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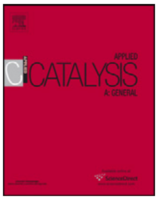

Conversion of 1-tetralone over HY zeolite: An indicator of the extent of hydrogen transfer

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ABSTRACT

The conversion of pure 1-tetralone and its mixtures with *n*-decane, decalin, tetralin, or 1,5-dimethyl tetralin (DMT) has been investigated over HY zeolite. The dominant reactions undergone by 1-tetralone are the dehydrogenation to 1-naphthol and the subsequent isomerization to 2-naphthol. In the presence of hydrocarbons, the hydrogen transfer/dehydration of naphthols is accelerated, and naphthalene is formed in different amounts, depending on the nature of the co-fed hydrocarbon. In this contribution, it is demonstrated how the product distribution from the tetralone conversion can be used as an indicator of the hydrogen transfer ability of a particular hydrocarbon, or mixture of hydrocarbons. The relative order of hydrogen transfer ability of the various hydrogen donating compounds, as inferred from the naphthalene-to-naphthol product ratio, is DMT > tetralin ≈ decalin > *n*-decane. This trend agrees well with the hydride dissociation energy of individual donors calculated by DFT.

1. Introduction

The extent of hydrogen transfer in fluid catalytic cracking (FCC) processes has an important effect on the product distribution and catalyst stability [1–4]. While hydrogen transfer has well known benefits, such as improved liquid yield and reduce coke formation, an excessive rate of hydrogen transfer may have negative effects. A major concern is the potential loss of olefinicity in the product by excessive hydrogen transfer, which has the undesired consequence of reducing octane number in the gasoline fractions [5–7].

It is widely accepted that, in the transition state, the carbenium ions on the acid sites can accept hydride ions from hydrogen-donor molecules and that the extent of this transfer can be modified by the nature of the catalyst, e.g., density or proximity of acid sites, presence of rare earth, etc. [8,9]. However, hydrogen transfer is a bimolecular reaction; therefore, the nature of both the hydride donor and hydride acceptor can impact the hydrogen transfer process. Therefore, it is anticipated that varying the nature of the hydrogen donor, the extent and rate of hydrogen transfer can be varied. In the majority of the previous studies about the extent of hydrogen transfer [8,9], the focus has been on the effect of different zeolite catalyst parameters, such as zeolite structure, number of Al per unit cell, and acidity strength, rather than the intrinsic properties of the different hydrocarbons that may act as H-donors. A simple method that can predict a-priori the ability of a given feed component or a mixture of components may have interesting applications in FCC technology. This is the focus of this contribution.

Being important components of typical FCC catalysts, HY, REY, and USHY zeolites have been the subject of many studies related to cracking and hydrogen transfer [10]. In our previous study on 1-tetralone conversion on HY zeolites [11], we showed that naphthol is a dominant product, which can further transform to naphthalene via hydride transfer-dehydration reactions. It was suggested that naphthalene formed predominantly in the presence of hydrogen donor molecules. In this study, we have investigated the reactivity of 1-tetralone in the presence of different hydrogen donor molecules, which typically exist in FCC feed stream such as paraffins, naphthenics, and aromatics. Using tetralone as an indicator is highly convenient since it only produces a small number of products, which facilitates the analysis and the quantification of the effects of the hydrogen donor. We have selected molecules with similar number of carbon atoms but with varying functionalities, which we anticipate that results in varying hydrogen transfer capacity [12–16]. The relative rates of the possible conversion paths of 1-tetralone were found to depend on the hydrogen-donation capacity of the hydrocarbons co-fed to the reactor. DFT calcula-

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tions were used to provide a correlation between the energy of hydride dissociation and the extent of hydrogen transfer observed experimentally.

2. Experimental

2.1. Catalytic activity testing

The model hydrogen donors used in this study were *n*-decane, decalin, tetralin, and 1,5-dimethyl tetralin (DMT), while 1-tetralone was used as a hydrogen acceptor. These compounds are fairly heavy and their boiling points varied in a wide range. To avoid using a solvent that might interfere with the process of hydrogen transfer and minimize condensation in the system, the feed was introduced to the reactor using a vapor saturation vessel made of glass through which the carrier gas was bubbled. By adjusting the temperature of the saturator, the vapor pressure of the individual compounds can be readily controlled. When mixtures were co-fed into the reactor, each component was controlled independently in a separate saturator. The feed rate was regulated by the carrier gas flow, and an additional inert gas line was added to keep the total gas flow rate constant.

The reactions were conducted in a ¼″ stainless steel reactor. Commercial HY zeolite from Zeolyst International (Si/Al = 15 and 40) used as the catalyst was placed at the center of the reactor. Since the zeolites were purchased in the proton form, the only pretreatment needed was to heat them up in-situ under He flow at 450 °C for 1 h to remove adsorbed water or any other contaminants. The top and bottom parts of the packed bed were filled with 3 mm-diameter glass beads. The operating conditions were as follows: atmospheric pressure, 450 °C, He carrier gas, space-time, W/F = 1.6 h, with respect to the mass flow rate of 1-tetralone in both pure and mixed feeds. Prior to each run, the feed was sent through the by-pass line until the concentration stabilized. At this point, it was switched to enter the reactor. The carbon mass balance was checked for every run by the analysis of the by-pass and the reactor outlet. The reaction products were sampled every 0.5 h on stream and analyzed on-line using an HP5890 gas chromatograph, equipped with an HP-5 column and an FID detector. A carbon elemental analyzer was used to measure the amount of coke deposits on the catalysts.The acid properties of the various zeolites were characterized by temperature programmed desorption of ammonia (NH_3-TPD), conducted in a 0.25 in. o.d. quartz reactor. Before each experiment, the 50 mg of zeolite sample was pretreated for 0.5 h in flowing He (30 mL/min) at 600 °C to eliminate any adsorbed water. Then, the temperature was lowered to 100 °C, and the sample exposed to a 2% NH_3/He, 30 mL/min stream for 30 min to reach saturation. After exposure, pure He was passed for 0.5 h over the sample to remove any weakly adsorbed NH_3. To conduct the TPD, the temperature was increased at a heating rate of 10 °C/min up to 650 °C. The evolution of desorbed species was continuously monitored by a Cirrus mass spectrometer (MKS) recording the signals $m/z = 17$ and 16 (corresponding to NH_3). The density of acid sites was quantified by calibrating the MS signals with the average of ten 5-mL-pulses of 2% NH_3/He.

2.2. Computational methods

To correlate the different extent of hydride transfer observed experimentally for the various compounds with their intrinsic molecular properties, density functional theory (DFT) calculations were carried out using the Gaussian 03 suite of programs [17]. Molecular geometries and zero-point energies (ZPE) for all species were optimized by the Berny analytical gradient method [18], and verified to be local minima by computing the Hessian matrix. DFT calculations for the doublet states of the radicals (i.e., protonated species) employed an unrestricted formalism. This study was computed at B3PW91 density functional with using the 6–31 + G(d,p) basis set, which were claimed to provide a good estimation for hydrogen transfer reactions [19].

Table 1
Catalytic reaction of pure compounds over HY zeolites.

Feed	1-Tetralone	*n*-Decane	Decalin	Tetralin	DMT
Conversion	97.7	9.4	19.3	26.3	100.0
Product yields (wt%)					
C_1–C_6	0.0	9.4	10.7	3.5	32.1
Cyclic olefins (C_6–C_{10})	0.0	0.0	6.1	3.3	0.0
Alkylbenzenes	0.0	0.0	2.6	5.9	44.1
n-Decane	0.0	90.6	0.0	0.0	0.0
trans-Decalin	0.0	0.0	65.4	0.0	0.0
cis-Decalin	0.0	0.0	15.3	0.0	0.0
Tetralin	0.0	0.0	0.0	73.7	0.0
1,5-Dimethyltetralin	0.0	0.0	0.0	0.0	0.0
Alkylnaphthalenes	0.0	0.0	0.0	0.0	23.8
Naphthalene	4.4	0.0	0.0	13.6	0.0
1-Tetralone	2.3	0.0	0.0	0.0	0.0
1-Naphthol	74.0	0.0	0.0	0.0	0.0
2-Naphthol	11.3	0.0	0.0	0.0	0.0
Coupling products	8.1	0.0	0.0	0.0	0.0

Reaction conditions: 450 C, 1 atm He, HY (Si/Al = 15), W/F = 1.6 h, TOS 0.5 h.

Since, as discussed below, naphthol plays a central role in the hydride transfer mechanism [11], it was important to determine which protonated intermediate is most likely to form. Using DFT, the proton affinity (PA) of naphthol in different protonated structures was compared, according to the expression [20,21]:

$$PA = -\{H(C_{10}H_9O^+) - [H(C_{10}H_8O) + H(H^+)]\} \tag{1}$$

where H(i) is the enthalpy of species i, being $C_{10}H_9O^+$ = the protonated naphthol in each specific structure; $C_{10}H_8O$ = naphthol; and H^+ = proton. That is, a large positive PA indicates a stable compound.

To compare the experimentally observed trends with the theoretical predictions, hydride dissociation energies of various donor molecules were calculated as follows:

$$E_{dis} = \{[H(R^+) + H(\text{hydride})] - H(R - H)\} \tag{2}$$

where R – H is the donor; and R^+ is a corresponding carbenium ion.

The relative activation energy of hydride dissociation (E_A) can be expressed by a ratio of hydride dissociation energy (E_{dis}) for each donor molecule over that for the C–H breaking of methane (482.6 kJ/mol);

$$E_A(x) = \frac{E_{dis}(x)}{E_{dis}(CH_4)} \tag{3}$$

where x is a particular donor molecule.

A lower E_A value indicates a better hydrogen transfer ability. In this simplified analysis, proton affinity and relative activation energy values are taken as intrinsic properties of the individual molecules and were determined in the gas phase basis, independent of their interaction with the solid catalyst.

3. Results

3.1. Catalytic reaction of pure compounds over HY zeolites

The total conversion and product distribution resulting from feeding the pure compounds (1-tetralone, *n*-decane, decalin, tetralin, and DMT) onto the HY (Si/Al = 15) zeolite are shown in Table 1. Observed cracking products are linear and branched alkenes/anes (C_1–C_6), cyclic olefins (C_6–C_{10}), and alkylbenzenes (e.g., ethylbenzene, toluene, and xylene). It is seen that DMT and 1-tetralone are significantly more reactive than the other compounds

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Table 2
Overall yields from catalytic reactions of mixture of hydrocarbons and 1-tetralone over HY zeolites.

Co-feed	*n*-Decane	Decalin	Tetralin	DMT
Product yields (wt%)				
C_1–C_6	2.3	1.7	1.5	5.4
Cyclic olefins (C_6–C_{10})	0.0	2.0	1.3	0.0
Alkyl benzenes	0.0	2.7	2.2	5.1
n-Decane	49.4	0.0	0.0	0.0
trans-Decalin	0.0	35.1	0.0	0.0
cis-Decalin	0.0	9.3	0.0	0.0
Tetralin	0.0	1.2	23.4	0.0
1,5-Dimethyltetralin	0.0	0.0	0.0	0.9
Alkyl naphthalenes	0.0	0.0	0.0	44.2
Naphthalene	5.1	27.3	52.5	34.5
1-Tetralone	0.9	2.4	1.8	2.4
1-Naphthol	31.1	12.5	11.0	5.6
2-Naphthol	8.9	1.8	3.6	0.7
Coupling products	2.4	4.1	2.6	1.2

Reaction conditions: % co-fed concentration = 50 ± 5%, 450 C, 1 atm He, HY (Si/Al = 15), W/F = 1.6 h, TOS 0.5 h.

Table 3
Conversion and selectivity from catalytic reactions of mixture of hydrocarbons and 1-tetralone over HY zeolites.

Co-feed	*n*-Decane	Decalin	Tetralin	DMT
Conversion of 1-tetralone	98.1	95.0	96.0	94.7
Conversion of hydrocarbons	4.4	14.7	57.3	98.4
Selectivity of 1-tetralone products (wt%)				
Naphthalene	10.7	59.7	60.3	82.1
1-Naphthol	65.4	27.4	25.3	13.4
2-Naphthol	18.8	3.9	8.3	1.6
Coupling products	5.1	9.0	6.0	2.9
Naphthalene/Naphthol ratio	0.13	1.91	1.79	5.47
Selectivity of hydrocarbons products (wt%)				
C_1–C_6	100.0	22.3	4.9	9.8
Cyclic olefins (C_6–C_{10})	0.0	26.2	4.3	0.0
Alkylbenzenes	0.0	35.6	7.0	9.4
n-Decane	–	0.0	0.0	0.0
trans-Decalin	0.0	–	0.0	0.0
cis-Decalin	0.0	–	0.0	0.0
Tetralin	0.0	15.8	–	0.0
1,5-Dimethyltetralin	0.0	0.0	0.0	–
Alkylnaphthalenes	0.0	0.0	0.0	80.8
Naphthalene	0.0	0.0	83.8	0.0

Reaction conditions: % co-fed concentration = 50 ± 5%, 450 C, 1 atm He, HY (Si/Al = 15), W/F = 1.6 h, TOS 0.5 h.

in the series. The crackability, i.e., conversion to lighter products, follows the order DMT > decalin > tetralin > *n*-decane. As expected, the presence of tertiary carbons in DMT and decalin increases the crackability of these molecules, as previously observed [22–24]. Dehydrogenated products (i.e., alkylnaphthalenes) were obtained from DMT, but in a lower extent. Some naphthalene was also obtained from dehydrogenation of tetralin, but not from decalin.

In contrast with the hydrocarbons, a major part of 1-tetralone conversion proceeded through dehydrogenation to form naphthols, without cracking. This is consistent with our previous study [11], in which dehydrogenation of 1-tetralone to 1-naphthol was found to be the dominant reaction pathway, and isomerization of 1-naphthol toward 2-naphthol was observed only at high temperatures (i.e., >400 °C). Only a small amount of naphthalene can be produced from 1-tetralone when fed alone.

The extent of overall dehydrogenation follows the order 1-tetralone > DMT > tetralin. That is, it appears that the presence of the aromatic ring and substituted groups (e.g., methyl) on the naphthenic ring readily improves the hydrogen transfer ability of the molecule, leading to an increased degree of dehydrogenation [25]. It can be seen that coupling products (e.g., multi-ring oxygenates) are only produced from 1-tetralone.

3.2. *Catalytic reaction of hydrocarbon with co-fed 1-tetralone over HY zeolites*

In this experiment, 1-tetralone was co-fed with the hydrocarbons, i.e., *n*-decane, decalin, tetralin, and DMT. The overall yields from catalytic reactions of the mixture feeds are shown in Table 2. Significantly different conversions and product selectivities, as compared with those from the pure feeds, were observed for each corresponding hydrocarbon (Table 3). Although the conversion of 1-tetralone remained close to 100%, the product selectivity, particularly towards naphthalene, was very sensitive to the nature of the hydrocarbon co-fed in to the reactor. It appears that, in the presence of a hydrocarbon that may act as a hydrogen donor, the naphthols deriving from 1-tetralone behave as hydrogen acceptors and subsequently undergo dehydration to produce naphthalene, as previously proposed [11]. The extent of this transformation depends on the co-fed hydrocarbon. Therefore, the intrinsic hydride transfer ability of a particular hydrocarbon species can be represented by the naphthalene-to-naphthol ratio derived from tetralone (Table 3). A clear trend is observed in this ratio, DMT > tetralin ≈ decalin > *n*-decane. It is likely that a relatively rapid formation of coke occurred at the beginning of the run (i.e., ~first 10 min), whereas a quasi-plateau in activity was obtained later [26]. The integrated amounts of coke formed over 1 h on stream are rather low (Table 4). Therefore, it can be expected that the contribution of to hydrogen from coke to the total to hydrogen transfer is negligible compared to the significant changes observed in product distribution.

In parallel to the changes in 1-tetralone products as a consequence of the enhanced hydrogen transfer, changes in overall conversions and product distribution from the individual hydrocarbons were clearly observed. For example, in the conversion of DMT in the presence of tetralone, dehydrogenated products (i.e., alkylnaphthalenes) became dominant rather than cracking products, which dominated in the pure DMT feed reaction. Similar behavior was observed with tetralin. In this case, the conversion significantly increased with a higher selectively towards the dehydrogenated product, naphthalene. The dehydrogenation of DMT and tetralin can be ascribed to their intrinsic hydride donor ability, which is promoted in the presence of the hydride acceptor, 1-tetralone. In contrast to DMT and tetralin, no significant dehydrogenation products (i.e., tetralin or alkylbenzene) were obtained from decalin despite the high naphthalene/naphthol ratio observed in the parallel 1-tetralone reaction. In fact, this ratio was as high as that obtained when co-feeding tetralin. This suggests that the hydrogen transfer occurs from the cracking products, most of which end up as cycloalkenes and alkylbenzenes. Also, isomerization of (*cis*-, *trans*-) decalin, which involves hydrogen exchange but not net hydrogen donation may accelerate the hydrogen transfer process for the conversion of 1-tetralone into naphthalene and water. Therefore, a

Table 4
Amount of coke on spent catalysts determined by an elemental analyzer.

Feed	Coke (%)
Tetralone	1.28
n-Decane	0.98
Decalin	1.16
Tetralin	1.77
DMT	1.59
n-Decane + Tetralone	1.96
Decalin + Tetralone	2.21
Tetralin + Tetralone	2.07
DMT + Tetralone	1.12

Reaction conditions: 450 C, 1 atm He, HY (Si/Al = 15).

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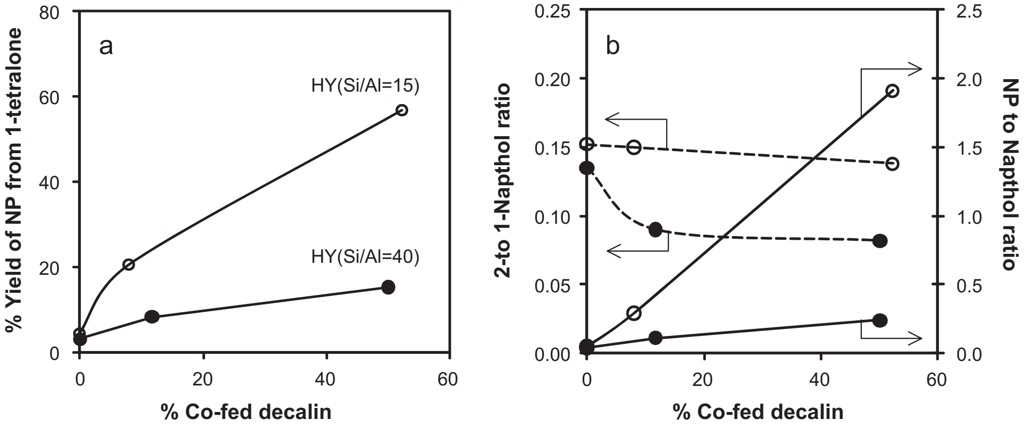

Fig. 1. Effect of % co-fed decalin on (a) yield of naphthalene (NP); and (b) 2-naphthol to 1-naphthol ratio, and NP to naphthol ratio . Reaction conditions: 450 C, 1 atm He, TOS = 0.5 h, HY (Si/Al = 15) (○), HY (Si/Al = 40) (●).

high yield of naphthalene was observed from 1-tetralone without a prominent change in the product distribution of decalin.

In the case of *n*-alkanes co-feed, their weaker hydrogen-donor ability had little effect in the naphthalene/naphthol product ratio of 1-tetralone (i.e., only a slight increase from about 0.05 for pure 1-tetralin alone to 0.13 for the mixed feed with added *n*-decane). It can be suggested a small amount of hydrogen transfer from *n*-decane can take place, essentially associated with cracking and coke formation. However, the cracking of both *n*-decane and decalin, lacking aromatic structure, is significantly suppressed in the presence of tetralone, due to a competitive adsorption of the oxygente.

At the same time, the yields of coupling products observed from all of the mixture feeds were significantly lower than that with pure 1-tetralone. This can be explained, again, by enhanced hydrogen transfer from the co-fed hydrocarbon, as well as by the dilution effect. The latter may be more important with the weaker hydrogen-donors (i.e., *n*-decane). However, a part of cracking products from decalin may participate in coupling formation, and result in a higher yield as compared to others.

3.3. Effect of decalin concentration on the product distribution of 1-tetralone conversion over HY zeolites with varying acidity (Si/Al ratio 15 and 40)

In addition to varying the nature of the hydrogen donor, we investigated the effect on hydrogen transfer of varying the concentration of the hydrocarbon as well as the acidity density of the catalyst. Increases in naphthalene yield were observed by increasing either the concentration of decalin (Fig. 1a) or the acidity of the catalyst (Fig. 2a). The contribution to naphthalene from decalin dehydrogenation is negligible under the reaction conditions investigated. Therefore, the enhanced concentration of naphthalene product can be solely ascribed to the tetralone conversion path, enhanced by hydrogen transfer. Since, in this path, hydrogen transfer enhances the conversion of naphthol to naphthalene, a good indicator of the extent of hydrogen transfer is the naphthalene/naphthol ratio. This ratio clearly increases with either increasing concentration of the hydrogen donor (Fig. 1b) or increasing acidity of the catalyst (Fig. 2b). At the same time, since conversion of naphthol to naphthalene competes with isomerization, the 2-naphthol/1-naphthol ratio was found to decrease with increasing decalin concentration (Fig. 1b). By contrast, when the acid density increases, both 1-naphthol isomerization and naphthalene production (i.e., hydrogen transfer) increase (Fig. 2b), as expected [27,28].

3.4. Proton affinity of naphthol from DFT calculation

As mentioned above, naphthalene formation occurs via the acid-catalyzed dehydration of naphthol. Therefore, it is important to determine what kind of protonated naphthol species is the most probable structure. Fig. 3 illustrates various possible protonated structures of naphthol and their corresponding proton affinity, which can be taken as a measure of their stability, i.e., the larger positive value the more stable. The various protonated species tested include the protonated keto-forms of 1-naphthol (**1**) and 2-

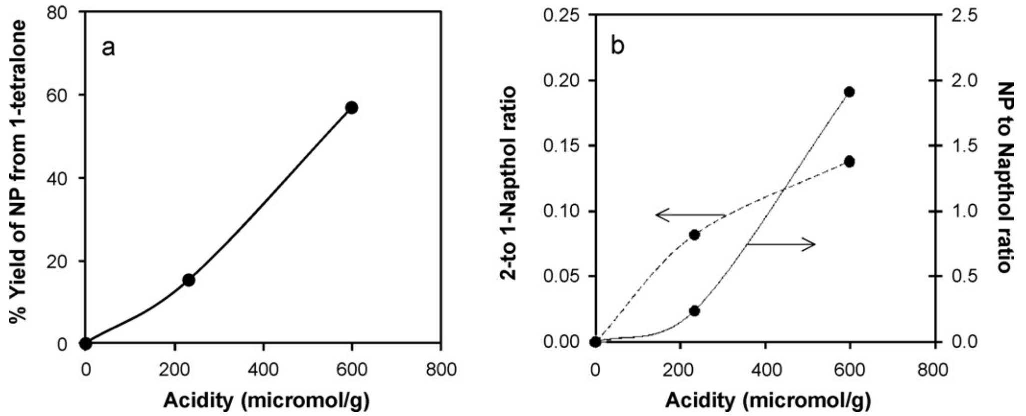

Fig. 2. Effect of acidity on (a) yield of naphthalene (NP); and (b) 2-naphthol to 1-naphthol ratio, and NP to naphthol ratio. Reaction conditions: co-fed concentration = 50 ± 5%, 450 C, 1 atm He, TOS = 0.5 h.

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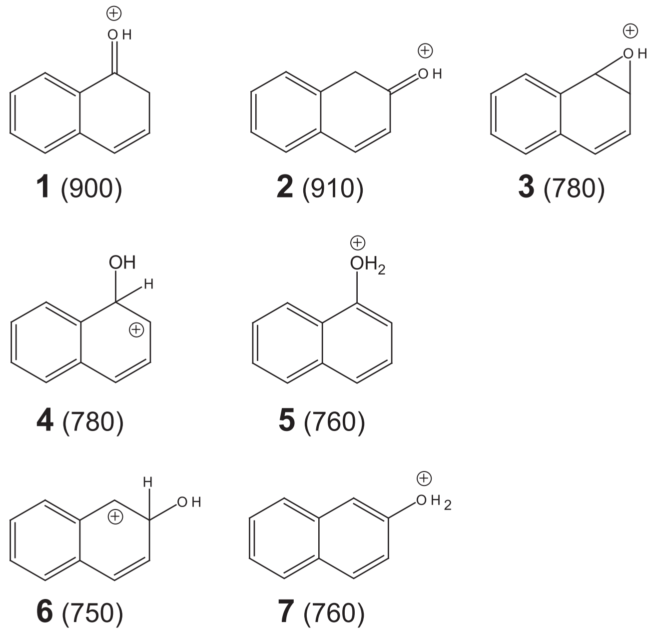

Fig. 3. Possible $C_{10}H_9O^+$ ions. Protonation of naphthol is compared for the keto-forms of 1-naphthol (**1**) and 2-naphthol (**2**) to form carbenium ions; the oxiranium cation (**3**); and the enol-forms of 1-naphthol (**4,5**) and 2-naphthol (**6–7**). The corresponding PAs in kJ/mol are shown in the parentheses.

naphthol (**2**) to form carbenium ions; the oxiranium cation (**3**); the protonated enol-forms of 1-naphthol (**4, 5**) and 2-naphthol (**6, 7**). The results of the calculations show that protonated keto-forms are the most favorable species (PA = 900 and 910 kJ/mol for (**1**) and (**2**), respectively). By contrast, the species protonated at C=C bond (enol-form of both 1- and 2-naphthol (**4, 6**)), as well as that protonated at the oxygen atom (**5, 7**) are less likely to be formed, i.e., they have low PA values. The favorable configuration of the protonated keto-forms difference could be ascribed to the direct conjugation of the positive charge on the oxygen atom with the π-system of the aromatic ring. Hence, the high electron density in the ring makes it favorable to shift towards the protonated site, enhancing stability of the oxonium ion species [20,21]

3.5. Hydrogen transfer ability of hydrocarbon species from DFT calculations

The hydride dissociation energies of various donor molecules calculated according to the Eqs. (2) and (3), relative to the C–H bond breaking in methane are shown in Fig. 4 for different positions in each of the hydrogen donor molecules investigated. We can anticipate that the lower is the dissociation energy for a given molecular position, the more effective the hydrogen transfer should be. For a particular molecule, the energy required to dissociate the first hydride is lowest at the tertiary carbon, e.g., those in decalin and methyl tetralin, while the terminal carbon shows highest energy, e.g., those in *n*-decane, as expected [29,30]. The dissociation from secondary carbons is relatively less probable as compared to that from tertiary carbons. Finally, the probability is particularly low (i.e., highest activation energy) for those from the aromatic ring, due to the higher electron density of carbons in the aromatic structure. The hydrogen on the aromatic ring is stabilized by sp^2 hybridization and least likely to be removed. By contrast, the hydrogen dissociation from the benzylic carbon is preferentially favorable since the positive charge formed can be stabilized by the delocalized π-electrons of the resonance structure. This effect is more pronounced by combining this effect with the presence of a tertiary carbon, as observed in methyl tetralin. According to the calculations, methyl tetralin should be the best hydrogen donor. Indeed, the trend of hydrogen transfer ability (DMT > tetralin ≈ decalin > *n*-decane) predicted according to the experimental naphthalene/naphthol ratios is consistent with the calculated relative activation energies for hydride dissociation.

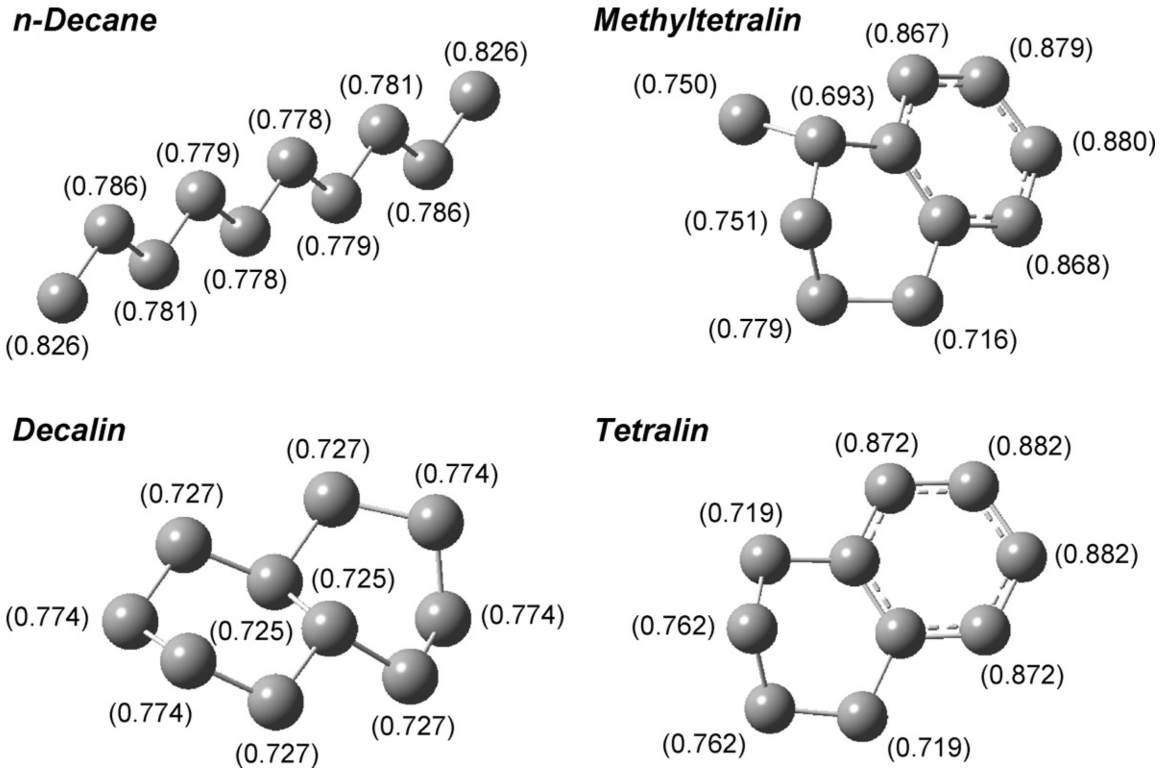

Fig. 4. Relative activation energy of hydride dissociation at different locations of the donor molecules. The calculated values relative to methane, and computed by DFT.

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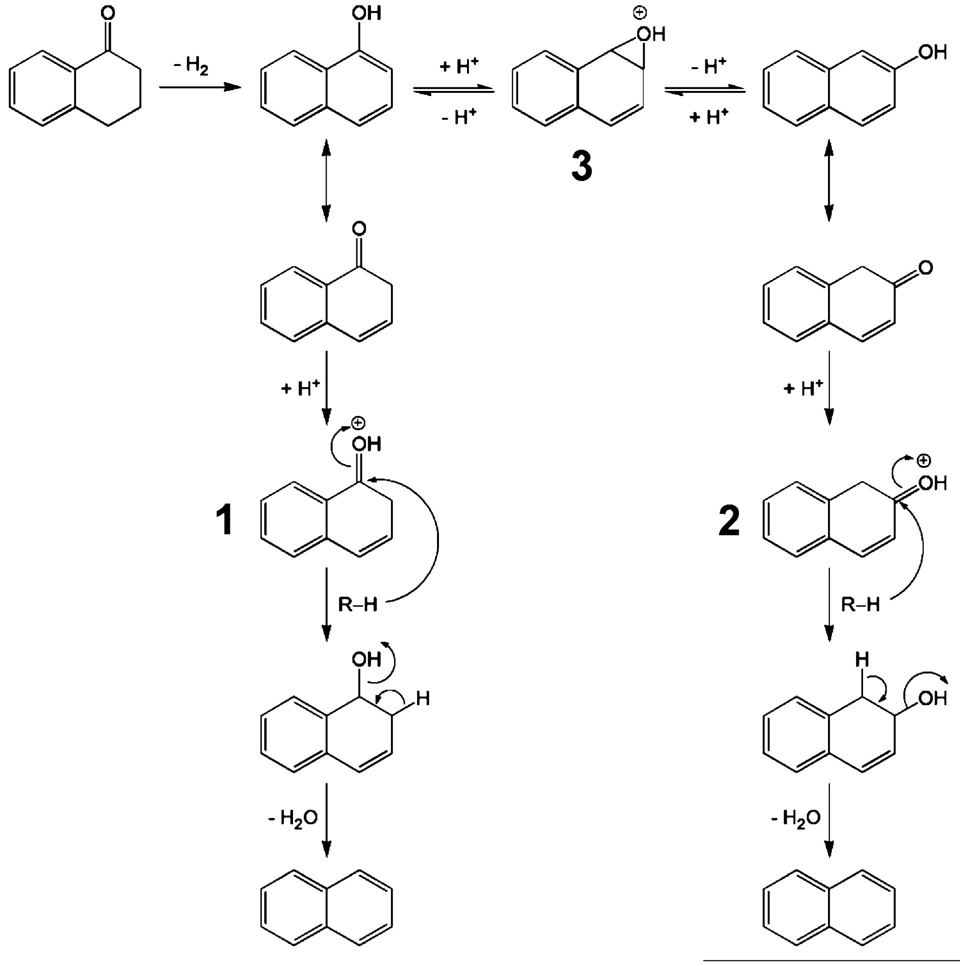
4. Discussion

The catalytic conversion of 1-tetralone yields 1-naphthol as a primary product. Over strong acid sites, 1-naphthol can be isomerized to 2-naphthol, most probably via an oxiranium cation (**3**) as shown in the scheme below. At the same time, among all of the possible protonated naphthol species, the most stable structure is then most probable participant in the hydride transfer process. Therefore, the two keto-forms of naphthols (**1**,**2**) can the protonated species that can act as hydride acceptors, leading to dehydrogenation and formation of naphthalene. Consequently, the rate of isomerization is low since the oxiranium cation (**3**) is less stable and therefore less probable in the intermediate state than the keto-form species.



Depending on their hydrogen transfer ability, hydrocarbons can donate a hydride to the carbonyl carbon of the protonated keto-form of naphthol, generating the corresponding alcohol which can be rapidly dehydrated to produce naphthalene, as summarized in the scheme above. Since dehydration is relatively fast over acid catalysts [31], the rate at which naphthalene is produced can be determined by the rate of hydrogen transfer. The hydrocarbon acting as hydrogen donor is also converted according to their hydrogen transfer ability, giving rise to products that are also enhanced by the hydrogen transfer reaction, i.e., dehydrogenation and skeleton isomerization. From the applications point of view, the yield of naphthalene from 1-tetralone can be taken as a measure of the hydrogen transfer. So, the product distribution of 1-tetralone conversion can be used as an indicator of the hydrogen transfer ability of a particular hydrocarbon or mixture of hydrocarbons for a given catalyst. A simple method like this could give refiners a tool to select feeds or predict what changes in olefinicity and octane number one could expect when the feed is changed.

DMT performed as the best hydrogen donor since it contains hydrogen on a tertiary benzylic carbon, which shows low relative activation energy for hydride dissociation ($E_A \sim 0.693$, Fig. 4). Likewise, tetralin exhibits a high rate of hydrogen transfer due to the presence of benzylic hydrogens ($E_A \sim 0.719$). Both DMT and tetralin convert mainly to their corresponding dehydrogenated product when co-fed with 1-tetralone. Due to the presence of tertiary carbons in its structure, decalin also possesses low relative activation energy for hydride dissociation ($E_A \sim 0.725$), but unlike the molecules containing one aromatic ring, decalin facilitates hydrogen transfer via isomerization (*cis-* and *trans-*). The small increase in the production of alkylbenzene from decalin is also an indication of hydrogen transfer. When co-feeding weak hydrogen donors, such as *n*-decane, the effects are much less apparent. Moreover, the competitive adsorption of 1-tetralone and its products on the surface readily suppress the overall conversion of *n*-decane. This inhibition is due to strong adsorption of 1-tetralone and naphthol on the acid sites of the zeolite compared to a rather weak adsorption of the paraffin, lowering its reaction rate.

5. Conclusion

The acid-catalyzed reaction of 1-tetralone produces 1-naphthol as primary product, followed by secondary isomerization of 1-naphthol to 2-naphthol. The presence of hydrocarbons in the feed, which can act as a hydrogen donor, promotes hydrogen transfer reaction to the surface protonated naphthol, facilitating the dehydration of the corresponding alcohols to form naphthalene.

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Therefore, the yield of naphthalene from 1-tetralone can be taken as a measure of the hydrogen transfer. So, the product distribution of 1-tetralone conversion can be used as an indicator of the hydrogen transfer ability of a particular hydrocarbon or mixture of hydrocarbons. Both, the experimental naphthalene/naphthol ratios obtained experimentally and the DFT calculations show that the hydrogen transfer ability of hydrocarbon species follows the order DMT > tetralin ≈ decalin > *n*-decane. It has been shown that the hydrogen transfer reaction is also sensitive to acid site density (Si/Al ratio) and by a hydrogen donor concentration.

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