_4 + H_2S$	− 32
Thiophane	$C_4H_8S + 2H_2 \rightarrow C_4H_{10} + H_2S$	− 27
Thiophene	$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$	− 62
Dibenzothiophene	$C_{12}H_8S + 2H_2 \rightarrow C_{12}H_{10} + H_2S$	− 11

Bimetallic catalysts

Platinum supported on chloride alumina (Pt/Al_2O_3–Cl) was the first prepared catalyst for naphtha reforming process (Haensel 1949; Haensel et al. 1949). High pressure of hydrogen was applied in order to decrease catalyst deactivation by coking which is not favored in thermodynamic point of view. The hydrogen surplus in naphtha reforming was decreased and catalytic activity increased by adding metal to the monometallic catalyst (D'Ippolito et al. 2009; Benitez et al. 2008). Metals such as Ge and Sn are inactive, while others such as Re, Rh and Ir have their own catalytic properties. Re addition to Pt contributes to the enhancement in aromatic yields, increase catalytic properties and reduce the rate of catalyst deactivation (Baghalha et al. 2010; Viswanadham et al. 2008). Tin (Sn) addition was studied in 1969 (Raffinage French Patent 2031). Sn addition results in Pt/Al_2O_3 stability by avoiding coke formation and improves the selectivity to aromatics (de Miguel et al. 1996; Bariås et al. 1996). Pt–Sn catalysts are typically applied in systems which the catalyst is regenerated continuously because they are regenerated easily (González-Marcos et al. 2005). In McCallister and O'Neal (1971), Ge addition in Pt-supported catalysts were considered. The addition of Ge causes to improvement in the Pt thioresistance at reaction conditions (Borgna et al. 1999). The addition of Ir and In was studied in (Sinfelt 1976; Antos 1977). It contributes to the decrease in the coke deposition on the catalyst surface, enhances the gasoline production and improves the aromatization/cracking ratio of the reforming reaction (Benitez et al. 2008; Benitez and Pieck 2010; Vicerich et al. 2014). The Pt–Ir catalyst has high capacity for hydrogenolytic, and sulfiding pretreatments must and be included in industrial scale in order to avoid risky exothermal runaway formed by feedstock immense C–C bond cleavage in the initial reaction stage (Boutzeloit et al. 2006).

The second metal has different properties. For instance, Ge and Sn are inactive toward the reaction of naphtha reforming. Thus, these two metals are not presulfided and are suitable for low-pressure naphtha reforming processes using continuous catalyst regeneration, because these catalysts require only simple activation techniques. On the other hand, Ir and In are active toward hydrogenolysis reactions; thus, these two catalysts are usually presulfided in situ during commercial practice to passivate their initial hyperactivity for exothermic demethylation reactions (Srinivasan and Davis 1992).

The addition of second metal can be contributed to modifying the electronic state of the metal, altering the geometry of adjacent Pt atom clusters and the final Pt particle size. A portion of the additives remains oxidized on the surface and modifies the amount and strength of the acid sites of the support. These changes affect the hydrogenation and dehydrogenation reaction kinetics and control effective size of Pt clusters, which result in better activity, selectivity and stability of the catalyst (Borgna et al. 2000; Rahimpour et al. 2013).

Trimetallic catalysts

The addition of third metals to bimetallic catalysts can enhance the catalysts function. The metal and acid functions of the bimetallic catalysts were improved by Ge which was added into Pt–Re/Al_2O_3 catalyst in Antos (1982).

Ge addition modified the properties of the metal and acid functions of the bimetallic catalysts. Ge parts are deposited on the supports which contribute to acidity modification of the catalyst.

In the previous study, Benitez et al. (2007) have prepared Pt–Ir–Ge and Pt–Re–Ge supported on Al_2O_3 catalysts. They found that Ge addition into bimetallic Pt–Ir and Pt–Re catalysts results in the strong inhibition activity of the dehydrogenating and hydrogenolytic, but Pt–Ir–Ge catalysts produce a greater metal function modification than Pt–Re–Ge. They also reported that using N_2 gas in the reduction process decreases the amount of Ge deposition compared to H_2 gas. For example, for a 0.3% theoretical amount of Ge a 0.2 wt% Ge in Pt–Ir and Pt–Re catalysts is obtained in the experiment under N_2. This result can be explained by considering that when H_2 is present in the solution, $GeCl_x$ species in contact or in the neighborhood of Pt particles are reduced by chemisorbed hydrogen and that simultaneously part of Ge is deposited over the surface by electrostatic adsorption over surface groups of the support.

The selectivity toward toluene and the catalyst stability can be increased by adding Sn to the bimetallic Pt–Ir. The previous research (Epron et al. 2005) shows that the same yield of toluene was achieved with Pt–Ir–Sn and Pt–Sn supported on Al_2O_3 catalysts, but less tin is needed in the case of the trimetallic catalyst. The catalyst metal and acid functions are affected by adding Sn. It also stops the catalyst metal and acid functions to such different degrees that a very suitable metal/acid activity ratio was achieved, consequential in an enhancement of catalyst selectivity, activity and stability.

TPR analysis of catalysts shows that hydrogen chemisorption decreases more than carbon monoxide chemisorption when the Sn is added to Pt (Gomez et al. 1993; Margitfalvi et al. 1999). In Verbeek and Sachtler's (1976) research, Pt and Pt–Sn alloys showed that "dissociative adsorption of hydrogen is likely to require two Pt atoms; moreover, it may be necessary for these to be adjacent." They found that when Sn is added to Pt, the space between the Pt atoms is enlarged and contributes to altering this adsorption to an activated process. When Sn is added to Pt–Re, the stability and the isomerization activity improved and the hydrogenolytic activity decreased (Mazzieri et al. 2005). One of the significant issues of the pollution in naphtha reforming process is reducing the benzene/i-C7 ratio. This can be possible by adding Sn to Pt–Re catalysts. Pt–Re–Sn catalyst would also result in eliminating the complex sulfiding pretreatment (Mazzieri et al. 2005).

The application of other trimetallic catalysts such as Ni–Mo–W/Al_2O_3 and Ni–Mo–W/SBA-15 was also patented. It was found that the best catalytic performance in HDS process belongs to NiMoW/SBA-15 catalyst (Mendoza-Nieto et al. 2013). This result was because of characteristic difference of Mo and W species in this trimetallic catalyst as confirmed by HRTEM, DRS and TPR techniques. The HRTEM characterization also shows the better active phase dispersion observation of trimetallic NiMoW/SBA-15 compared with bimetallic ones. Another study (Absi-Halabi et al. 1998) used Ni–Mo–W trimetallic catalyst supported on Al_2O_3 for residual oil hydroprocessing. The results revealed that the Ni–MO–W catalyst was more active for various conversions than either the Ni–Mo or Ni–W catalyst.

Zeolite

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. Currently, the reported zeolite-based supports for HDS catalysts mainly included alumina-mixed zeolites, other component-mixed zeolites, nanosized zeolites and hierarchical zeolites. The combination of zeolite and alumina is able to produce hierarchical pores in support because of the rich meso-/macropores in alumina, which would improve both the diffusion of reactant and the dispersion of active phase. Most of the studies indicated that zeolite–alumina-supported catalyst showed higher activity than alumina-supported catalyst (Isoda et al. 1996; Nakano et al. 2013; Wan et al. 2010a, b; Yao et al. 2012; Sankaranarayanan et al. 2011; Ali et al. 2002; Marín et al. 2005).

Several studies have applied zeolites for naphtha reforming and cracking processes. Akiyama et al. (2017) used H-ZSM5 zeolite for catalytic cracking of naphtha. They found that H-ZSM5 silylated by cyclic siloxanes such as tetramethylcyclotetrasiloxane (TMCTS) and pentamethylcyclopentasiloxane (PMCPS) has more durability for the catalytic cracking of *n*-hexane than H-ZSM5 silylated by other silylation compounds. Hodala et al. (2016) examined modified ZSM5 with zinc and gallium (ZnGa/H-ZSM5) for aromatization of *n*-hexane (model compound for light naphtha). They reported that the ZnGa/H-ZSM5 catalyst produced aromatics in high yields (64.8% for light naphtha), especially high quantities of toluene with toluene/benzene ratio (T/B) ~ 2. Soto and Marín (2000) investigated Pt supported on zeolites for hydrocracking of heavy straight-run naphtha. They reported that among Y zeolite-supported catalysts, Pt/dealuminated Y zeolites are more active than Pt/Y. Saxena et al. (2014) studied the enhanced catalytic isomerization of naphtha over BEA zeolite. They found that the catalyst (Pt-BEA-2) exhibited promising catalytic activity for the production of branched paraffins from pure paraffin compound n-heptane as well as from naphtha-1 and naphtha-2. They reported that low acid density, high acid strength (strong acidity measured by heat of adsorption of ammonia > 100 kJ/mol), enhanced mesopores in combination with highly dispersed Pt sites on the Pt-BEA-2 zeolite catalyst seem to be responsible for the effective formation of isomers to contribute to the significant increase in the RON of the product suitable for gasoline applications. Corma et al. (2013) applied IM-5 zeolite for steam catalytic cracking of naphtha. They mentioned that the incorporation of phosphorous in IM-5 zeolite is able to reduce the deactivation by dealumination during steam catalytic cracking process. This treatment significantly reduces the strong dependency of the dealumination with the temperature in this zeolite. Viswanadham et al. (2013) examined Pt over zeolites such as nano-ZSM-5 (NZ), BEA (BZ) and mordenite (MZ) for naphtha reforming process. As shown in Table 5, the conversion of nC_7 is maximum on MZ (~ 41%), followed by BZ and NZ. They stated that the higher conversions on MZ can be ascribed to the strong acidity of the mordenite. It also can be seen that the octane boosting is high on MZ catalyst but not on BZ. This can be understood from the composition of isoparaffins, where the high amount of lower isoparaffins (iC_4–iC_6) formed through cracking on MZ contributes more to the octane gain. Though the high acidity of MZ causes decrease in C_7+ isomer yield, the formation of lower isoparaffins (iC_5–iC_6) facilitated through cracking on this catalyst contributes to the octane boosting reaction. Higher iC_4–iC_6 formation on MZ may also be due to its narrow range pores and diffusion limitation of longer isoparaffins through the side pockets of the mordenite.

Historical aspects of zeolite

Researchers have dedicated great studies to develop a new process that can defeat the lack of steam cracking. In order to attain higher light olefin yield, various kinds of catalysts have been deliberated in the catalytic hydrocarbon cracking (Wei et al. 2005; Rahimi and Karimzadeh 2011). From the time of 1960, the use of SrO, $A1_2O_3$, ZrO_2, MnO_2, MgO, In_2O_3, TiO_2, Mn_2O_3, K_2O metal oxides in the production of olefin has been explored. Dependent on the type of feed and the reaction condition, 15–22% of propylene yield and 24–40% of ethylene yield have been achieved using metal oxide catalysts (Zhagfarov et al. 2005). It was found that the ethylene yield from naphtha was improved by 5–10%, at 1043–1093 K in comparison with the conventional steam cracking (Mukhopadhyay and Kunzru 1993; Basu and Kunzru 1992; Lee et al. 2004). There are studies were focused

Table 5 *n*-Heptane isomerization performance of Pt/zeolites. (Reproduced with permission from Viswanadham et al. 2013)

Catalysts	NZ	MZ	BZ	BZ1	BZ1	BZ1	BZ1
Pressure (bar)	20	20	20	10	15	20	25
Conversion (wt%)	26.8	40.6	35.5	68.4	70.7	72.2	74.2
Gas yield (wt%)	7.8	14.2	4.4	5	3.5	3.5	4.2
Liquid yield (wt%)	92.2	85.8	95.6	95	96.5	96.5	95.8
Product composition (wt%)							
Total paraffins	81	73.6	68.9	36.6	32.8	31.3	30
Cracked paraffins (C_1–C_6)	7.8	14.2	4.4	5	3.5	3.5	4.2
n-heptane	73.2	59.4	64.5	31.6	29.3	27.8	25.8
Total i-paraffins	17.8	26.4	27.5	62.5	64.4	66.4	67.2
Lower i-paraffins (iC_4–iC_6)	4.8	7.7	5.1	9.2	8	9.4	9.8
C_7 + i-paraffins	13	18.7	22.4	53.3	56.4	57	57.4
Mono-branched	11.3	14.7	18.2	41.1	43.4	43.4	44.2
Di-branched	1.7	4	2.7	11.7	12.4	13.1	13
Multi-branched	0	0	1.5	0.5	0.6	0.5	0.2
Olefins	0.1	0	1.2	0.1	0.1	0	0.1
Naphthenes	1	0	2.3	0.7	2.5	2.2	2.4
Aromatics	0	0	0	0	0.1	0	0.1
Unidentified	0.1	0	0.1	0.1	0.1	0.1	0.2
Total	100	100	100	100	100	100	100
Research octane number (RON)	16.2	25.3	35	47.3	45.3	47.3	48.6

Reaction condition: temperature = 280 °C, WHSV = 2 h^{-1}, H_2/HC = 4 mol/mol on the production of light olefin from hydrocarbons catalytic cracking using zeolites before 1990s. Due to completely developed process of industrial steam cracking, less investigation was done on the light olefin production (especially ethylene) over zeolites (Bellussi and Pollesel 2005). Researchers after 1990s have investigated on catalysts formulation that can increase the selectivity to both propylene and ethylene and in hydrocarbons catalytic cracking.

Zeoforming process

In order to produce lead-free high-octane gasoline by low-octane gasoline fractions refining, zeoforming technique using zeolite catalyst is recommended. It was developed by the SEC Zeosit of the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (BIC SB RAS), Novosibirsk, and industrially adopted (Stepanov and Ione 2003). It is a first-generation technology and allows for the manufacturing of different types of high-octane automotive gasolines without compoundation and the use of anti-knocking agents. The process is utilized for the conversion of straight-run gasoline fractions with a boiling temperature below 200 °C into high-octane fuels in the presence of zeolite catalysts. Zeoforming is based on acid–base active catalysts (type IC-30) containing artificial zeolites with a high content of silica. The catalyst was developed by BIC SB RAS (Stepanov and Ione 2003; Velichkina 2009).

The reactions of the aromatization of intermediately formed olefins, alkylation and the disproportioning of aromatics result in the formation of hydrocarbon fractions boiling above 150 °C; moreover, the increase in the temperature of the process (to obtain a higher octane number of gasolines manufactured) favors a boiling temperature elevation to 220–280 °C. This determines the necessity of the following separation of the resulting mixtures in a rectification column to separate the gasoline fraction and a higher boiling residue. The formation of heavier gasoline fractions during zeoforming allows for the processing of relatively low boiling hydrocarbon fractions (BP = 100–140 °C) to prepare gasolines boiling in the range of 35–215 °C.

The use of a stabilization column in the technological scheme provides the way to regulate the pressure of gasoline saturated vapor within a wide range, determined by standards GOST (State Standard) 2084-77 or GOST (State Standard) R 51105-97 (Stepanov and Ione 2003).

Advantageously, the process of zeoforming is not sensitive toward various compounds of sulfur, which are always present in oil and liquid gas petroleum. During the process, in an IC-30 type of catalyst a sequence of reactions occurs and sulfur-containing species is converted into paraffins, aromatic hydrocarbons and hydrogen sulfide. As shown in Fig. 3, the C–S bond of mercaptanes, sulfides, thiophenes or their derivatives is cleaved and the molecules of hydrogen sulfide and olefins are released. Then, the intermediate olefins undergo the following conversions leading to paraffins and aromatics, while hydrogen sulfide is separated along with side products of the entire process—a gaseous C_1–C_4 species.

The catalytic activity of the catalysts for the zeoforming process is highly stable in the absence of gaseous hydrogen (non-reductive media); thus, technologically the catalyst can be organized as an immobile permanent layer. The verification of the process was performed in 1982–1990 using pilot equipment and original authentic raw materials (Stepanov and Ione 2003; Stepanov 2005).

The process was accepted in industry both in Russia and abroad (Krumpelt et al. 2005; Zinnen 1999). The first pilot plant based on the process of zeoforming was employed in the Nizhnevartovsk gas processing plant in August 1992 with a production capacity of 5000 tons of raw material per annum. The octane number has been achieved at a rate of 80–82 (MON) with a production yield of 82–85%. The period between service regeneration depended on the quality of the starting materials and varied in the range 220–300 h. The Glimar oil refinery (Gorlice, Poland) started to produce unleaded gasoline of the type Eurosuper-95 with an

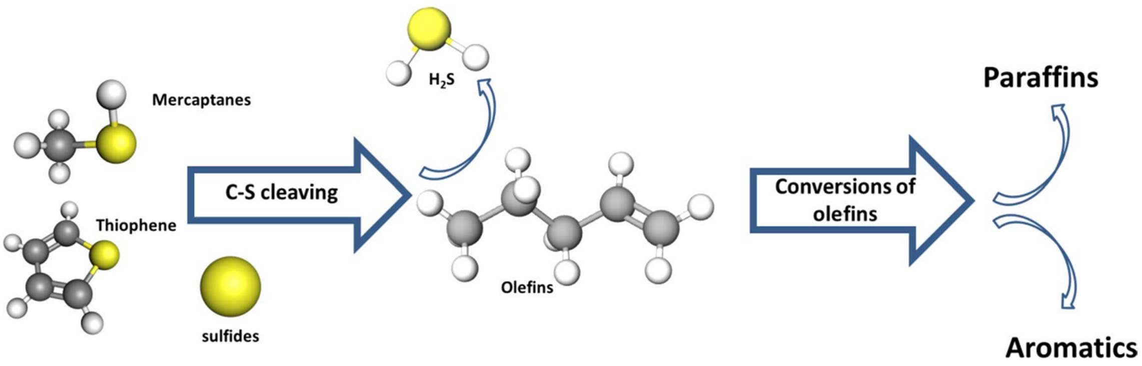

Fig. 3 Conversion of sulfur-containing species during the zeoforming process

octane number of 85 (MON) or 95 (RON) using straight-run gasoline as a starting material in February 1997. The production capacity was 40000 tons of raw materials per annum. The yields of the target products achieved—gasoline Eurosuper-95 and liquidized natural gas—were 62–70 and 22–30%, respectively. The period between service regeneration varied within 250–350 h with a full period of activity of not less than 2 years. Another plant based on the process of zeoforming was launched at the Azot production complex (Rustavi, Georgia) with a production capacity of 30,000–40,000 tons of raw material per annum (depending on the scheme of manufacturing). The plant produces the following target products: gasolines of AI-80, AI-92 and AI-95 types (depending on the scheme), as well as liquidized gas (technical-grade mixture of propane and butanes).

The technology of zeoforming is easy in maintenance and requires minor amounts of supporting materials only. Therefore, plants of different capacity can be set as a part of oil refinery complexes, as well as separate units at remote oil and liquid petroleum gas mining sites.

At present, two different versions of zeoforming have been developed—zeoforming itself (original version) and zeoforming combined with the pyrolysis of light hydrocarbons (Stepanov and Ione 2003). The last version allows for the use of other types of raw materials for gasoline production, namely a broad fraction of light hydrocarbons and light components C2–C4 of flashed gases and of well sites of liquid petroleum gas. As said before, the conversion of heavier fractions (BP up to 360 °C) by means of the zeoforming process is possible but not efficient due to the lower yields and lower cetane number of diesel fractions which can be achieved.

In general, the method requires rather low start-up and maintenance costs, its technical realization is rather simple, and it represents a much lower (in comparison with catalytic reforming) fire and explosion danger due to the absence of gaseous hydrogen and low sensitivity toward the composition and quality of raw materials. All of these make the method a profitable and preferable solution for low-capacity plants far from big oil refineries (production capacity 5000–100,000 tons of raw materials per annum) located in remote regions near oil or liquid petroleum gas well sites as a supply of motor fuel (automotive gasoline and diesel fuel) in these regions. Larger zeoforming-based plants (up to 300,000 tons of raw materials per annum) can be operated effectively as part of a big oil refinery complex.

Zeolite-based-supported hydrodesulfurization catalysts

Currently, the reported zeolite-based supports for hydrodesulfurization (HDS) catalysts mainly included alumina-mixed zeolites, other component-mixed zeolites, nanosized zeolites and hierarchical zeolites.

Alumina-mixed zeolites as support The combination of zeolite and alumina is able to produce hierarchical pores in support because of the rich meso-/macropores in alumina, which would improve both the diffusion of reactant and the dispersion of active phase. Most of the studies indicated that zeolite–alumina-supported catalyst showed higher activity than alumina-supported catalyst (Isoda et al. 1996; Nakano et al. 2013; Wan et al. 2010a, b; Yao et al. 2012; Sankaranarayanan et al. 2011; Ali et al. 2002; Marín et al. 2005). Ding et al. (2006) studied the catalytic performance over alumina-Beta and alumina-Y-supported catalyst. The results displayed that alumina-Beta-supported catalyst gave relatively low sulfur content and polyaromatics in the HDS reaction of light cycle oil (LCO). Moreover, the effect of the content of Beta in support on catalytic performance was also investigated. The results showed that the catalyst with 10 wt% Beta had superior HDS and hydrodearomatization (HDA), activity in the presence of 1-methylnaphthalene (Table 6). Certainly, the optimal content could be different due to the difference of used zeolite. For example, Duan et al. (2011) and Wan et al. (2009) found that the catalyst with 32 wt% Beta synthesized by in situ hydrothermal crystallization method was the most efficient in HDS reaction. The similar phenomenon was also observed by Yao et al. (2012).

On the other hand, preparation method of catalyst had an influence on catalytic performance. Duan et al. (2009) prepared the alumina-USL-supported catalysts by the direct mixed method and in situ synthetic method. The result showed that the catalyst obtained by in situ synthetic method had higher HDS and hydrodenitrogenation (HDN) activity than that by direct mixed method. The catalyst with 10 wt% USL exhibited the highest activity. Additionally, Kunisada et al. (2004) synthesized the alumina-USY support by the coating technique. They found that the HDS catalyst supported on such support had less cracking of hydrocarbons than that supported on direct mixed support (Kunisada et al. 2004). Further, Nakano et al. (2013) suggested that the HDS activity could be controlled by the change in the coating ratio and the sulfur content could be reduced to 4.8 from 15,400 ppm in diesel.

Table 6 Optimal content of zeolite in the alumina-mixed zeolite support. (Reproduced with permission from Wang et al. 2014)

Catalyst	Loading content (%)	Optimal content
NiMo/Al_2O_3-Beta	0–20	10
NiMo/Al_2O_3-nanobeta	0–46	32
NiMo/Al_2O_3-nanobeta	7.5 and 15	15
NiMo/Al_2O_3-HNaY	0–20	5
NiMo/Al_2O_3-USL	0–40	10

Acidity of zeolites

The global acidity of a given zeolite is the result, among other things, of two parameters characteristic of Brønsted sites, i.e., their density (or their concentration) and their strength (Marcilly 2006). The density of Brønsted acid sites decreases when the Si/Al ratio of the zeolitic framework increases (Rahimi and Karimzadeh 2011; Marcilly 2006; Maxwell and Stork 2001), since the ion exchange capacity corresponds to the Al^{3+} content of the zeolites (Hagen 2006). The zeolites are categorized according to increasing Si/Al ratio and the associated with the properties of acid/base (Table 7).

The Brønsted site strength can be determined by the interaction between the proton and the zeolitic framework or the environment of the framework Al (Marcilly 2006). The strongest Brønsted acid site type can be created by completely isolated Al tetrahedron. The chemical composition of the zeolite and its structural characteristics are the two main governing parameters of the Brønsted site acid strength. The structural characteristic of the zeolite is related to the proton lability that depends on the angle formed between the two adjacent tetrahedral T at the oxygen carrying the proton (Marcilly 2006). The number of aluminate tetrahedral that are adjacent to a silicate tetrahedron group are controlling the acid strength in regard to the composition of chemical (Marcilly 2006; Hagen 2006). The highest proton–donor strengths are exhibited by zeolites with the lowest concentrations of AlO_4^- tetrahedral such as HZSM-5 and the ultrastable zeolite HY.

The Lewis acid sites are related to the formation of positively charged oxide clusters or ions within the porous structures of the zeolites (Amin and Ammasi 2006). They are typically related to the metal ions exchanged for the acid site protons or the species of extra-framework Al (EFAL) formed by aluminum extraction from the lattice (Marcilly 2006; Corma and Orchillés 2000). These metal cations together with the adjacent framework oxygens may polarize bonds in reacting molecules and will act as Lewis acid/base pair (Amin and Ammasi 2006). It has been also suggested that the reduction in the Brønsted acid site concentration in the framework cause by the extra-framework trivalent Al species (formation of hydroxyaluminate species in the microporosity) (Marcilly 2006). Commonly, the strength of the nearby OH Brønsted acid sites is increased due to the presence of Lewis acid sites; it is because of a synergistic or an inductive effect between the Brønsted and the Lewis acid sites (Marcilly 2006; Babitz et al. 1999). Additionally, most of the thiophene sulfur compounds in transportation fuels are Lewis base, which are adsorbed at Lewis acid sites easily according to Lewis acid–base theory (Zhang et al. 2015).

Comparison of different active phases

Navarro et al. (Navarro et al. 1999) evaluated the catalytic performance of different noble and semi-noble metals supported on HUSY. The results suggested that the order of catalytic activity is Ir > Pt > Pd > Ru ≫ Ni (Table 8). The comparison between zeolite-supported NiMo and CoMo catalysts seemed to depend on the reaction temperature. Azizi et al. (2013) found that alumina-coated zeolite-supported CoMo catalyst was more active at high temperature (360 °C) but less active at 340 °C than that supported NiMo catalyst.

Table 8 Comparison between different active phases on zeolites. (Reproduced with permission from Wang et al. 2014)

Support	Reaction temperature (°C)	Active phases
HUSY	320	Ir > Pt > Pd > Ru ≫ Ni
Alumina-coated zeolite	340	NiMo > NiW
Alumina-coated zeolite	360	CoMo > NiMo
Beta	400	CoMo > NiMo
Beta	400	W > Mo
Alumina-beta	375	NiMo > NiW
Alumina-nanobeta	375	NiW > NiMo
Alumina-ASA-beta/USY	380–410	NiW > NiMo

Table 7 Classification of acidic zeolites according to increasing Si/Al ratio. (Reproduced with permission from Hagen 2006)

Si/Al ratio	Zeolites	Acid/base properties
Low (1–1.5)		Relatively low stability of lattice Low stability in acids High stability in bases High concentration of acid groups of Medium strength
Medium (2–5)	Erionite, chabazite, chinoptilolite, mordenite, Y	
High (ca. 10–∞)	ZSM-5; Dealuminated Erionite, mordenite, Y	Relatively high stability of the lattice High stability in acids Low stability in bases Low concentration of acid groups of High strength

The other group also observed that Beta-supported CoMo catalyst gave higher activity than that supported NiMo catalyst at a reaction temperature of 400 °C (Kumaran et al. 2006). The comparison between active phase W and Mo is difficult because the optimal content of two metals in support could be different. For instance, the optimal loading content is 6 wt% for Mo and 17 wt% for W over pure Beta zeolite, respectively (Kumaran et al. 2006a, b).

The comparison of active phase NiMo and NiW took place over the desulfurization of vacuum gasoil (2890 ppmw) with the loading content of 4% wt NiO and 15 wt% MoO3/WO3 (10% Mo and 11.9% W, respectively) (Ali et al. 2002). The results suggested that NiW supported on alumina-ASA-USY/Beta generally had relatively high catalytic activity in the range of reaction temperature from 380 to 410 °C. However, NiW catalyst was very sensitive to the particle size of zeolite support and NiMo catalyst was inert. For example, microsized Beta-supported NiW catalyst showed lower activity than that supported NiMo catalyst. But nanosized Beta-supported NiW catalyst showed higher activity than that supported other catalysts (Ding et al. 2009).

Catalyst deactivation

The loss of catalyst activity during the reforming reaction or deactivation is one of the major problems related to the operation of heterogeneous catalysis. This process is of both chemical and physical nature and occurs simultaneously with the main reaction. Deactivation can occur by a number of different mechanisms, both chemical and physical in nature. These are commonly divided into four classes, namely poisoning, coking or fouling, sintering and phase transformation. Other mechanisms of deactivation include masking and loss of the active elements via volatilization, erosion and attrition (Forzatti and Lietti 1999).

Choice of reactor

Similar to other catalytic materials development, there have been several methods regarding the reactor and processes design. These methods came up in order to address the major problem of coke formation and enhance process performance. For study of catalytic reactions in laboratory, different reactors have been used. Laboratory reactors are mainly used for measuring reaction kinetics and catalyst activity at different conditions of temperature and pressure. For the continuous process of zeoforming, the fluidized-bed reactor is preferred. In the fluidized-bed reactors, the deposited coke on the catalyst surface can be gasified easily. As a result, it allows for more continuous process (Galdámez et al. 2005). Fluidized-bed reactors are capable of handling large amounts of feed and catalyst. But fixed-bed reactors were commonly used in previous researches with solid catalysts for catalytic reforming process. The packed-bed or fixed-bed reactors are most common used for study of gas phase reactants using solid catalyst for the synthesis of large-scale basic chemicals and intermediates (Andrigo et al. 1999; Eigenberger and Ruppel 2000). In addition to the valuable chemicals synthesis, fixed-bed reactors have been progressively applied in recent years for toxic and harmful materials treatment (Andrigo et al. 1999). Figure 4 shows a schematic flow diagram of fixed-bed reactor. It is typically made up of a cylindrical vessel packed with catalyst pellets. Moreover, it is easy to design, control and operate. The lower maintenance cost and reduced catalyst loss due to attrition and wear are other advantages of fixed-bed reactor over the fluidized bed. These make the fixed-bed reactor more preferred for zeoforming process.

Recommendations

Researches related to reforming of naphtha have taken new dimensions toward improving it to become an efficient candidate technology in the future global energy scenario. In summary, further work on the development of catalyst and new process for naphtha reforming is proposed as follows

a. To explore new material to achieve high activity with low reaction temperature.
b. Investigation on the catalytic performance of nano- and macrostructure catalysts.
c. Better reactor configuration and scale-up procedure such as using plasma reactor for reforming reaction.
d. Optimization of naphtha reforming for high-octane gasoline production by response surface methodology.

Conclusion

In this work, an overview of catalytic naphtha reforming process in order to produce high-octane gasoline including sulfur compounds in naphtha, HDS, catalysts used and zeoforming process is presented. The presence of sulfur in naphtha has a negative effect on the performance of catalysts. HDS is a catalytic chemical process widely used to remove sulfur from refined petroleum products. From the studies reported so far, adding third metals to bimetallic catalysts can enhance the catalysts function. The metal and acid functions, activity and resistance to coke deposition can be improved by third metal in HDS process. Another option is using zeolites in the reforming of naphtha (zeoforming) instead of noble metals. In high-octane gasoline production and long-term stability, zeolites are recognized as suitable catalysts due to their basic

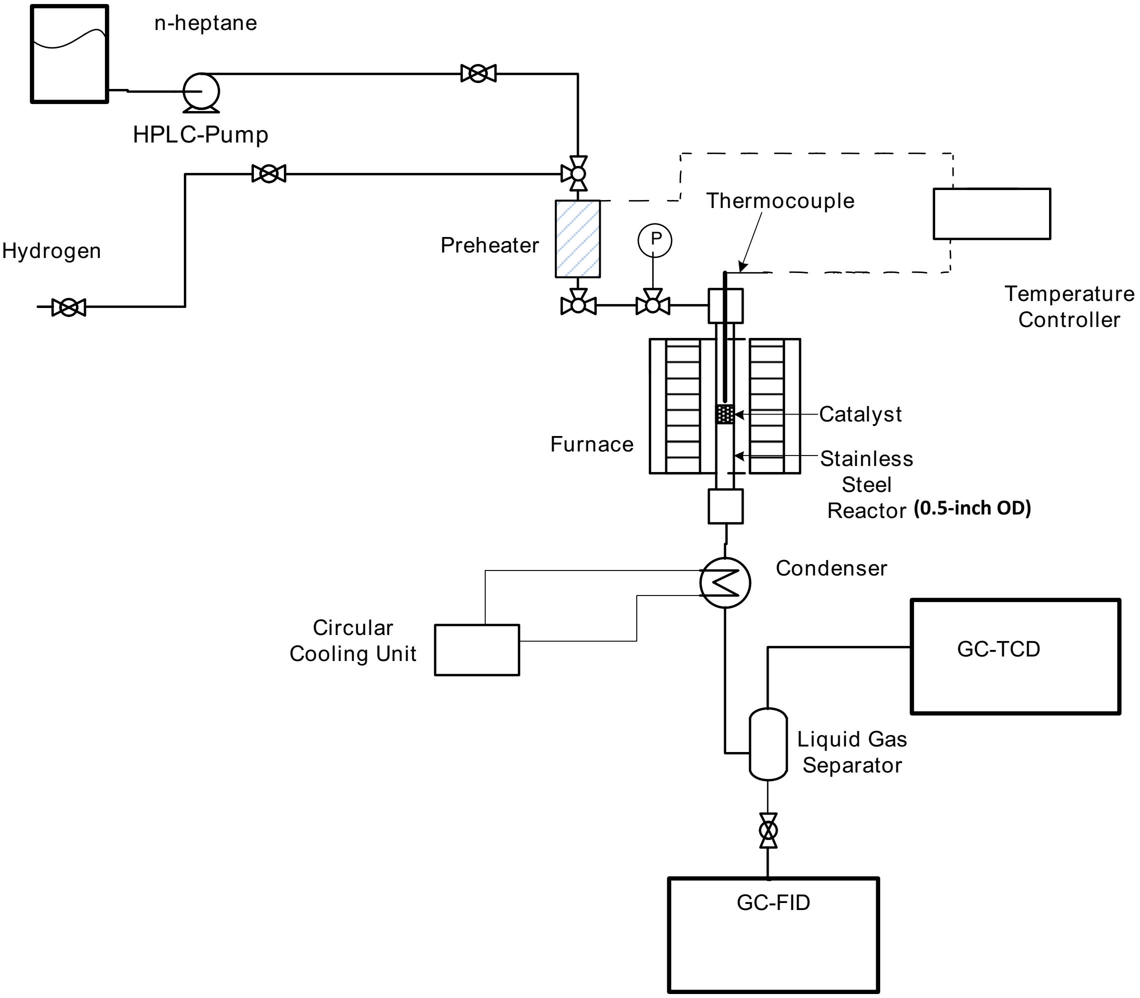

Fig. 4 Schematic diagram of a fixed-bed reactor system used

character. Additionally, the process of zeoforming is not sensitive toward various compounds of sulfur; thus, zeoforming process appears to be the ultimate option for high-octane gasoline production. Among the naphtha reforming techniques, reforming of naphtha using fixed-bed reactor can be regarded as the most suitable method. It can be concluded that zeoforming process will be much more efficient than the conventional processes because the zeolite-based catalysts do not need noble active metal and desulfurization process.

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References

Absi-Halabi M, Stanislaus A, Al-Dolama K (1998) Performance comparison of alumina-supported Ni–Mo, Ni–W and Ni–Mo–W catalysis in hydrotreating vacuum residue. Fuel 77:787–790. https://doi.org/10.1016/S0016-2361(97)00228-7

Akiyama S, Mochizuki H, Yamazaki H, Yokoi T, Tatsumi T, Kondo JN (2017) The effective silylation of external surface on H-ZSM5 with cyclic siloxane for the catalytic cracking of naphtha. Mol Catal 433:48–54. https://doi.org/10.1016/j.mcat.2016.12.005

Ali MA, Tatsumi T, Masuda T (2002) Development of heavy oil hydrocracking catalysts using amorphous silica-alumina and zeolites as catalyst supports. Appl Catal A 233:77–90. https://doi.org/10.1016/S0926-860X(02)00121-7

Amin NAS, Ammasi S (2006) Dual-bed catalytic system for direct conversion of methane to liquid hydrocarbons. J Nat Gas Chem 15:191–202. https://doi.org/10.1016/S1003-9953(06)60026-1

Andrigo P, Bagatin R, Pagani G (1999) Fixed bed reactors. Catal Today 52:197–221. https://doi.org/10.1016/S0920-5861(99)00076-0

Antos GJ (1977) Dehydrocyclization with an acidic multimetallic catalytic composite. US Patent 4032587

Antos GJ (1982) Attenuated superactive multimetallic catalytic composite. US Patent 4229319

Antos GJ, Aitani AM (2004) Catalytic naphtha reforming, revised and expanded. Taylor & Francis, Oxfordshire

Azizi N, Ali SA, Alhooshani K, Kim T, Lee Y, Park J-I et al (2013) Hydrotreating of light cycle oil over NiMo and CoMo catalysts with different supports. Fuel Process Technol 109:172–178. https://doi.org/10.1016/j.fuproc.2012.11.001

Babitz SM, Williams BA, Miller JT, Snurr RQ, Haag WO, Kung HH (1999) Monomolecular cracking of *n*-hexane on Y, MOR, and ZSM-5 zeolites. Appl Catal A 179:71–86. https://doi.org/10.1016/S0926-860X(98)00301-9

Baghalha M, Mohammadi M, Ghorbanpour A (2010) Coke deposition mechanism on the pores of a commercial Pt–Re/γ-Al_2O_3 naphtha reforming catalyst. Fuel Process Technol 91:714–722. https://doi.org/10.1016/j.fuproc.2010.02.002

Bariås OA, Holmen A, Blekkan EA (1996) Propane dehydrogenation over supported Pt and Pt–Sn catalysts: catalyst preparation, characterization, and activity measurements. J Catal 158:1–12. https://doi.org/10.1006/jcat.1996.0001

Basu B, Kunzru D (1992) Catalytic pyrolysis of naphtha. Ind Eng Chem Res 31:146–155. https://doi.org/10.1021/ie00001a021

Bellussi G, Pollesel P (2005) Industrial applications of zeolite catalysis: production and uses of light olefins. Stud Surf Sci Catal 158:1201–1212. https://doi.org/10.1016/S0167-2991(05)80466-5

Benitez VM, Pieck CL (2010) Influence of indium content on the properties of Pt–Re/Al_2O_3 naphtha reforming catalysts. Catal Lett 136:45–51. https://doi.org/10.1007/s10562-009-0202-x

Benitez V, Boutzeloit M, Mazzieri VA, Especel C, Epron F, Vera CR et al (2007) Preparation of trimetallic Pt–Re–Ge/Al_2O_3 and Pt–Ir–Ge/Al_2O_3 naphtha reforming catalysts by surface redox reaction. Appl Catal A 319:210–217. https://doi.org/10.1016/j.apcata.2006.12.006

Benitez VM, Vera CR, Rangel MAC, Yori JC, Grau JM, Pieck CL (2008) Modification of multimetallic naphtha-reforming catalysts by indium addition. Ind Eng Chem Res 48:671–676. https://doi.org/10.1021/ie800933s

Borgna A, Garetto TF, Apesteguía CR, Moraweck B (1999) Formation of bimetallic alloys in naphtha reforming Pt–Ge/Al_2O_3 catalysts: an EXAFS study. Appl Catal A 182:189–197. https://doi.org/10.1016/S0926-860X(99)00010-1

Borgna A, Garetto TF, Apesteguía CR (2000) Simultaneous deactivation by coke and sulfur of bimetallic Pt–Re(Ge, Sn)/Al_2O_3 catalysts for *n*-hexane reforming. Appl Catal A 197:11–21. https://doi.org/10.1016/S0926-860X(99)00528-1

Boutzeloit M, Benitez VM, Mazzieri VA, Especel C, Epron F, Vera CR et al (2006) Effect of the method of addition of Ge on the catalytic properties of Pt–Re/Al_2O_3 and Pt–Ir/Al_2O_3 naphtha reforming catalysts. Catal Commun 7:627–632. https://doi.org/10.1016/j.catcom.2006.01.029

Brunet S, Mey D, Pérot G, Bouchy C, Diehl F (2005) On the hydrodesulfurization of FCC gasoline: a review. Appl Catal A 278:143–172. https://doi.org/10.1016/j.apcata.2004.10.012

Carvalho LS, Pieck CL, Rangel MC, Fígoli NS, Grau JM, Reyes P et al (2004a) Trimetallic naphtha reforming catalysts. I. Properties of the metal function and influence of the order of addition of the metal precursors on Pt–Re–Sn/γ-Al_2O_3–Cl. Appl Catal A 269:91–103. https://doi.org/10.1016/j.apcata.2004.04.004

Carvalho LS, Pieck C, Rangel M, Fıgoli N, Vera C, Parera JM (2004b) Trimetallic naphtha reforming catalysts: II. Properties of the acid function and influence of the order of addition of the metallic precursors on Pt–Re–Sn/γ-Al_2O_3–Cl. Appl Catal A 269:105–116. https://doi.org/10.1016/j.apcata.2004.04.006

Corma A, Orchillés AV (2000) Current views on the mechanism of catalytic cracking. Microporous Mesoporous Mater 35:21–30. https://doi.org/10.1016/S1387-1811(99)00205-X

Corma A, Martínez C, Ketley G, Blair G (2001) On the mechanism of sulfur removal during catalytic cracking. Appl Catal A 208:135–152. https://doi.org/10.1016/S0926-860X(00)00693-1

Corma A, Mengual J, Miguel PJ (2013) IM-5 zeolite for steam catalytic cracking of naphtha to produce propene and ethene. An alternative to ZSM-5 zeolite. Appl Catal A 460–461:106–115. https://doi.org/10.1016/j.apcata.2013.02.030

D'Ippolito SA, Vera CR, Epron F, Samoila P, Especel C, Marécot P et al (2009) Influence of tin addition by redox reaction in different media on the catalytic properties of Pt-Re/Al_2O_3 naphtha reforming catalysts. Appl Catal A 370:34–41. https://doi.org/10.1016/j.apcata.2009.09.012

de Miguel S, Castro A, Scelza O, Fierro JLG, Soria J (1996) FTIR and XPS study of supported PtSn catalysts used for light paraffins dehydrogenation. Catal Lett 36:201–206. https://doi.org/10.1007/bf00807620

Ding L, Zheng Y, Zhang Z, Ring Z, Chen J (2006) Hydrotreating of light cycled oil using WNi/Al_2O_3 catalysts containing zeolite beta and/or chemically treated zeolite Y. J Catal 241:435–445. https://doi.org/10.1016/j.jcat.2006.05.004

Ding L, Zheng Y, Yang H, Parviz R (2009) LCO hydrotreating with Mo–Ni and W–Ni supported on nano-and micro-sized zeolite beta. Appl Catal A 353:17–23. https://doi.org/10.1016/j.apcata.2008.10.023

Duan A, Gao Z, Huo Q, Wang C, Zhang D, Jin M et al (2009) Preparation and evaluation of the composite containing USL zeolite-supported NiW catalysts for hydrotreating of FCC diesel. Energy Fuels 24:796–803. https://doi.org/10.1021/ef901098m

Duan A, Wan G, Zhang Y, Zhao Z, Jiang G, Liu J (2011) Optimal synthesis of micro/mesoporous beta zeolite from kaolin clay and catalytic performance for hydrodesulfurization of diesel. Catal Today 175:485–493. https://doi.org/10.1016/j.cattod.2011.03.044

Duarte FA, Mello P, Bizzi CA, Nunes MAG, Moreira EM, Alencar MS et al (2011) Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process. Fuel 90:2158–2164. https://doi.org/10.1016/j.fuel.2011.01.030

Eigenberger G, Ruppel W (2000) Catalytic fixed-bed reactors. Ullmann's encyclopedia of industrial chemistry. Wiley, London. https://doi.org/10.1002/14356007.b04_199.pub2

Epron F, Carnevillier C, Marécot P (2005) Catalytic properties in n-heptane reforming of Pt–Sn and Pt–Ir–Sn/Al_2O_3 catalysts prepared by surface redox reaction. Appl Catal A 295:157–169. https://doi.org/10.1016/j.apcata.2005.08.006

Forzatti P, Lietti L (1999) Catalyst deactivation. Catal Today 52:165–181. https://doi.org/10.1016/S0920-5861(99)00074-7

Galdámez JR, García L, Bilbao R (2005) Hydrogen production by steam reforming of bio-oil using coprecipitated Ni–Al catalysts. Acetic acid as a model compound. Energy Fuels 19:1133–1142. https://doi.org/10.1021/ef049718g

Gomez R, Bertin V, Bosch P, Lopez T, Del Angel P, Schifter I (1993) Pt–Sn/Al_2O_3 sol–gel catalysts: metallic phase characterization. Catal Lett 21:309–320. https://doi.org/10.1007/bf00769483

González-Marcos MP, Iñarra B, Guil JM, Gutiérrez-Ortiz MA (2005) Development of an industrial characterisation method for naphtha reforming bimetallic Pt-Sn/Al_2O_3 catalysts through n-heptane reforming test reactions. Catal Today 107–108:685–692. https://doi.org/10.1016/j.cattod.2005.07.052

Haensel V (1949) US Patents 2479109, 2479110. UOP

Haensel V, Hills C, Gerald CF (1949) Reforming process. US Patent 2478918

Hagen J (2006a) Industrial catalysis: A Practical Approach. Wiley, London, p 2006

Hagen J (2006b) Shape-selective catalysis: zeolites. Industrial catalysis: a practical approach, vol 2. Wiley, London, pp 239–259. https://doi.org/10.1002/3527607684.ch7

Hamoule T, Peyrovi MH, Rashidzadeh M, Toosi MR (2011) Catalytic reforming of n-heptane over Pt/Al-HMS catalysts. Catal Commun 16:234–239. https://doi.org/10.1016/j.catcom.2011.09.020

Hansel V (1949) U.S. Patents 2479101 and 2479110. UOP

Harandi MN, Greeley JP, Chuba MR, Lu BC (2017) Production of low sulfur gasoline. US Patent 20170015915

Hodala JL, Halgeri AB, Shanbhag GV, Reddy RS, Choudary NV, Rao PVC et al (2016) Aromatization of C5-rich light naphtha feedstock over tailored zeolite catalysts: comparison with model compounds (n-C5–n-C7). Chem Sel 1:2515–2521. https://doi.org/10.1002/slct.201600412

Isoda T, Nagao S, Ma X, Korai Y, Mochida I (1996) Hydrodesulfurization pathway of 4, 6-dimethyldibenzothiophene through isomerization over Y-zeolite containing CoMo/Al_2O_3 catalyst. Energy Fuels 10:1078–1082. https://doi.org/10.1021/ef960048r

Krumpelt M, Kopasz JP, Ahmed S, Kao RL, Randhava SS (2005) Autothermal hydrodesulfurizing reforming method and catalyst. US Patent 6967063

Kulprathipanja S, Nemeth LT, Holmgren JS (1998) Process for removing sulfur compounds from hydrocarbon streams. US Patent 5807475

Kumaran GM, Garg S, Soni K, Prasad V, Sharma L, Dhar GM (2006a) Catalytic functionalities of H-β-zeolite-supported molybdenum hydrotreating catalysts. Energy Fuels 20:1784–1790. https://doi.org/10.1021/ef060134j

Kumaran GM, Garg S, Kumar M, Viswanatham N, Gupta J, Sharma L et al (2006b) Origin of hydrocracking functionality in β-zeolite-supported tungsten catalysts. Energy Fuels 20:2308–2313. https://doi.org/10.1021/ef0602527

Kunisada N, Choi K-H, Korai Y, Mochida I, Nakano K (2004a) Optimization of silica content in alumina–silica support for NiMo sulfide to achieve deep desulfurization of gas oil. Appl Catal A 273:287–294. https://doi.org/10.1016/j.apcata.2004.06.045

Kunisada N, Choi K-H, Korai Y, Mochida I, Nakano K (2004b) Novel zeolite based support for NiMo sulfide in deep HDS of gas oil. Appl Catal A 269:43–51. https://doi.org/10.1016/j.apcata.2004.03.051

Lee KX, Valla JA (2017) Investigation of metal-exchanged mesoporous Y zeolites for the adsorptive desulfurization of liquid fuels. Appl Catal B 201:359–369. https://doi.org/10.1016/j.apcatb.2016.08.018

Lee W-H, Jeong SM, Chae JH, Kang J-H, Lee W-J (2004) Coke formation on KVO3–B2O3/SA5203 catalysts in the catalytic pyrolysis of naphtha. Ind Eng Chem Res 43:1820–1826. https://doi.org/10.1021/ie030522y

Leflaive P, Lemberton JL, Pérot G, Mirgain C, Carriat JY, Colin JM (2002) On the origin of sulfur impurities in fluid catalytic cracking gasoline—reactivity of thiophene derivatives and of their possible precursors under FCC conditions. Appl Catal A 227:201–215. https://doi.org/10.1016/S0926-860X(01)00936-X

Lü H, Ren W, Wang H, Wang Y, Chen W, Suo Z (2013) Deep desulfurization of diesel by ionic liquid extraction coupled with catalytic oxidation using an Anderson-type catalyst [(C4H9)4N]4NiMo6O24H6. Appl Catal A 453:376–382. https://doi.org/10.1016/j.apcata.2012.12.047

Lü H, Deng C, Ren W, Yang X (2014) Oxidative desulfurization of model diesel using [(C4H9)4N]6Mo7O24 as a catalyst in ionic liquids. Fuel Process Technol 119:87–91. https://doi.org/10.1016/j.fuproc.2013.10.023

Marcilly C (2006) Acido-basic catalysis: application to refining and petrochemistry. Technip Ophrys Editions, Paris

Margitfalvi JL, Borbáth I, Hegedűs M, Gőbölös S, Lónyi F (1999) New approaches to prepare supported Sn–Pt bimetallic catalysts. React Kinet Catal Lett 68:133–143. https://doi.org/10.1007/bf02475495

Marín C, Escobar J, Galván E, Murrieta F, Zárate R, Vaca H (2005) Light straight-run gas oil hydrotreatment over sulfided CoMoP/Al_2O_3-USY zeolite catalysts. Fuel Process Technol 86:391–405. https://doi.org/10.1016/j.fuproc.2004.05.007

Maxwell IE, Stork WHJ (2001) Chapter 17 Hydrocarbon processing with zeolites. Stud Surf Sci Catal 137:747–819. https://doi.org/10.1016/S0167-2991(01)80259-7

Mazzieri VA, Grau JM, Vera CR, Yori JC, Parera JM, Pieck CL (2005a) Role of Sn in Pt–Re–Sn/Al_2O_3–Cl catalysts for naphtha reforming. Catal Today 107–108:643–650. https://doi.org/10.1016/j.cattod.2005.07.042

Mazzieri VA, Grau JM, Vera CR, Yori JC, Parera JM, Pieck CL (2005b) Pt-Re-Sn/Al_2O_3 trimetallic catalysts for naphtha reforming processes without presulfiding step. Appl Catal A 296:216–221. https://doi.org/10.1016/j.apcata.2005.08.028

McCallister K, O'Neal T (1971) French Patent 2078056. UOP

Mendoza-Nieto JA, Vera-Vallejo O, Escobar-Alarcón L, Solís-Casados D, Klimova T (2013) Development of new trimetallic NiMoW catalysts supported on SBA-15 for deep hydrodesulfurization. Fuel 110:268–277. https://doi.org/10.1016/j.fuel.2012.07.057

Mukhopadhyay R, Kunzru D (1993) Catalytic pyrolysis of naphtha on calcium aluminate catalysts. Effect of potassium carbonate impregnation. Ind Eng Chem Res 32:1914–1920. https://doi.org/10.1021/ie00021a015

Myrstad T, Seljestokken B, Engan H, Rytter E (2000) Effect of nickel and vanadium on sulphur reduction of FCC naphtha. Appl Catal A 192:299–305. https://doi.org/10.1016/S0926-860X(99)00405-6

Nakano K, Ali SA, Kim H-J, Kim T, Alhooshani K, Park J-I et al (2013) Deep desulfurization of gas oil over NiMoS catalysts supported on alumina coated USY-zeolite. Fuel Process Technol 116:44–51. https://doi.org/10.1016/j.fuproc.2013.04.012

Navarro R, Pawelec B, Fierro J, Vasudevan P, Cambra J, Guemez M et al (1999) Dibenzothiophene hydrodesulfurization on HY-zeolite-supported transition metal sulfide catalysts. Fuel Process Technol 61:73–88. https://doi.org/10.1016/S0378-3820(99)00031-4

Otsuki S, Nonaka T, Takashima N, Qian W, Ishihara A, Imai T et al (2000) Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. Energy Fuels 14:1232–1239. https://doi.org/10.1021/ef000096i

Pieterse JAZ, van Eijk S, van Dijk HAJ, van den Brink RW (2011) On the potential of absorption and reactive adsorption for desulfurization of ultra low-sulfur commercial diesel in the liquid phase in the presence of fuel additive and bio-diesel. Fuel Process Technol 92:616–623. https://doi.org/10.1016/j.fuproc.2010.11.019

Raffinage French Patent 2031984. CFD1969

Rahimi N, Karimzadeh R (2011) Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: a review. Appl Catal A 398:1–17. https://doi.org/10.1016/j.apcata.2011.03.009

Rahimpour MR, Jafari M, Iranshahi D (2013) Progress in catalytic naphtha reforming process: a review. Appl Energy 109:79–93. https://doi.org/10.1016/j.apenergy.2013.03.080

Rashidzadeh M, Mondegarian R, Peyravi MH (1999) Catalytic reforming of N-Heptane on Pt-Nd/Alumina. Int J Chem 9:37–46

Rausch R (1973) Platinum-tin uniformly dispersed hydro-carbon conversion catalyst and process. US Patent 3745112

Salem ABSH, Hamid HS (1997) Removal of sulfur compounds from naphtha solutions using solid adsorbents. Chem Eng Technol 20:342–347. https://doi.org/10.1002/ceat.270200511

Sankaranarayanan TM, Banu M, Pandurangan A, Sivasanker S (2011) Hydroprocessing of sunflower oil–gas oil blends over sulfided Ni–Mo–Al–zeolite beta composites. Bioresour Technol 102:10717–10723. https://doi.org/10.1016/j.biortech.2011.08.127

Saxena SK, Viswanadham N, Garg MO (2014) Porosity and acidity patterns of steam treated BEA zeolite material for enhanced catalytic isomerization of naphtha. J Ind Eng Chem 20:3875–3883. https://doi.org/10.1016/j.jiec.2013.12.093

Shiraishi Y, Tachibana K, Hirai T, Komasawa I (2002) Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid–liquid extraction. Ind Eng Chem Res 41:4362–4375. https://doi.org/10.1021/ie010618x

Sinfelt JH (1976) Polymetallic cluster compositions useful as hydrocarbon conversion catalysts. US Patent 3953368

Song C, Ma X (2003) New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. Appl Catal B 41:207–238. https://doi.org/10.1016/S0926-3373(02)00212-6

Soto HO, Marín LJH (2000) Hydrocracking of heavy straight run naphtha with Pt supported on zeolites Y, USY, ZSM5 and β. In: Corma A, Melo FV, Mendioroz S, Fierro JLG (eds) Studies in surface science and catalysis. Elsevier, New York, pp 2489–2494. https://doi.org/10.1016/S0167-2991(00)80843-5

Srinivasan R, Davis BH (1992) The structure of platinum-tin reforming catalysts. Platin Metals Rev 36:151–163

Stanislaus A, Marafi A, Rana MS (2010) Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. Catal Today 153:1–68. https://doi.org/10.1016/j.cattod.2010.05.011

Stepanov V (2005) Low scale production of motor fuels on remote oil fields. Khim Tekhnol Topl Masel 1:3–11

Stepanov V, Ione K (2003) Low-and intermediate-scale production of motor fuels using a novel catalytic process zeoforming, Katal. Promsti

Vasudevan PT, Fierro JLG (1996) A review of deep hydrodesulfurization catalysis. Catal Rev 38:161–188. https://doi.org/10.1080/01614949608006457

Velichkina LM (2009) Hydrogen-free domestic technologies for conversion of low-octane gasoline distillates on zeolite catalysts. Theor Found Chem Eng 43:486–493. https://doi.org/10.1134/s004057950904023x

Verbeek H, Sachtler WMH (1976) The study of the alloys of platinum and tin by chemisorption. J Catal 42:257–267. https://doi.org/10.1016/0021-9517(76)90260-8

Vicerich MA, Oportus M, Benitez VM, Reyes P, Pieck CL (2014) Influence of time and temperature on the regeneration of PtReIn/Al_2O_3 naphtha reforming catalysts. Catal Lett 144:1178–1187. https://doi.org/10.1007/s10562-014-1282-9

Viswanadham N, Kamble R, Sharma A, Kumar M, Saxena AK (2008) Effect of Re on product yields and deactivation patterns of naphtha reforming catalyst. J Mol Catal A Chem 282:74–79. https://doi.org/10.1016/j.molcata.2007.11.025

Viswanadham N, Saxena SK, Garg MO (2013) Octane number enhancement studies of naphtha over noble metal loaded zeolite catalysts. J Ind Eng Chem 19:950–955. https://doi.org/10.1016/j.jiec.2012.11.014

Vrinat ML (1983) The kinetics of the hydrodesulfurization process: a review. Appl Catal 6:137–158. https://doi.org/10.1016/0166-9834(83)80260-7

Wan G, Duan A, Zhang Y, Zhao Z, Jiang G, Zhang D et al (2009) Hydrodesulfurization of fluidized catalytic cracking diesel oil over NiW/AMB catalysts containing H-type β-zeolite in situ synthesized from kaolin material. Energy Fuels 23:3846–3852. https://doi.org/10.1021/ef900178n

Wan G, Duan A, Zhang Y, Zhao Z, Jiang G, Zhang D et al (2010a) NiW/AMBT catalysts for the production of ultra-low sulfur diesel. Catal Today 158:521–529. https://doi.org/10.1016/j.cattod.2010.08.021

Wan G, Duan A, Zhang Y, Zhao Z, Jiang G, Zhang D et al (2010b) Zeolite beta synthesized with acid-treated metakaolin and its application in diesel hydrodesulfurization. Catal Today 149:69–75. https://doi.org/10.1016/j.cattod.2009.07.098

Wang Y, Wang B, Rives A, Sun Y (2014) Hydrodesulfurization of transportation fuels over zeolite-based supported catalysts. Energy Environ Focus 3:45–52. https://doi.org/10.1166/eef.2014.1088

Wei Y, Liu Z, Wang G, Qi Y, Xu L, Xie P et al (2005) Production of light olefins and aromatic hydrocarbons through catalytic cracking of naphtha at lowered temperature. Stud Surf Sci Catal 158:1223–1230. https://doi.org/10.1016/S0167-2991(05)80468-9

Yao S, Zheng Y, Ng S, Ding L, Yang H (2012) The role of nanobeta zeolite in NiMo hydrotreating catalysts. Appl Catal A 435:61–67. https://doi.org/10.1016/j.apcata.2012.05.038

Yin C, Zhu G, Xia D (2002a) Determination of organic sulfur compounds in naphtha. Part I. Identification and quantitative analysis of sulfides in FCC and RFCC naphthas. Prepr Am Chem Soc Div Petrol Chem 47:391–395

Yin C, Zhu G, Xia D (2002b) Determination of organic sulfur compounds in naphtha. Part II. Identification and quantitative analysis of thiophenes in FCC and RFCC naphthas. Prepr Am Chem Soc Div Petrol Chem 47:398–401

Zeelani GG, Ashrafi A, Dhakad A, Gupta G, Pal SL (2016) Catalytic oxidative desulfurization of liquid fuels: a review

Zhagfarov FG, Grigor'eva NA, Lapidus AL (2005) New catalysts of hydrocarbon pyrolysis. Chem Technol Fuels Oils 41:141–145. https://doi.org/10.1007/s10553-005-0036-1

Zhang J, Qiu G, Fan L, Meng X, Cai Q, Wang Y (2015) Enhanced sulfur capacity of durable and regenerable mesoporous sorbents for the deep desulfurization of diesel. Fuel 153:578–584. https://doi.org/10.1016/j.fuel.2015.03.056

Zinnen HA (1999) Removal of organic sulfur compounds from FCC gasoline using regenerable adsorbents. US Patent 5935422