Catalysis Science & Technology

PERSPECTIVE

View Article Online
View Journal | View Issue

Cite this: *Catal. Sci. Technol.*, 2016, **6**, 2528

Bifunctional noble metal/zeolite catalysts for upgrading low-quality diesel fractions *via* selective opening of naphthenic rings

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Received 19th January 2016,
Accepted 3rd April 2016

DOI: 10.1039/c6cy00135a

www.rsc.org/catalysis

Current regulations for diesel fuels primarily involve severe reductions in the concentrations of sulfur and polyaromatics and a minimum cetane number (51 according to current EU standards). Low-quality distillate fractions, such as the LCO fraction abundantly produced in fluid catalytic cracking (FCC) units, cannot be directly used as a blending diesel component due to their high polyaromatics content and consequently poor cetane number (CN < 25) and ignition quality. For such fractions, the increase in CN achieved by deep hydrogenation of the polyaromatics is not enough to meet the fuel specifications. Further upgrading through selective ring opening (SRO) of the produced naphthenes has been proposed as a suitable technological solution to bring the CN to the required values. As will be shown in this article, bifunctional catalysts based on noble metals loaded on acidic zeolites (and mesoporous molecular sieves) exhibit good prospects for the SRO of multi-ring naphthenes as those contained in hydrogenated distillates. Moreover, the high hydrogenation ability of the noble metal(s) makes these bifunctional catalysts suitable for the coupled hydrogenation of (poly)aromatics and the subsequent opening of the naphthenic rings. As will be illustrated here for model naphthenic and aromatic compounds, fine tuning of the hydrogenation and hydrogenolysis activities of the metallic function and the acidity and porous structure of the molecular sieve carrier becomes crucial for achieving optimum performance in SRO reactions. Finally, the relevant issue of the sulfur tolerance of these noble metal-based bifunctional SRO catalysts and their performance in the upgrading of sulfur-containing industrial feedstocks will also be addressed in this perspective article.

Introduction

Increasingly stringent standards regarding the quality of transport fuels are continuously being implemented in developed economies with the aim of mitigating the detrimental impact of the exhaust emissions on the environment as well as on human health, particularly in the most populated areas. Environmental issues are of particular concern for diesel (the most demanded transport fuel in the EU) due to their higher tendency to emit more particulate matter (PM) and nitrogen oxides (NO_x) as compared to gasoline. The presence of polyaromatic compounds in diesel is known to increase PM and NO_x emissions while negatively impacting cetane number (CN). Hence, current requirements for diesel fuel in the EU, covered by standard EN 590, include a minimum CN of 51, a maximum concentration of polycyclic aromatics of 8 wt%, and a sulfur content of 10 ppm maximum. In the US, a sulfur limit of 15 ppm and a minimum CN of 41 are effectively applied since 2010 for ultra-low sulfur diesel (ULSD) for highway use, while a maximum aromatic content of 10 wt% is allowed in certain states like California.

Cetane number (CN) is a key property determining the quality of the diesel fuel. Low CN values result in knocking and noise issues and increase the amount of emitted PM. The CN of hydrocarbons is closely related to their molecular structure. As a general trend, for hydrocarbons with a given number of carbon atoms, the CN increases in the order: (poly)aromatics < naphthenes < iso-paraffins < *n*-paraffins. Thus, ideally converting aromatics into linear paraffins would produce the highest achievable increase in CN starting from low quality highly aromatic refining fractions. In practice, however, a certain (and controlled) degree of branching in the paraffinic hydrocarbons is required to improve the cold flow properties of the diesel fuel while still keeping a relatively high CN. One of the most interesting refinery streams requiring upgrading in order to be used as diesel blending component is the LCO (light cycle oil) fraction produced in FCC (fluid catalytic cracking) units. LCO has a boiling point range similar to diesel and represents about 20–30 wt% of the FCC product slate. However, it typically contains 50–70

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wt% aromatics, 0.2–2 wt% sulfur, and an unacceptably low CN value of 15–25. Currently, upgrading of LCO mainly relies on severe hydrotreating with transition metal sulfide catalysts, during which aromatics are hydrogenated and the concentrations of sulfur and nitrogen pollutants are substantially reduced. Nonetheless, even if hydrogenation of the aromatics present in this type of feeds brings a significant increase in CN, the final CN values are still far from those stipulated in the regulations. For instance, full hydrogenation of naphthalene (a common aromatic structure in LCO) to decalin increases the CN from 1 to 36. On the other hand, upgrading of such highly aromatic refining fractions by hydrocracking produces middle distillates of good quality, although at the expense of a substantial yield loss due to cracking into undesired lighter components, mainly into naphtha. In zeolite-based hydrocracking catalysts, the middle distillates/naphtha ratio in the hydrocracked products can be controlled to a certain extent by tuning the zeolite pore structure and acidity. For instance, hydrocracking of LCO (CN = 27, 0.5 wt% sulfur) on Pt supported on an HY zeolite with a low Si/Al ratio (2.6) was more suitable for producing middle distillates than Pt/beta, giving 65% selectivity at 85% conversion.[1] These noble metal/zeolite catalysts, however, experience a rapid initial deactivation due to poisoning of the metal by sulfur and coke deposition on the support acid sites until a pseudo-stable state is attained.[2,3] The activity in the pseudo-stable state strongly depends on the zeolite acidity and the nature of the noble metal phase, with the bimetallic Pt–Pd composition supported on low Si/Al ratio HY (*i.e.* with a high amount of acid sites) exhibiting the best catalytic performance.[2]

An alternative technological solution that has been proposed to further enhance the CN is to perform the selective ring opening (SRO) of the naphthenes produced in a preceding hydrotreating/hydrogenation step, ideally to the linear (or slightly branched) paraffin with the same number of carbon atoms as the original cyclic hydrocarbon.[4–6] In this case, as shown in Fig. 1 starting from naphthalene, the SRO of decalin to *n*-decane entails an increase in CN from 36 to 77. Thus, SRO of naphthenic compounds could be considered, *a priori*, a suitable strategy for upgrading low-quality refining fractions like LCO. As an additional advantage, SRO increases the volume of fuel available for selling due to the gradual decrease in density when going from the aromatic to the corresponding paraffin (Fig. 1).

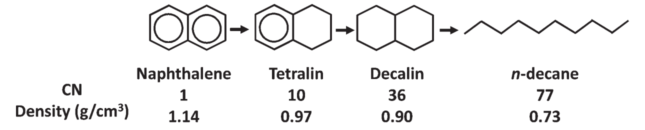

Fig. 1 Improvement in CN and fuel density through hydrogenation of aromatics and subsequent selective opening of naphthenic rings.

Although, apparently, the reaction path leading to the high-cetane *n*-paraffin hydrocarbons from aromatics might look relatively simple, it is in fact very challenging, and the chemistry behind SRO is, as will be shown in the next sections for model compounds, quite complex. The problem becomes much more intricate when dealing with real feedstocks as most of the catalysts which are being developed for SRO are based on noble metals that are readily poisoned by sulfur even if present in very low concentrations. Moreover, as properly pointed out by Resasco and co-workers, not every ring opening product has a CN higher than that of the starting naphthenic compound.[7] Therefore, a profound knowledge of the chemistry involved in the SRO reaction is crucial for designing effective catalysts that selectively promote the formation of specific ring opening products (ROP) that would bring a net gain in CN. It should be remarked that the goal of SRO is to produce the targeted ring opening products while minimizing (or ideally avoiding) carbon losses through consecutive reactions.

Selective opening of naphthenic rings can take place through different mechanisms depending on the type of catalyst employed (see next section). Regardless of the main operating mechanism, it is well documented that C_6 naphthenic rings are more difficult to open than C_5 rings. Consequently, an acid function is needed to catalyze the C_6-to-C_5 ring contraction (RC) step preceding ring opening.[6] In this respect, zeolites and related molecular sieves might be suitable catalysts for the C_6-to-C_5 ring isomerization provided that the acidity and pore architecture are finely adjusted so as to minimize unwanted acid-catalyzed dealkylation and cracking reactions. In turn, besides catalyzing the precedent RC (skeletal isomerization) step, the zeolite may also be active for breaking endocyclic C–C bonds in the naphthenic molecules *via* carbenium ion chemistry on the Brønsted acid sites. Thus, as will be shown in this article, zeolites, and more generally molecular sieves, are essential components in many of the most effective catalysts that are being developed for SRO. The flexibility of these materials to tune, within a relatively wide range, the density and strength of the acid sites as well as the pore structure leaves ample room for the fine tuning of their properties in the development of improved generations of SRO catalysts.

In this article, we discuss the most relevant advances in the SRO of multi-ring naphthenic compounds as an appealing catalytic route to increasing the CN of low-value diesel fractions, with a special focus on the role that micro- and mesoporous molecular sieves are playing in the design of highly efficient ring opening catalysts. First, the salient aspects of the chemistry involved in SRO, which is closely related to the type of catalyst employed, will be discussed. Next, the ring opening of model bicyclic naphthenic and aromatic compounds in the absence of sulfur using bifunctional catalysts comprising noble metals loaded on acidic micro- and mesoporous materials will be addressed. Then, we will deal with the relevant issue of the sulfur resistance of the noble metal-based catalysts during the SRO of model compounds. Finally, the studies performed with real feedstocks will be considered, to end up with final remarks and perspectives regarding the viability of SRO for upgrading poor diesel fractions and the potential of molecular sieves for designing more efficient SRO catalysts. Kinetic modeling studies are not covered in this article.

A brief outlook on the chemistry of SRO

The SRO of single-ring naphthenes like methylcyclopentane, cyclohexane, and their derivatives has been deeply investigated in the past.[8–12] Since SRO on metal catalysts is known to be a structure-sensitive reaction, most of the earlier works employed SRO of these simple mononaphthenes as a model reaction to characterize the properties of metal surfaces.[13–16] Nonetheless, these previous studies have largely contributed to a more solid understanding of the underlying chemistry in SRO reactions and set the basic concepts for a guided design of catalysts with improved activity and selectivity for the ring opening of more complex multi-ring naphthenes. In this section, the conspicuous aspects of the chemistry behind the SRO of model naphthenic compounds on different types of catalysts are addressed. A thorough discussion of the reaction pathways and mechanisms involved in the SRO chemistry is, however, outside the scope of this article, and the reader is referred to comprehensive reviews on the topic for more detailed information.[17–19]

Opening of endocyclic C–C bonds in naphthenic rings can occur through three main pathways depending on the nature of the employed catalyst: 1) *via* carbenium ion intermediates on Brønsted acid sites, 2) *via* hydrogenolysis on metal surfaces, and 3) through a bifunctional route involving both metal and Brønsted acid sites.

In purely acidic catalysts (*e.g.* H-zeolites), breaking of endocyclic C–C bonds in naphthenes proceeds on Brønsted acid sites (BAS) *via* carbenium ion intermediates according to the cracking mechanism extensively described for alkanes.[20] The reaction is consensually assumed to be initiated by the attack of a proton to an endocyclic C–C bond followed by the release of H_2 and formation of a cyclic carbenium ion with the same number of carbon atoms as the original naphthene (protolytic dehydrogenation). Then, the adsorbed cyclic carbocation undergoes skeletal isomerization (C_6-to-C_5 ring contraction) *via* cyclopropane intermediates, hydride transfer, and finally β-scission (ring opening). ROP may also form, in principle, *via* protolytic cracking (PC) of the reactant naphthene.[21] This cracking mechanism, also known as Haag–Dessau cracking,[22] involves the formation of a non-classical (three-center, two-electron bond) carbonium ion upon protonation of the reactant at a Brønsted acid site. This monomolecular cracking route is favored on medium pore zeolites (*i.e.* HZSM-5) imposing steric restrictions to the classical bimolecular β-scission mechanism and becomes relevant at temperatures higher than those typically applied in SRO reactions (>400 °C).[22] Interestingly, the addition of minute amounts (10–100 ppm) of a noble metal like Pd to HZSM-5 significantly increased the contribution of the non-classical Haag–Dessau mechanism to the ring opening of methylcyclohexane.[23] Protolytic cracking of skeletal isomers is, however, more likely to occur under SRO conditions.[24] In the presence of alkyl substituents, acid-catalyzed cleavage of exocyclic C–C bonds occurs 3–4 times faster than that of endocyclic C–C bonds, particularly for alkyl chains with three or more carbon atoms.[25] As a consequence, cracking at the alkyl chain and dealkylation are favored against ring opening on acid catalysts. In turn, the monofunctional acid pathway typically leads to highly branched ring opening products with a lower CN than their linear counterparts. Moreover, such highly isomerized ROP are more prone to crack than the original naphthene causing a significant reduction in molecular weight. These issues make SRO of naphthenic rings *via* monofunctional acid catalysis very challenging. It should be mentioned that in the presence of H_2 monofunctional H-zeolites are able to activate H_2 and promote hydrogenation reactions provided sufficiently high H_2 pressures are applied.[26,27] In these cases, H-zeolites may behave as bifunctional catalysts in the cracking of cycloalkanes (hence changing the main cracking mechanism) by simultaneously catalyzing hydrogenation and cracking reactions, increasing the formation of skeletal isomers and saturated products.[28] In the case of HZSM-5, the presence of H_2 was also seen to enhance the contribution of the non-classical monomolecular (Haag–Dessau) cracking mechanism yielding higher amounts of methane and ethane from methylcyclopentane.[28]

SRO of naphthenes can also proceed on certain noble metals like Pt, Pd, Ir, Rh, and Ru *via* hydrogenolysis (cleavage of C–C bonds on metal surfaces in the presence of H_2) of endocyclic C–C bonds. Ir-based catalysts typically display higher activity and RO selectivity than the other metals under equivalent reaction conditions. Ring opening *via* hydrogenolysis may take place through different mechanisms depending on the type of metal and metal properties (particle size, morphology, *etc.*). SRO on Ir and Rh catalysts mainly takes place *via* the so-called dicarbene (or doublet) mechanism irrespective of metal particle size. In this mechanism, cleavage of C–C bonds in the ring occurs at unsubstituted secondary carbon atoms, resulting in the preferential formation of less desired highly branched paraffins.[8] In Pt, however, the prevailing mechanism was seen to depend on the metal particle size. Thus, on very small Pt particles (*i.e.* highly dispersed catalysts), ring opening predominantly occurs through a non-selective π-adsorbed olefin (or multiplet) mechanism which gives a statistical product distribution, whereas the dicarbene mechanism is dominant on large Pt ensembles and on Pt surfaces with low Miller indexes.[8] Additionally, a third hydrogenolysis mechanism involving a metallocyclobutane intermediate has also been proposed.[8] These three hydrogenolysis mechanisms are illustrated in Fig. 2. Besides selectivity, which is governed by the prevailing mechanism, particle size may also influence the hydrogenolysis activity of the noble metals. For instance, for Al_2O_3-supported catalysts, the intrinsic activity (or TOF) for the hydrogenolysis of cyclopentane has been shown to decrease with decreasing particle sizes of Pt, Rh, and (to a lesser extent) Pd, while for

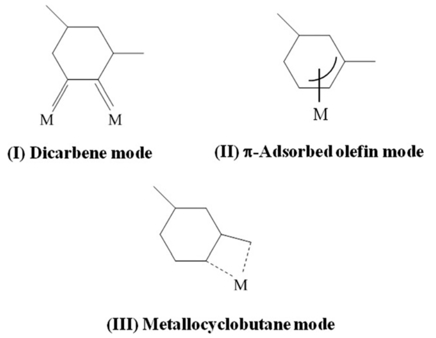

Fig. 2 Ring opening mechanisms on metal catalysts. Adapted from ref. 30.

Ir the TOF was practically insensitive to the metal particle size.[8,29] The precise reasons behind such particle size effects, however, have not yet been fully elucidated.

Both the multiplet and metallocyclobutane mechanisms can result in the cleavage of substituted C–C bonds giving linear paraffins that are more desirable to effectively increase the CN. The differences in the distribution of ROP arising from the different operating mechanisms are illustrated in Table 1 for the SRO of methylcyclopentane (MCP) and *n*-pentylcyclopentane (PCP) on highly dispersed Pt/Al_2O_3 and Ir/Al_2O_3 catalysts.[6]

The chemical nature and acid–base character of the support may influence the properties of the supported metals as well through electronic effects and, hence, induce changes in the hydrogenolysis activity as well as in the prevailing mechanism and consequently in the structure of the formed ROP. For instance, compared to Ir/SiO_2, Ir/Al_2O_3 and Ir/TiO_2 catalysts exhibit a higher preference for cleaving substituted C–C bonds and are thus preferred for improving the CN.[30] Moreover, ring opening of MCP on Pt sites was seen to proceed with much higher selectivity when the metal is supported on basic (neutral) supports in comparison to acidic carriers.[31] In turn, too acidic supports such as low Si/Al ratio H-zeolites may strengthen the interaction of the metal with the acid sites impairing its hydrogenolysis ability.[32] On the other hand, the degree of substitution of the naphthenic rings may also affect the overall reactivity as well as the relative rate of cleavage of substituted and unsubstituted C–C bonds and, hence, the CN of the formed ROP. In Ir/Al_2O_3, for instance, SRO of 1,2,4-trimethylcyclohexane proceeds at a much lower rate than that of methylcyclohexane and with higher preference for cleavage at substituted C–C bonds.[6]

A common aspect to the different hydrogenolysis mechanisms is the much higher reactivity of the metals to open C_5 rings as compared to C_6 rings.[6] Since C_6 naphthenic rings are formed upon hydrogenation of the aromatics present in real feeds, a C_6-to-C_5 ring contraction step needs to be performed prior to ring opening in order to attain high conversion rates at moderate temperatures. As Ir preferentially breaks unsubstituted C–C bonds, higher RO rates can be achieved if ring contraction occurs without increasing the number of alkyl substituents (non-branching isomerisation), as exemplarily shown in Fig. 3 for methylcyclohexane (MCH).[6] As shown by McVicker and co-workers, non-branching isomerisation can be performed with solid acids having low to moderate acid strength such as amorphous SiO_2–Al_2O_3 or highly dealuminated USY and ECR-32 zeolites.[6] For instance, the conversion of MCH over 2% Ir/Al_2O_3 substantially increases from 25% to 55% when admixed with a ring contraction 0.9% Pt/USY catalyst (Pt was incorporated into the zeolite to prevent extensive coking) while still keeping a high RO selectivity of about 70–73% under the studied conditions.[6]

Finally, SRO can also take place through a bifunctional route involving both metal and Brønsted acid sites similarly to catalytic hydrocracking.[18] According to the classical bifunctional mechanism,[33,34] the reaction starts with the dehydrogenation of the naphthene to the corresponding cyclic olefin on the metal sites. The formed olefin is protonated at a Brønsted acid site to give an adsorbed carbenium ion that subsequently undergoes skeletal isomerisation prior to ring opening *via* β-scission of an endocyclic C–C bond. The products are desorbed from the acid sites as olefins which are then hydrogenated on the metal. Alternatively, the final saturated products may desorb directly from the acid sites by hydrogenation of the adsorbed carbenium ions *via* surface diffusion of hydrogen species activated on the metal sites (hydrogen spillover).[35] A simplified reaction scheme for the ring opening of decalin on bifunctional metal/acid catalysts is presented in Fig. 4. As in monofunctional acid catalysts, ROP are predominantly formed from the skeletal isomers by β-scission of an endocyclic C–C bond in the C_5 ring.

Table 1 Product distributions obtained in the ring opening of five-membered-ring naphthenes on highly dispersed Pt/Al_2O_3 and Ir/Al_2O_3 catalysts. Adapted from ref. 6

Feed	Products	Pt/Al_2O_3 (%)	Multiplet[a] (%)	Ir/Al_2O_3 (%)	Dicarbene[a] (%)
MCP[b]	n-C_6	41	40	<1	0
	2-MC_5	42	40	70	67
	3-MC_5	17	20	29	33
PCP[c]	n-C_{10}	55	40	3	0
	4-MC_9	31	40	64	67
	3-EtC_8	14	20	33	33

[a] Theoretical product distribution. [b] 2850 kPa MCP, WHSV = 15 h^{-1} for Pt and 30 for Ir; H_2/MCP = 5. [c] 20% PCP/n-C_7; 3540 kPa; LSHV = 0.5 h^{-1} for Pt and 5 h^{-1} for Ir; H_2/PCP = 15.

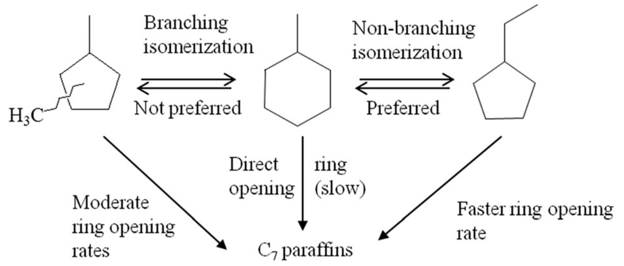

Fig. 3 Non-branching isomerisation of MCH to ECP is preferred over both branching isomerisation to DMCP and direct MCH ring opening. Adapted from ref. 6.

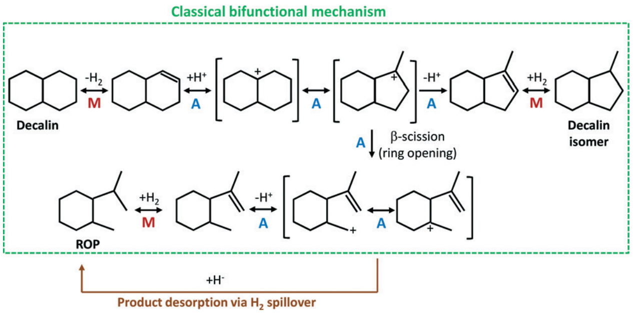

Fig. 4 Simplified scheme for the ring opening of decalin on bifunctional metal (M)/acid (A) catalysts.

Differently from hydrogenolysis, the main role of the metal in the bifunctional mechanism is the dehydrogenation of the starting naphthene and the hydrogenation of the olefinic intermediates. As it generally occurs in bifunctional reactions, a proper balance between the two catalytic functions is required for achieving optimum performance.

SRO of model multi-ring naphthenes and aromatics

SRO on bifunctional zeolite-based catalysts

As stated before, ring opening of naphthenic compounds may take place on monofunctional acid catalysts, such as H-zeolites, *via* carbocation intermediates. However, even in the presence of H_2, H-zeolites experience a gradual deactivation with time, in which the extent is determined by both zeolite acidity and pore structure, resulting in unacceptably low yields of the targeted ROP.[24] As an example, a maximum ROP yield of only 8 mol% was obtained in the conversion of decalin on a highly active H-beta zeolite (atomic Si/Al ratio of 25).[24] Much higher ring opening rates as well as a more stable catalytic performance can be achieved by using bifunctional catalysts in which a metal function, typically a noble metal, is added to the H-zeolite.[36–38] Thus, addition of 2 wt% Pt to H-beta (Si/Al = 25) increased the maximum ROP yield from 8 mol% to 30 mol%.[37] Additionally, secondary cracking and condensation reactions are strongly suppressed in the bifunctional Pt/H-zeolites, resulting in increased selectivities to the skeletal feed isomers and ring opening products.[36,37] The decreased formation of heavy condensation products has been attributed to the hydrogenation activity of Pt,[37] while the suppression of cracking has been related to a reduction in the average strength of the zeolite BAS due to electronic interactions with small Pt crystallites located within the zeolite channels.[37,39] In Pt/H-zeolites, SRO of binaphthenes like decalin mainly proceeds through the bifunctional mechanism (Fig. 4), although a certain contribution of the Pt sites to the formation of ROP from decalin isomers *via* hydrogenolysis has been suggested.[37]

Most of the studies using decalin employed commercial reagents comprising a mixture of *cis*- and *trans*- stereoisomers as model reactants. Generally, a gradual decrease in the *cis*/*trans* ratio is observed at increasing decalin conversions. The reason behind this behaviour is, however, not exempt of a certain controversy. Thus, while some authors exclusively attribute this effect to the stereoisomerization of *cis*-decalin to the thermodynamically favoured *trans*-decalin,[37,40] others propose a higher reactivity of *cis*-decalin as compared to the *trans*- isomer as the major cause of the decrease in the *cis*/*trans* ratio.[36,41–43] Moreover, by reacting pure *cis*- and *trans*-decalin on HY and Pt/H-Y catalysts, a more selective conversion of *cis*-decalin to ROP was concluded, whereas *trans*-decalin was seen to react in a less selective way giving higher yields of cracking products.[36] If this was the case, and given that the *trans* isomer is thermodynamically favoured, a kinetic control through the judicious choice of the catalyst and reaction conditions would be required to keep the *trans*-to-*cis* ratio as low as possible in the hydrogenation of diaromatics like tetralin and naphthalene so as to maximize the formation of ROP in the subsequent SRO catalytic step.[43]

As shown in Table 2, Pt/H-beta and Pt/H-Y outperformed Pt/H-mordenite in the SRO of decalin giving much higher yields of ROP even at a lower reaction temperature.[37] Moreover, Pt/H-beta performed slightly better than Pt/H-Y probably due to the higher Brønsted acidity of the employed H-beta sample.[37] Indeed, the opposite trend was observed in the ring opening of decalin in 1.5% Pt–0.75% Ir catalysts loaded on an HY zeolite having about twice the amount of acid sites of H-beta, as measured by NH_3-TPD.[44]

Therefore, in catalysts comprising noble metals dispersed on a large-pore 3D zeolite bearing relatively strong BAS, the activity for conversion of decalin is dominated by the zeolite

Table 2 Yields (mol%) to the main products[a] obtained in the hydroconversion of decalin on bifunctional Pt/H-zeolites (2 wt% Pt) at the temperature of maximum ROP yield (2.0 MPa, 360 min). Adapted from ref. 37

		Yield (mol%)			
Catalyst	Temp. (°C)	iso-D	ROP	CP	HP
Pt/H-beta	250	42.0	30.2	16.4	3.6
Pt/H-Y	250	35.2	27.2	26.3	4.1
Pt/H-mordenite	270	60.3	8.8	3.2	0.8

[a] iso-D: decalin isomers; ROP: ring opening products; CP: cracking products; HP: heavy products.

acidity. However, differences in product selectivity were noticed depending on the nature of the metal. Thus, Ir-modified H-beta and H-Y zeolites exhibited slightly higher selectivity to ROP than their Pt-modified counterparts, albeit at the expense of an increase in the selectivity to cracking products.[45] Even more importantly, while C_{10}-alkylmononaphthenes were the only ROP formed in the Pt catalysts, formation of C_{10}-paraffins was observed for the Ir/H-zeolite samples, evincing the higher hydrogenolysis activity of Ir for opening the second C_5 ring in decalin isomers.[45] Accordingly, the formation of ROP in the conversion of decalin over bimetallic Pt–Ir/HY (Si/Al = 3.16) catalysts was enhanced by increasing the Ir content,[46] with the catalysts containing equivalent amounts of Pt and Ir (Pt/Ir = 1) exhibiting the best ROP selectivity.[47]

C_{10}-paraffins, also called open-chain decanes (OCD), are more desirable than C_{10}-alkylmononaphthenes due to the higher CN values of the former products. Identification of OCD in the complex reaction mixture obtained in the hydroconversion of decalin (usually comprising more than 100 products) represents, however, a great analytical challenge, so, not surprisingly, OCDs were not even mentioned in most of the SRO studies. This issue was solved by researchers at Eni by using comprehensive two-dimensional GC with mass selective detection (GCxGC-MSD) offering an enhanced peak resolution as compared to conventional GC-FID and GC-MS techniques, enabling an easier identification of the C_{10} hydrocarbons produced by ring opening of decalin.[48] By applying this methodology, researchers at Eni in collaboration with the group of Weitkamp nicely showed, in subsequent studies, that unprecedented high yields (>25 wt%) to the most desirable OCDs can be obtained with bifunctional catalysts comprising a noble metal with high hydrogenolysis activity (typically Pt or Ir) dispersed on large pore zeolites with low Brønsted acidity. In these catalysts, coined by the authors as "high-performance ring-opening catalysts" (HIPEROCs),[49] the main function of the low-acidic zeolite is to catalyze the non-branching C_6-to-C_5 ring isomerization minimizing consecutive cracking reactions, while subsequent opening of the C_5 naphthenic rings in feed isomers proceeds almost exclusively and with high selectivity *via* hydrogenolysis on the metal sites. Examples of HIPEROCs comprise Pt or Ir loaded on Y and beta zeolites exchanged with alkali cations, and particularly with Na^+, Cs^+, K^+, and Rb^+,[49,50] in which the few BAS of low acid strength present were practically those generated upon reduction of the noble metal with H_2. In these studies, the metals were generally incorporated by ionic exchange from cationic metal complexes so as to achieve a high degree of dispersion on the zeolite surface. The catalytic performance of representative HIPEROCs in the SRO of decalin is illustrated in Table 3.

As seen in the table, 3.4% Ir/Cs,H-beta resulted particularly effective for the SRO of decalin, giving very high conversion (94%) and yield of total ROP (59%) and OCDs (44%) at mild reaction temperatures. In turn, the distribution of OCDs was markedly different for Pt and Ir. As shown in Fig. 5, Ir/Na,H-Y favoured the formation of multiply branched hydrocarbons, as expected from the dicarbene mechanism operating on Ir, while less branched products formed on Pt/Na,H-Y in concordance with the "multiplet" mechanism prevailing on Pt. Consequently, a higher CN would be expected for the reaction product obtained with the Pt-containing catalyst. Moreover, no signs of deactivation were evidenced for any of these catalysts in runs lasting 36–50 h.

The coupled hydrogenation and ring opening of aromatics can also be accomplished using metal–acid bifunctional catalysts as those described previously for decalin. The simplified reaction scheme for the hydroconversion of tetralin on bifunctional Pt/H-zeolites is shown in Fig. 6.[51] First, tetralin is hydrogenated to a mixture of *cis* and *trans* decalins. Although the hydrogenation of the aromatic ring is a typical metal-catalyzed reaction, supporting the metal on solid acids like H-zeolites is known to enhance the hydrogenation activity through adsorption of the aromatic on the acid sites and its hydrogenation *via* H_2 spillover.[38,52–54] Next, decalins are isomerized to methyl-bicyclononanes and dimethyl-bicyclooctanes (iso-decalins) which subsequently undergo ring opening to yield C_{10}-alkylcyclohexanes and C_{10}-alkylcyclopentanes as main ROP. Further opening of the naphthenic ring in C_{10}-cycloalkanes to produce C_{10}-paraffins (open chain decanes or OCDs) may also occur, although their formation, though being of paramount importance from the viewpoint of cetane, is barely described in most of the studies using model aromatic reactants. Finally, C_{10}-cycloalkanes may undergo dealkylation and cracking reactions to produce alkylnaphthenes and paraffins with less than 10 carbon atoms.

As expected from the bifunctional mechanism, the efficiency of the metal/zeolite catalysts for decalin isomerization and ring opening increases with a closer proximity between the metal and acid sites and with a proper metal/acid site ratio.[36,51] Differently from decalin, under equivalent metal

Table 3 Hydroconversion of decalin on representative HIPEROC systems under reaction conditions maximizing the yield of OCD. Adapted from ref. 49 and 50

Catalyst	Temp (°C)	X_{Dec} (%)	$Y_{\mathrm{ROP}}{}^{a}$ (%)	$Y_{\mathrm{OCD,max}}$ (%)	S_{OCD} (%)
3% Ir/Na,H-Y	300	86	54	31	36
3% Pt/Na,H-Y	361	96	54	39	41
3.4% Ir/Cs,H-beta	262	94	59	44	47

[a] ROP include both C_{10}-alkylmononaphthenes and OCDs.

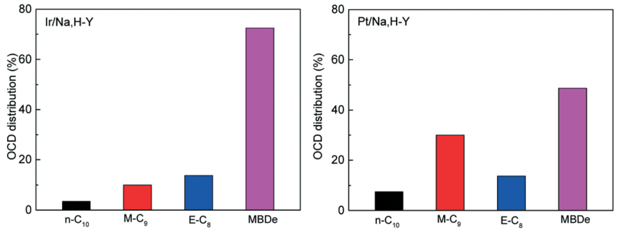

Fig. 5 Distribution of OCD products for a) Ir/Na,H-Y (T = 300 °C, X_{Dec} = 86%, Y_{OCD} = 31%) and b) Pt/Na,H-Y (T = 361 °C, X_{Dec} = 96%, Y_{OCD} = 39%) catalysts (E: ethyl; M: methyl; MBDe: multiply branched iso-decanes). Adapted from ref. 50.

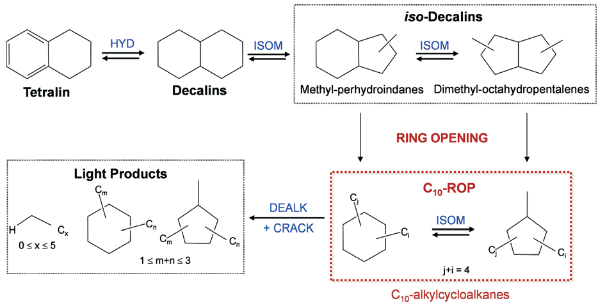

Fig. 6 Proposed reaction pathway for the hydroconversion of tetralin on bifunctional Pt/H-zeolites. Adapted from ref. 51.

loading and reaction conditions, the hydrogenation and ring opening of aromatics proceed more efficiently on Pt-modified than on Ir-modified H-zeolites due to the much poorer hydrogenation ability of Ir in comparison to Pt, as shown in Table 4 for the hydroconversion of tetralin over USY-based catalysts loaded with 1 wt% metal.[51] As also seen in Table 4, at the same total metal content (2 wt%), no practical differences in activity and product yields were observed for bimetallic Ir-Pt/USY (Ir/Pt = 1 wt/wt) and monometallic Pt/USY catalysts.[51] This result indicates that Ir did not provide the Pt/USY catalyst with additional ring opening activity and that the formation of iso-decalins and ROP from tetralin is mainly determined by the zeolite acidity.

Table 4 Hydrogenation and ring opening of tetralin on Pt- and Ir-modified USY[a] catalysts. Reaction conditions: T = 275 °C, P_{tot} = 3.0 MPa, H_2/tetralin = 10 mol/mol, WHSV = 2.5 h^{-1}, TOS = 7–8 h. Adapted from ref. 51

	Metal and loading (wt%)			
	1% Pt	1% Ir[b]	1% Ir + 1% Pt	2% Pt
Conversion (%)	99.9	31.7	100	99.2
Product yields[c] (wt%)				
LP + LN	9.6	0.9	13.4	13.6
DEC	23.6	21.2	12.5	11.9
iso-DEC	49.5	6.6	50.4	52.0
ROP	16.0	0.3	21.1	20.1
HP	0.1	1.7	1.5	0.6

[a] Bulk Si/Al ratio = 2.6; framework Si/Al ratio = 16.6. [b] Reaction temperature = 300 °C. [c] LP: light (C_{9-}) paraffins; LN: light (C_{9-}) naphthenes; DEC: decalin; iso-DEC: iso-decalins; ROP: ring opening products; HP: heavy (C_{11+}) products.

Regarding acidity, an enhancement in the yield and selectivity to ROP in the conversion of tetralin was reported for Pt/USY upon neutralization of the strongest BAS, on which consecutive (hydro)cracking reactions are favored, by impregnation of the zeolite with an appropriate amount of K prior to metal deposition.[55] In this case, a maximum ROP yield of 35.6% (at 90% C_{10} yield) was obtained for the catalyst loaded with 2.0 wt% K.[55] A similar effect was observed for Pt/H-beta upon submitting the zeolite to acid and steam dealumination treatments.[56] As shown in Fig. 7, the yield of ROP was maximized (*ca.* 26%) for the H-beta zeolite dealuminated with steam at high temperature (700 °C) due to both a lower amount and strength of the BAS and a higher mesoporosity in comparison to the acid-treated zeolites.[56] Also note in Fig. 7 that the decrease in zeolite acidity upon dealumination shifts the temperature of maximum ROP yield toward higher values. Overall, these results highlight the relevance of diffusional issues in the SRO of multi-ring compounds on zeolite-based catalysts. In this line, an enhanced activity for tetralin hydrogenation and ring opening has been reported for nano-sized H-beta having high external surface area and inter-crystal mesoporosity as compared to a commercial H-beta sample.[56,57]

As in the case of decalin, SRO of tetralin occurs more efficiently on 12-ring as compared to 10-ring zeolites.[58] Among the large-pore zeolites, the 3D USY and beta zeolites performed better than the 1D mordenite, with beta being somewhat more effective than USY in the SRO of tetralin.[58] The relevance of the zeolite pore architecture for the efficient conversion of tetralin to ROP is also inferred from the work by Arribas *et al.* using a Pt/ITQ-21 catalyst.[59] ITQ-21 (Fig. 8) is a 3D 12-ring zeolite with a pore structure closely related to that of FAU, both comprising large cavities of about 1.18 nm diameter. The main structural difference between these two zeolites relies on the number of 12-ring windows through which the supercages are accessed, being four in FAU and six in ITQ-21.[60] As a result of the better access to the large

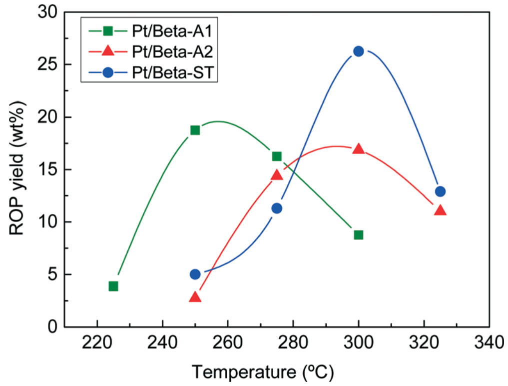

Fig. 7 Yield of ROP as a function of reaction temperature in the SRO of tetralin over dealuminated Pt/beta catalysts: Pt/beta-A1 and Pt/beta-A2 were produced by treatment of a commercial TEA-beta with, respectively, 8 N and 9.2 N HNO_3 solutions; Pt/beta-ST was obtained by steaming of H-beta at 700 °C for 3 h. Reaction conditions: 3.0 MPa, H_2/tetralin = 10 mol/mol, WHSV = 2.5 h^{-1}. Adapted from ref. 56.

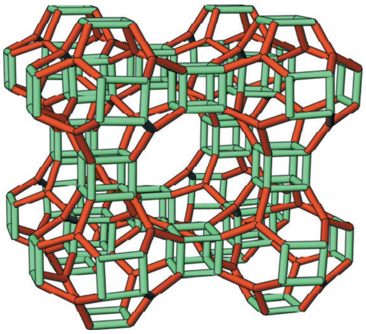

Fig. 8 Perspective view of the structure of the ITQ-21 zeolite.

cavities in ITQ-21, the bifunctional Pt/ITQ-21 catalyst outperformed those based on USY and H-beta leading to higher ROP yields (at constant cracking yield of 15 wt%) in the conversion of tetralin (Fig. 9).[59]

The porosity of the zeolite becomes of particular importance when dealing with bulkier alkylated diaromatics. For instance, while for a similar density of BAS Pt/H-beta was more active than Pt/USY in the ring opening of tetralin, the trend was reversed in the case of 1-methylnaphthalene (1-MN) due to a more impeded diffusion of the ROP (mainly C_{11}-alkylbenzenes and C_{11}-alkylcycloalkanes) in the pores of BEA, as supported by molecular docking simulations.[58] On the other hand, the role of the zeolite acidity in the ring opening of 1-MN was addressed by Arribas and Martínez by preparing a series of Pt(1 wt%)/USY samples with different concentrations of framework (FAL) and extraframework (EFAL) Al species.[38] The results from this study are presented in Table 5. These results show that the formation of ROP was favoured on the USY zeolites with low FAL and high EFAL concentrations (USY-2 and USY-4) and thus with low density of BAS. For the Pt/USY-2 catalyst, ROP represented about 20 wt% of the total C_{11} products (at constant C_{11} yield of 75 wt%) corresponding to a yield of 15 wt%.[38] Conversely, USY zeolites with higher Brønsted acidity (high FAL and low EFAL contents) promoted cracking and dealkylation reactions and experienced, at low temperatures (300 °C), a partial deactivation by coking.

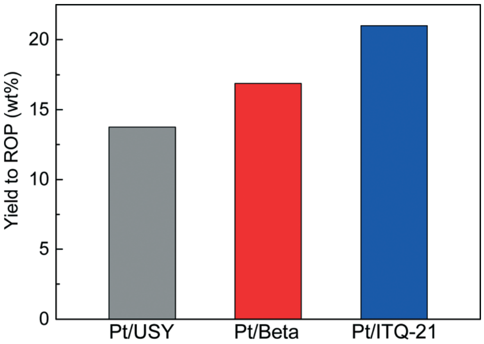

Fig. 9 Comparison of ROP yields (at constant cracking yield of 15 wt%) in the hydroconversion of tetralin on bifunctional Pt/USY, Pt/beta, and Pt/ITQ-21 catalysts. Reaction conditions: T = 275 °C, P = 3.0 MPa, WHSV = 2.5 h^{-1}. Adapted from ref. 59.

Table 5 Distribution of C_{11} products at a constant C_{11} yield of 75 wt% obtained in the coupled hydrogenation and ring opening of 1-methylnaphthalene (1-MN) on 1% Pt/USY catalysts with different chemical compositions and acidities. Reaction conditions: 4.0 MPa, WHSV = 2 h^{-1}, and H_2/1-MN = 30 mol/mol. Adapted from ref. 38

	USY-1	USY-2	USY-3	USY-4	USY-5
FAL/u.c.[a]	33.4	10.9	10.9	1.9	1.9
EFAL/u.c.[a]	19.9	42.4	16.5	51.4	4.8
BAS (μmol g^{-1})[b]	89	14	55	10	20
T_{75} (°C)[c]	325	350	330	355	330
Distribution (wt%)[d]					
MT + DMI	78.3	41.2	76.1	51.9	81.2
MD + iso-MD	10.4	37.7	15.0	31.3	10.4
ROP	8.1	20.1	7.8	15.8	7.9

[a] Number of framework (FAL) and extraframework (EFAL) Al atoms per unit cell. [b] Density of Brønsted acid sites measured by FTIR-pyridine after desorption at 250 °C. [c] Temperature required for achieving 75 wt% C_{11} yield. [d] MT: methyltetralin, DMI: dimethylindanes, MD: methyldecalins, iso-MD: methyldecalin isomers, ROP: C_{11}-alkylbenzenes + C_{11}-alkylcyclohexanes + C_{11}-alkylcyclopentanes.

SRO on bifunctional mesostructured catalysts

As inferred from the previous discussions, large-pore 3D zeolites with moderate Brønsted acidity produce the most efficient bifunctional SRO catalysts. On these premises, it seems logical that acidic ordered mesoporous materials (OMM) of the MCM-41 and SBA-15 types were also employed as supports in the preparation of bifunctional SRO catalysts. Moreover, the high surface area of these materials was anticipated to enhance the dispersion and, hence, the hydrogenation/hydrogenolysis activity of the supported noble metals, while the combination of a weak Brønsted acidity and uniformly-sized mesopores could be beneficial for limiting the extent of undesired consecutive reactions leading to light products and coke precursors.

The most widely applied acidic OMM for preparing bifunctional SRO catalysts are Zr- and Al-doped mesoporous silicas. These materials were loaded with different noble metal compositions and evaluated for the ring opening of two-fused ring naphthenic[61,62] and aromatic[62–72] model compounds. When decalin was used as a model reactant, the maximum yields achieved with bifunctional noble metal/OMM catalysts were, however, notably lower than those attained on analogous zeolite-based catalysts even at higher reaction temperatures. For instance, the maximum yield of ROP over a bimetallic Ir–Pt/Zr–MCM-41 (Si/Zr atomic ratio = 5) catalyst with an optimized metal composition of 1.5 wt% Ir and 0.75 wt% Pt amounted to only 15% (with 26% selectivity) at 350 °C and 5 MPa.[61] The nature and concentration of the metallic phases supported on Zr-doped mesoporous silica (Zr-MS, Si/Zr = 5) have been shown to impact the activity and selectivity of the catalyst in the hydrogenation and ring opening of two-fused ring aromatics. Zr-MS impregnated with 2 wt% Pt, Pd, Rh, and Pd–Pt exhibited relatively high conversions (>85%) in the hydroconversion of tetralin at temperatures of 250–350 °C and 6 MPa.[65] In the lower temperature range (250–300 °C), tetralin was mainly converted to the hydrogenation product decalin (mainly to *trans*-decalin), while increasing amounts of hydrogenolysis/ring opening products were formed above 300 °C in yields of up to 20–40%, with the Rh-containing catalyst giving the best yields among the investigated metals. In another study from the same group, Ru (5 wt%) supported on Zr-MS was seen to display high activity for the hydrogenation of tetralin but poor efficiency for the subsequent hydrogenolysis/ring opening of the formed decalins.[67] Zr-MS impregnated with 5 wt% Os showed, however, the opposite behavior reaching relatively high yields (30–35%) to hydrogenolysis/ring opening products.[67] On the other hand, raising the concentration of metals from 0.5 to 2.0 wt% in bimetallic Pd–Pt catalysts (Pd/Pt mole ratio = 4) supported on Zr-MS improved the activity for the total hydrogenation of naphthalene to decalins but concomitantly lowered the activity for hydrogenolysis/ring opening due to a reduced acidity at higher metal loadings.[70] Therefore, the catalyst with intermediate loading (1 wt%) was that giving the best balance between both reactions, yielding *ca.* 29% hydrogenolysis/ring opening products and 98.5% naphthalene conversion at 340 °C and 6 MPa.[70] Nonetheless, under analogous reaction conditions, bifunctional noble metal catalysts loaded on Zr-MS were less active for the hydroconversion of naphthalene than those supported on a more acidic commercial amorphous silica–alumina (Si/Al = 40/60 wt/wt).[69]

Thus, bifunctional catalysts based on mesoporous aluminosilicates (abbreviated here as Al-MS) exhibiting a higher Brønsted acidity than Zr-MS appear to be more appropriate for promoting the desired ring opening reactions. Indeed, an improvement in the catalytic performance for the hydrogenation and ring opening of tetralin and naphthalene was seen for bimetallic PdRh catalysts loaded on a mesoporous aluminosilicate carrier upon reducing the Si/Al ratio from 20 to 10 (*i.e.* with increasing acidity).[64] In the reaction with naphthalene, for instance, a maximum yield of hydrogenolysis/ring opening products of 47.9% at 83% conversion was obtained over 2 wt% PdRh (Pd/Rh = 2/1 mol/mol) loaded on the Al-MS sample with a Si/Al ratio of 10 at 300 °C and 6.0 MPa.[64] The catalytic performance for the hydroconversion of naphthalene of noble metal-doped Zr- and Al-MS materials is compared under the same reaction conditions in Table 6.[63,64,68–70,73] These results clearly highlight the benefit of the higher acidity of Al-MS with respect to Zr-MS for promoting ring opening. It can also be inferred from the results presented in Table 6 that, for a given support, the product distribution is highly influenced by the nature and concentration of the supported metal phase. Hence, for Rh/Al-MS (Si/Al ratio of 20), the yield of hydrogenolysis/ring opening products (lumped in the HMW group) increased from 15 to 31% with increasing the concentration of Rh from 1 to 2 wt%. For the same support and at equivalent total metal loading (2 wt%), a higher HMW yield of 40% was attained for the bimetallic Pd–Pt catalyst, albeit at the expense of increasing the yield of undesired gaseous products (LMW group).

Regrettably, in the above studies, the selective ROP products (that is, those with the same number of carbon atoms as the starting reactant) were lumped together with less interesting lighter products resulting from consecutive hydrogenolysis and/or ring opening reactions of the selective ROP (HMW group in Table 6), thus precluding a rigorous assessment of the SRO performance of such bifunctional Zr- and Al-MS-based catalysts.

On the other hand, 0.5 wt% Pt loaded on mesoporous Al–SBA-15, in which Al was directly incorporated during the synthesis using $Al_2(SO_4)_3$ as Al source, was seen to produce relatively high yields (26.4%) of selective (C_{10}) ROP in the conversion of decalin,[62] albeit at higher temperatures (380 °C) than those typically required for zeolite-based catalysts. The main ROP obtained on the 0.5% Pt/Al–SBA-15 catalyst were C_{10}-alkylcyclohexanes and C_{10}-cyclohexenes, with only a small contribution (0.4% yield) from the most preferred OCD products. This low yield contrasts with the outstanding OCD yields above 25%, characteristic of the high-performance zeolite-based catalysts (Table 3). Dispersing Pt on an Al–SBA-15–Al_2O_3 composite improved the activity for the hydrogenation of 1-methylnaphthalene (1-MN) in comparison to Pt/Al–SBA-15 and Pt/Al_2O_3.[71] The enhanced hydrogenation ability of the composite material was ascribed to the preferential deposition and high dispersion of the metal on the Al_2O_3 phase while providing sufficient activated H_2 species to the acid sites of Al–SBA-15 *via* spillover. However, even under the most favorable reaction conditions (380 °C, 5.0 MPa H_2

Table 6 Comparison of the catalytic performance for the hydrogenation and ring opening of naphthalene on bifunctional metal-doped mesoporous catalysts under equivalent reaction conditions (T = 300 °C, P = 6.0 MPa, τ = 6.8 s, and H_2/naphthalene = 21 mol/mol) as a function of the catalyst composition. Adapted from ref. 63, 64, 68–70, and 73

Catalyst[a]	Conv. (%)	Yield (%) Tetralin	Decalin	HMW[b]	LMW[b]
2% Rh/Al-MS(20)	99	29	35	31	4
1% Rh/Al-MS(20)	97	51	20	15	11
2% (Pd–Pt)/Al-MS(20)	99	0	10	40	50
1% (Pd–Pt)/Zr-MS(5)	100	1	75	10	14
2% (Pd–Rh)/Al-MS(10)	83	2	25	48	8

[a] Values in parentheses are the atomic Si/Al(Zr) ratios of the metal-doped mesoporous silica. Metal contents are given in wt%. [b] HMW: high molecular weight (C_7–C_{10}) products resulting from hydrogenolysis and/or ring opening reactions. LMW: low molecular weight cracking products.

pressure, WHSV of 2 h^{-1}), the yield of ROP achieved with the most active 2.5% Pt/Al–SBA-15–Al_2O_3 composite barely reached 6 wt% with a concomitantly low selectivity of 6%. The relatively poor ring opening performance of these materials is probably due, at least in part, to an insufficient Brønsted acidity resulting from an inefficient incorporation of tetrahedral Al in the walls of SBA-15 during the direct synthesis, as inferred from the much higher Si/Al ratio in the final Al–SBA-15 material (136) as compared to that employed in the synthesis gel (20).[71] In this regard, the use of alternative synthesis or post-synthesis approaches that would bring a more effective incorporation of Al in tetrahedral coordination into the siliceous SBA-15 structure should produce more acidic Al–SBA-15 materials with expectedly improved catalytic performance in SRO.

Overall, the above results highlight, as in zeolite-based catalysts, the crucial role played by the acidity of the mesoporous molecular sieve in the hydrogenation and ring opening reactions. However, even in the most favorable cases, the acidity of these materials seems to be too low to effectively promote ring opening at favorably low temperatures. In this respect, it is interesting to mention here that relatively high yields of selective C_{10}-ROP of *ca.* 30% were attained at 300 °C and 6 MPa in the ring opening of decalin over 2 wt% Ir loaded on hybrid micro/mesoporous materials comprising embedded MCM-41 with a BEA zeolite exhibiting a higher Brønsted acidity than the purely mesoporous Al–MCM-41 aluminosilicate.[74] Although these ROP yields are similar to those achieved with many zeolite-based catalysts, further studies would thus be required to better assess the real possibilities of such acidic hybrid materials with hierarchical micro–mesoporosity for SRO, particularly from the point of view of producing the most desired open chain alkanes.

SRO of model compounds in the presence of sulfur

Noble metals are known to be readily poisoned by sulfur compounds present in real feedstocks, which restrict their practical application to dual-stage processes in which the feed is first submitted to severe hydrotreating to reduce the sulfur concentration to a few ppm before entering the SRO reactor. Poisoning of the noble metals by sulfur is believed to occur by weakening of the metal–support interaction that promotes metal particle growth resulting in a progressive loss of the available metallic surface. Given the high sensitivity of noble metals to sulfur, developing more sulfur tolerant noble metal-based SRO catalysts is of pivotal importance for their hypothetical industrial implementation. The main strategies proposed for improving the sulfur tolerance of noble metals rely on the modification of their electronic properties *via* dispersion on acidic carriers or alloying.[75]

Supporting the noble metals on acidic carriers is known to improve the sulfur tolerance as a result of a weakening of the metal–sulfur bond arising from electron transfer from the metal to the acidic support. However, Pt/USY catalysts containing 0.5–2 wt% Pt experienced a gradual deactivation with time-on-stream during the SRO of tetralin in the presence of 100 ppm sulfur (added to the feed as 2-methylthiophene).[51] The Pt/USY catalyst loaded with 1 wt% Pt exhibited the best thioresistance, with a decrease in the yield of iso-decalins and ROP of *ca.* 20% after about 7 h on stream relative to the yields obtained in the absence of sulfur. Interestingly, the addition of 1 wt% Ir to 1 wt% Pt/USY drastically reduced the thiotolerance of the catalyst resulting in the almost suppression of ring opening activity after *ca.* 7 h on stream in the presence of sulfur (Fig. 10). According to XPS measurements, the lower thioresistance of 1% Ir–1% Pt/USY relative to the monometallic Pt/USY catalysts was ascribed to an increased electron density of Pt in the bimetallic Pt–Ir particles.[51] Similarly, Piccolo *et al.* observed an increased thiotolerance during the conversion of tetralin in the presence of 100 ppm H_2S with decreasing concentration of Ir in bimetallic Pd–Ir particles supported on amorphous silica–alumina.[76] These results clearly indicate a lower sulfur tolerance of Ir as compared to Pt and Pd in bifunctional zeolite-based catalysts.

As inferred from the data presented in Fig. 10, the presence of sulfur exerted a higher inhibiting effect on the skeletal isomerization of decalin (and in consequence on the subsequent ring opening of iso-decalins) than on the preceding hydrogenation of tetralin to decalin. On the other hand, increasing the concentration of sulfur (added as H_2S) from 200 to 1600 ppm during the hydroconversion of 1-methylnaphthalene (1-MN) on 0.5% Pt–0.3% Pd/USY barely affected the rate of the hydrogenation of 1-MN to methyltetralins but significantly lowered the hydrogenation rate of methyltetralins (MTs) to methyldecalins while increasing the isomerization and ring opening of MTs to, respectively, methylindanes and alkylbenzenes.[77] The deactivating effect of sulfur in the hydrogenation of the aromatic depended on the source of sulfur, increasing from H_2S to thiophene and further to dibenzothiophene.[78]

The sulfur tolerance of noble metals supported on acidic ordered mesoporous materials has also been studied. In the

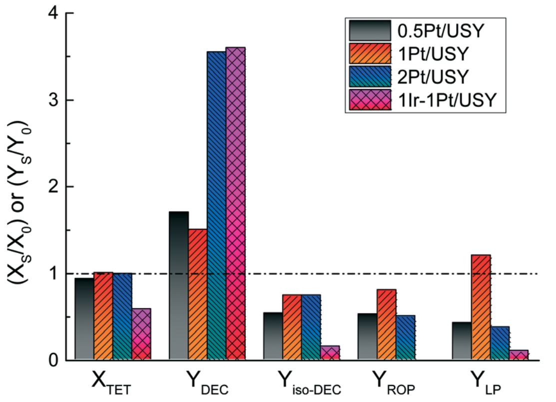

Fig. 10 Relative changes in the conversion of tetralin and yields of the main reaction products after 7 h on stream on bifunctional Pt- and Pt–Ir/USY catalysts upon addition of 100 ppm sulfur. Reaction conditions: 275 °C, 3.0 MPa, H_2/tetralin = 10 mol/mol, WHSV = 2.5 h^{-1}, 100 ppm sulphur added as 2-methylthiophene. Adapted from ref. 51.

presence of 100 ppm of dibenzothiophene (DBT), 1 wt% monometallic (Pt, Pd, Rh) catalysts loaded on a mesoporous aluminosilicate (Al-MS) with an atomic Si/Al ratio of 20 displayed significant deactivation during the hydroconversion of naphthalene, producing mainly tetralin and gaseous cracking products in detriment of decalin and hydrogenolysis/ring opening products.[73] A similar progressive decrease in the hydrogenation and hydrogenolysis/ring opening reactions with a concomitant increase in the formation of tetralin and light products was also observed for bimetallic (2 wt%) PdPt (Pd/Pt = 4/1 mol/mol) and PdRh (Pd/Rh = 2/1 mol/mol) compositions supported on Al-MS with Si/Al = 10–20 during the conversion of naphthalene in the presence of different amounts of DBT.[64,68] The influence of the concentration of DBT in the feed (0–3000 ppm) on naphthalene conversion and yields of the relevant products is presented in Fig. 11 for the bimetallic 2% PdRh (2 : 1)/Al-MS (Si/Al = 10) catalyst.[64] As seen in the figure, drastic changes in product yields already occurred at a DBT concentration of 100 ppm.

The precedent discussions make clear the need for improving the thioresistance of the noble metal-based catalysts and/or to drastically reduce the sulfur content in the feed to very low levels (deep hydrodesulfurization) to allow the SRO to proceed efficiently. In the following section, the upgrading of sulfur-containing industrial feedstocks *via* SRO is addressed.

SRO of industrial feedstocks

In comparison to the studies dealing with SRO of model naphthenic and aromatic compounds, the works employing industrial feedstocks are very scarce, due partly to the higher experimental and analytical complexity associated with the use of real feeds. In this section, the most relevant results regarding the upgrading of industrial LCO feedstocks *via* SRO on bifunctional catalysts comprising noble metals and acidic micro- and mesoporous molecular sieves, as those described before for model compounds, are discussed.

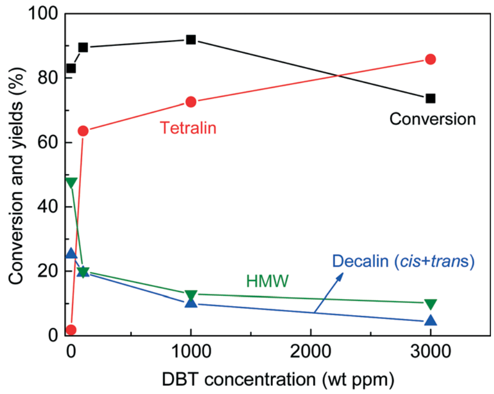

Fig. 11 Influence of the increasing concentration of DBT on naphthalene conversion and product yields for the bimetallic PdRh/Al-MS catalyst (Pd + Rh = 2 wt%, Pd/Rh = 2, Si/Al = 10). Reaction conditions: *T* = 300 °C, *P* = 6 MPa, H_2/naphthalene = 21 mol/mol, contact time = 6.8 s. Adapted from ref. 64.

Bimetallic Pd–Pt catalysts (2 wt%, Pd/Pt molar ratio of 4) supported on a mesoporous aluminosilicate (Al-MS) with a Si/Al ratio of 20 was applied for the hydrogenation and ring opening of a hydrotreated 85% LCO/15% SR feed mixture containing 32 ppm sulphur and 10 ppm nitrogen under industrially relevant conditions (270–345 °C, 6.0 MPa, LSHV 1 h^{-1}, H_2/feed ratio of 600 vol/vol).[68] A CN increase of 7.5 points, representing an improvement of 22% with respect to the feed (CN = 36.6), was achieved at 300 °C over the Pd–Pt/Al-MS catalyst.[3] Under these conditions, about 90% of the initial aromatics were saturated. Interestingly, at 300 °C, the increase in CN occurred with a concomitantly low loss in product yield (1%). In a posterior study, these authors observed a 7-point CN gain at 300 °C and 6 MPa in the conversion of a hydrotreated 85% LCO/15% SR feed (33 ppm sulphur, density of 0.8732 g cm^{-3}, and CN of 32.9) over a bimetallic PdRh (Pd/Rh molar ratio 1/1) supported on the same mesoporous Al-MS carrier (Si/Al = 20).[64] Interestingly, these bimetallic MAS-supported catalysts displayed better performance at lower temperatures than a zeolite-based reference catalyst. The composition and properties for the reference catalyst, however, were not reported.

As mentioned previously, upgrading of LCO fractions *via* aromatics saturation (ASAT) followed by selective ring opening (SRO) provides higher improvements in CN and product density as compared to the complete saturation of aromatics. However, the consumption of H_2 in the combined ASAT + SRO process is also higher, which may jeopardize the process economics. An alternative approach with less H_2 requirements could be to perform the partial hydrogenation of aromatics in the first step followed by ring opening of the formed benzo-naphthenic compounds. In a recent study, Calemma and co-workers have compared Pt and Ir catalysts loaded on several supports showing distinct acidic properties for the hydrogenation and ring opening of a hydrodesulphurized LCO feed (16 ppm sulfur, cetane index of 34.2).[79] It was seen that the catalyst based on Ir loaded on a mesoporous silica–alumina (Al-MS, Si/Al ~ 25) with mild Brønsted acidity leads to a product exhibiting a cetane gain equivalent to that produced by full hydrogenation of the aromatics but still leaving 27% of aromatics, which represent a 20–30% saving in H_2 consumption. This behaviour is illustrated in Fig. 12 showing the cetane index (CI) *versus* the aromatics content in the reaction products obtained on the different Pt and Ir catalysts.[79] The behavior of Ir/Al-MS was related to the higher activity of Ir (as compared to Pt) for opening the naphthenic rings in the benzo-naphthenic structures present in the HDS-LCO feed and the mild acidity and mesoporous structure of the Al-MS support. In turn, while for the Ir catalysts the performance was strongly dependent on the nature (*i.e.* acidity) of the support, saturation of aromatics was the main reaction on the Pt catalysts irrespective of the support, which was ascribed to the much higher hydrogenating power of this metal. In another study, a 0.9% Ir/K-USY (Si/Al = 40, 0.75 wt% K) catalyst was applied for the

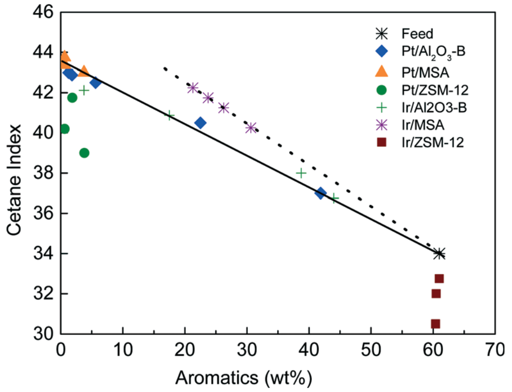

Fig. 12 Cetane index (CI) *versus* aromatic content of conversion products of a HDS-LCO feed on bifunctional Pt and Ir catalysts. Adapted from ref. 79.

hydrogenation and ring opening of untreated LCO having high aromatics (72.3%) and sulphur (2.513 ppm) contents, high density (0.9366 g cm^{-3}), and a very low CN of 18.[80] The reaction was conducted in a batch reactor at 300 °C and *ca.* 30 bar H_2 pressure for 1 h. Under the studied conditions, the CN was increased from 18 to 27 due to an increase in the concentration of monoaromatics and aliphatics. Furthermore, the total aromatics content after the conversion with the 0.9% Ir/K-USY catalyst remained high (62%). Indirectly, these results indicate that upgrading of LCO requires a previous hydrotreating step to severely reduce the amount of polyaromatics and sulphur before further upgrading *via* SRO.

A summary of the most relevant results obtained in the upgrading of LCO by SRO on the above bifunctional noble metal catalysts supported on microporous and mesoporous molecular sieves is given in Table 7.

It is worth noting that the final CN values achieved in these studies are still below the minimum value of 51 required by EU standards. Remarkably, CN values meeting the current specifications in the conversion of a hydrotreated LCO were reported in a recent work by Calemma *et al.* using the so-called "high performance ring opening catalysts" (HIPEROC) comprising Ir (3 wt%) or Pt (4 wt%) loaded on Na-exchanged Y zeolites with a low concentration of BAS.[81] The reactions were carried out in a continuous bench scale fixed bed reactor at 7.0 MPa, a H_2/feed ratio of 0.15 wt/wt, WHSV of 1–3 h^{-1}, and a temperature in the range of 290–350 °C. At 80% gas oil yield, increases in CI of 11 and 7 points were obtained for the 4% Pt/Na,H-Y and 3% Ir/Na,H-Y catalysts, respectively. The higher CI increase achieved with the Pt catalyst was related to the multiplet mechanism prevailing on this metal, which preferentially cleaves substituted C–C bonds leading to less branched (higher cetane) products, in opposition to the dicarbene mechanism favoured on Ir and which preferentially cleaves unsubstituted C–C bonds resulting in more branched products with a lower CN. Interestingly, these catalysts lead, at constant cracking yields, to higher CN than conventional bifunctional 2% Ir/USY and 2% Ir/MSA catalysts owing to a higher ring opening activity of the former resulting in a higher % of ring disappearance, as presented in Fig. 13. It should be noted, however, that the dearomatized LCO used in this study contained very low (<0.5 ppm) sulfur content, which may benefit the hydrogenation and ring opening activity of the noble metals.

Concluding remarks

As we have shown in this perspective article, bifunctional catalysts comprising noble metals and acidic molecular sieves have good prospects for improving the cetane number of low-quality distillate fractions like LCO *via* selective ring opening (SRO) of naphthenic compounds. Large-pore three-dimensional zeolites such as Y, beta, and ITQ-21 are better suited to the SRO of bicyclic naphthenic and aromatic compounds as those present in middle distillates than medium-pore zeolites due to the steric constraints imposed to the formation and diffusion of the targeted ring opening products (ROP) in the latter. Besides the porous structure, the acidity of the zeolite is a crucial parameter for maximizing the yield of ROP. Brønsted acid sites (BAS) are required to catalyze the skeletal isomerisation (C_6-to-C_5 ring contraction) of the naphthenes as an essential step preceding ring opening. However, a too high Brønsted acidity promotes the formation of undesired light hydrocarbons from skeletal isomers and ROP through consecutive dealkylation and cracking reactions resulting in low ROP selectivities and significant yield losses and may induce catalyst deactivation by coking as well. In fact, catalysts

Table 7 LCO quality enhancement after SRO on bifunctional zeolite-supported noble metal catalysts

Catalyst	CN	Density (kg dm^{-3})	Sulfur (ppm)	PAH[a] (wt%)	Ref.
(Feed)	36.6	0.891	32	10.3	
Pd–Pt/Al-MS	45.0	0.840	<1	<3.0	68
(Feed)	32.9	0.873	33	5.5	
PdRh/Al-MS	40.0	0.840	<1	<3	64
(Feed)	34.2	0.888	16	68.4[b]	
Pt/USY	44.0	—	—	<1[b]	
Pt/Al-MS	43.4	—	—	<2[b]	79
Ir/Al-MS	42.4	0.849	—	21.0[b]	
(Feed)	18	0.937	2513	4.8	
Ir/K-USY	27	0.889	—	0.39	80

[a] PAH: polycyclic aromatics. [b] Total aromatics.

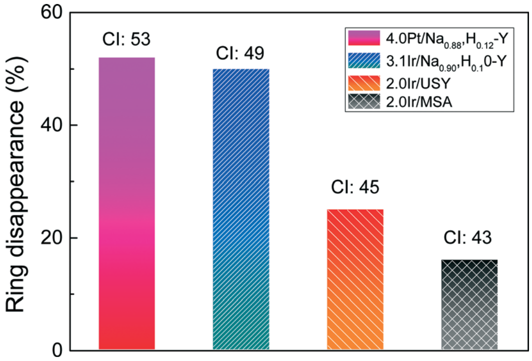

Fig. 13 Comparison of high-performance ring opening catalysts with bifunctional catalysts showing the ring disappearance (%) at a constant cracking yield of 20 wt% in the hydroconversion of a dearomatized LCO feed. Adapted from ref. 81.

comprising noble metals displaying high hydrogenolysis activity, such as Pt and Ir, dispersed on low acidic Y and beta zeolites in which protons are exchanged with alkali cations, particularly with Na^+ and Cs^+, appear the most promising for SRO. On such catalysts, the principal role of the zeolite is to catalyze the C_6-to-C_5 ring isomerisation, preferentially without increasing the degree of branching of the molecule, enabling the subsequent opening of C_5 rings in skeletal isomers to proceed easier and with high selectivity on the noble metals *via* hydrogenolysis. These so-called "high-performance" SRO catalysts produced unprecedented high yields (>30%) of the most desired open chain alkanes bearing higher cetane numbers than the corresponding alkylcycloalkanes with the same number of carbon atoms.

Noble metals loaded on acidic ordered mesoporous materials with Zr or Al incorporated into the siliceous matrix have also been studied for the SRO of naphthenic and aromatic compounds. However, even for the most acidic Al-doped mesoporous silicas, the maximum ROP yields attained did not reach, in most of the cases, the values achieved with the zeolite-based catalysts. When starting from bicyclic aromatics like tetralin and naphthalene (and alkylated derivatives), these catalysts generally show good hydrogenation performance at favourably low reaction temperatures albeit relatively poor activity for hydrogenolysis/ring opening reactions. In this respect, hierarchical micro–mesoporous materials possessing a Brønsted acidity intermediate between that of purely mesoporous aluminosilicates and H-zeolites and high accessibility to the active sites might be suitable supports for preparing more efficient bifunctional SRO catalysts, particularly for treating bulky multi-ring compounds.

The thiotolerance of these bifunctional catalysts is of particular concern for practical applications. On the whole, the studies performed using model aromatics in the presence of sulfur indicate a relatively low resistance against sulfur poisoning of the noble metal-based SRO catalysts, despite the fact that the sulfur resistance of noble metals is known to be enhanced when supported on acidic carriers like zeolites. Moreover, Ir-containing catalysts seem to be less thiotolerant than those based on Pt or Pd. In general, the presence of sulfur exerts a stronger inhibiting effect on the skeletal isomerisation and ring opening reactions than on the hydrogenation of the aromatic rings. Therefore, development of more thioresistant SRO catalysts based on noble metals is advised, albeit very challenging. Possible strategies in this direction could be, for instance, the tuning of the metal–support interaction strength by proper modification of the preparation and/or activation conditions, *via* shape-selective exclusion through the encapsulation of the metal clusters within the zeolite pores,[82] and the preparation of bimetallic particles with the appropriate degree of alloying, composition, and size.

The initial expectations derived from the SRO studies using model S-free naphthenic and aromatic molecules were not fulfilled when dealing with industrial hydrotreated LCO feedstocks. In this case, even if significant increases in CN with respect to the feed were achieved, the final CN values did not reach the minimum of 51 demanded by the EU regulations. Probably, the lower-than-expected increases in CN are related, at least partly, to the relatively low sulfur resistance of the bifunctional noble metal-based catalysts. Indeed, the only study reporting CN values above 51 used "high-performance" Pt(Ir)/Na,H-Y catalysts for the SRO of a dearomatized LCO feed containing less than 0.5 ppm sulfur. It seems, thus, that severe hydrotreating of the LCO feed would be compulsory prior to performing SRO as a final upgrading step. In turn, one has to take into account that not every ROP formed has a CN higher than the starting naphthene. Moreover, the high compositional complexity of the reaction products derived from industrial feedstocks precludes the assessment of the real contribution of SRO (besides hydrogenation of aromatics and hydrocracking) to the observed CN gains. Nonetheless, it should be remarked that, in spite of the limited increase in CN observed with industrial hydrotreated LCO feedstocks, SRO may offer other potential benefits to refiners such as an improvement in the cloud point of the diesel and in the volume of products available for selling due to the decrease in fuel density.

Acknowledgements

The authors gratefully acknowledge the support of the Spanish Ministry of Economy and Competitiveness (MINECO) through the Severo Ochoa Program for Centers of Excellence (SEV-2012-0267) and of the Conshelho Nacional de Pesquisa e Desenvolvimento (CNPq) of Brazil through project 401474/2014-3 (PVE 2014).

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