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Conversion of 1- and 2-Tetralone Over HY Zeolite

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Abstract Conversion of 1- and 2-tetralone was investigated over acid HY zeolite under various reaction conditions in the vapor phase. Reactions were conducted in a fixed-bed reactor at 300, 400 and 500 °C in hydrogen atmospheric pressure. It was found that 1- and 2-tetralone are thermally unstable and thermal reaction has a contribution, particularly at high temperatures. The reactivity of 2-tetralone was significantly higher than that of 1-tetralone. This behavior is more pronounced in the presence of acid HY zeolite. For both isomers, the main products were naphthol, coupling compounds (4-ring), naphthalene and tetralin. Trace amounts of dihydronaphthalene, ring-contraction and ring-opening product were also observed. At high temperatures, isomerization and dehydration of naphthol were observed over the HY zeolite. It seems that on the acidic zeolite, hydrogen transfer plays a significant role in determining the reaction path.

Keywords Oxygenated aromatic · 1-Tetralone · 2-Tetralone · Tetralin · Dihydronaphthalene · Naphthalene · Tetralol · Naphthol · Thermal reaction · HY · Zeolite

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1 Introduction

The projected demand for transportation fuels exceeds the current capacity for light sweet crudes [1]. Security and sustainability concerns enhance the need for access to alternative domestic sources. Unconventional crude oils (heavy oil, bitumen, tar sands, shale oils, and coals) are abundant in North America and may reduce the consumption of imported feedstocks [2]. Therefore, these complex carbon resources are expected to contribute a growing fraction of transportation fuel production. Heavy crude oils have a density (specific gravity) approaching or even exceeding that of water. They usually are extremely viscous, with a consistency ranging from that of heavy molasses to a solid at room temperature. Conversion of heavy feedstocks to fuels via severe hydrotreating or cracking processes has been practiced for many years. However, these technologies present drawbacks related to the high consumption of hydrogen and demanding reaction conditions that they require. To convert complex carbon resources with typical H/C atomic ratios of about 1.1–1.2 to the range of transportation liquid fuels (H/C ~1.8 to 2.0) a very significant amount of hydrogen is needed. At the same time, the high temperatures and pressures associated with these processes result in exceedingly high capital costs.

The use of heavy oil as a crude produces high aromaticity in the internal streams in the refinery (i.e. LCO) as well as a net increase in the volume of the heavier fractions (i.e. slurry oil) produced in the distillation units. One possible solution would be to recycle some of these heavier fractions through the catalytic cracking unit (FCC). However, it is well established that naphthalene, phenanthrene, and anthracene do not crack under typical FCC conditions, but instead they undergo condensation and form coke [3].

Functionalization with heteroatoms, such as S, N, and O may greatly affect the reactivity of the aromatic rings and allow unzipping the stable structure of the heavy molecules under milder conditions than those used in hydrotreating. Such functionalization may create reactive centers in the molecule that would help selectively activating the molecule via H-transfer, ring-opening, etc. Hence, this work focused on reaction of tetralones (1 and 2), as the representative molecules of oxygenated aromatics on HY zeolites.

2 Experimental

A commercial HY zeolite from Zeolyst International (CBV 780, Si/Al ratio 40) was used as a catalyst. The reactions were conducted in a ¼″ stainless steel reactor at atmospheric pressure of hydrogen. The reactor temperature in the range 300–500 °C was controlled in a tube furnace. The feed reactants, tetralin, 1-tetralone, 1-tetralol, 1-naphthol, and 2-tetralone, were purchased from Sigma-Aldrich and used as received. The feed was introduced to the reaction system by bubbling hydrogen through a saturator adjusted at an appropriate temperature to obtain the desired vapor pressure of the specific reactant. Space velocities were in the range 0.5–2.0 h^{-1}. Prior to each run, the feed was directed through a bypass until the concentration reached steady-state, and then it was switched to the reactor. Carbon mass balance closure was checked in every run by comparing the total mass determined from the analysis of the reactor outlet with that from the by-pass. The amount of coke formation during reaction was determined in an elemental analyzer and found to be less than 1 wt% of the total weight of the spent catalyst, which indicates that the coke formation per pass is very small and does not affect the carbon balance or product distribution in a significant manner. Products were analyzed every 0.5 h after the beginning of the run with an on-line HP5890 gas chromatograph equipped with HP-5 column and an FID detector. To minimize the effect of catalyst deactivation in the analysis of initial reactivity, the values reported in this work are those obtained in the first measurement (i.e., after 0.5 h on stream). The temperature program started at 40 °C, linearly increased to 280 °C with a 15 °C/min heating ramp, and finally held for 8 min.

3 Results and Discussion

3.1 Thermal Reactions of 1- and 2-Tetralone (Blank Reactor)

Before the catalytic measurements, runs without catalyst were conducted to determine the contribution of thermal reactions. The product yields obtained from 1- and 2-tetralone in a blank reactor filled with inert glass beads in the temperature range 300–500 °C are compared in Table 1. It is clear that the both compounds can be thermally decomposed and the conversion readily increases with temperature. Conversion of 2-tetralone is significantly higher than that of 1-tetralone at all temperatures. The higher reactivity of 2-tetralone is associated to its benzylic carbon that requires a relatively lower energy for C–H dissociation [4] and hence it can be thermally activated more readily than 1-tetralone [5].

For 1-tetralone conversion, naphthol is the main product. At 500 °C, production of naphthalene becomes significant. This suggests that at high temperatures hydrogen transfer may be occurring [6]. By contrast, 2-tetralone produces heavy coupling compounds (i.e. 4-ring) as the major product with a lower selectivity toward the

Table 1 Thermal reactions of 1- and 2-tetralone

Feed:	1-Tetralone			2-Tetralone		
Temperature:	300 °C	400 °C	500 °C	300 °C	400 °C	500 °C
Conversion (%)	5.6	11.0	42.4	15.0	22.6	56.0
Product yields (wt%)						
RO	0.0	0.3	1.7	0.0	0.0	0.0
RC	0.0	0.0	0.3	0.0	0.0	0.4
Tetralin	0.1	0.1	0.2	0.0	0.0	0.0
Dihydronaphthalene	0.6	0.8	1.8	0.0	0.0	0.0
Naphthalene	0.5	0.8	5.6	0.0	0.2	0.2
Tetralone	94.4	89.0	57.6	85.0	77.4	44.0
Tetralol	0.0	0.0	0.0	0.0	0.0	0.0
Naphthol	4.4	8.3	31.8	5.8	7.1	26.0
Heavies	0.0	0.7	1.0	9.2	15.4	29.3

Reaction conditions: 1 atm H_2, TOS 0.5 h

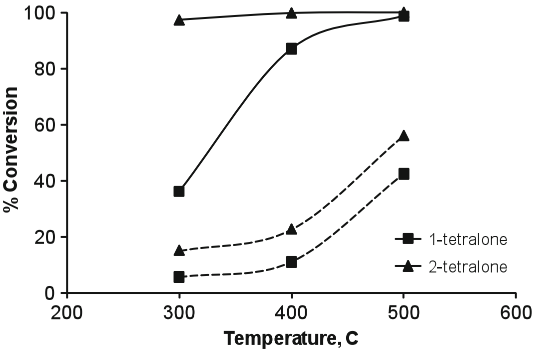


Fig. 1 Conversions of 1- and 2-tetralone as a function of temperature. Reaction conditions: 1 atm H_2, TOS 0.5 h, W/F = 1.723 h. *Solid and dashed lines* represent catalytic and thermal conversion, respectively

corresponding naphthol than 1-tetralone. At the same time, no naphthalene is obtained in the temperature range studied. Trace amounts of dihydronaphthalene, tetralin, ring-contraction (RO) and ring-opening (RO) products can be observed from 1-tetralone, while they do not appear from 2-tetralone conversion.

3.2 Catalytic Conversion of 1- and 2-Tetralone Reactions Over the HY Zeolite

As shown in Fig. 1, the presence of HY catalyst greatly enhances the conversion of both 1- and 2-tetralone compared to the runs in the blank reactor. As in the case of thermal conversion, 2-tetralone displays a much higher reactivity than 1-tetralone. Reactive adsorption of aromatic ketones on acid sites is well known [7, 8]. Our results show that the position of the carbonyl functionality not only has an effect on the reactivity toward thermal activation, but also toward catalytic activation.

Figure 2 shows the product distribution from 1- and 2-tetralone conversion over the HY zeolite as a function of temperature. It is seen that below 400 °C the acid-catalyzed reaction yields their corresponding naphthols as main products, suggesting an enhanced hydrogen transfer over the acid catalyst. Interestingly, as the temperature increases to 500 °C 2-naphthol was obtained from 1-tetralone and 1-naphthol from 2-tetralone, while the concentration of the corresponding naphthol decreased, suggesting that naphthol isomerization can take place over the acid HY zeolite at this high temperature.

Also, coupling products, i.e. 4-ring compounds, were produced at high temperatures in significant amounts, suggesting the contribution of hydrogen transfer/coupling reactions, catalyzed by Brønsted sites [5].

Production of naphthalene and tetralin was noticeably enhanced over the HY catalyst compared to the thermal reaction. This enhancement again suggests that hydrogen transfer is readily facilitated over acid sites [9–11], so deoxygenated products can be obtained. Only small amounts of ring-contraction and ring-opening products were found [12] in this acid-catalyzed reaction.

Figure 3 shows the evolution of product distribution and conversions of 1- and 2-tetralone with space time (W/F), over the HY zeolite at 300 °C. As described above, 2-tetralone is more reactive and sensitive to the presence of the acid catalyst than 1-tetralone. At this low temperature,

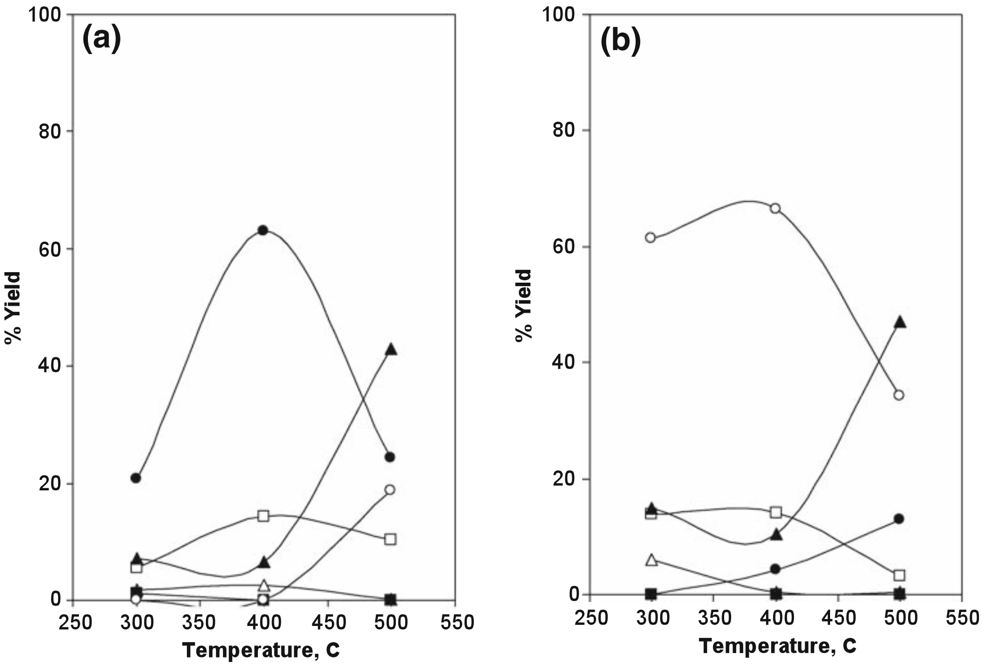


Fig. 2 Product yields from the reaction of **a** 1-tetralone and **b** 2-tetralone as a function of temperature over HY zeolite. Reaction conditions: 1 atm H_2, TOS = 0.5 h, W/F = 1.723 h. Tetralin (*open triangle*), dihydronaphthalene (*filled square*), naphthalene (*open square*), 1-naphthol (*filled circle*), 2-naphthol (*open circle*) and heavies (*filled triangle*)

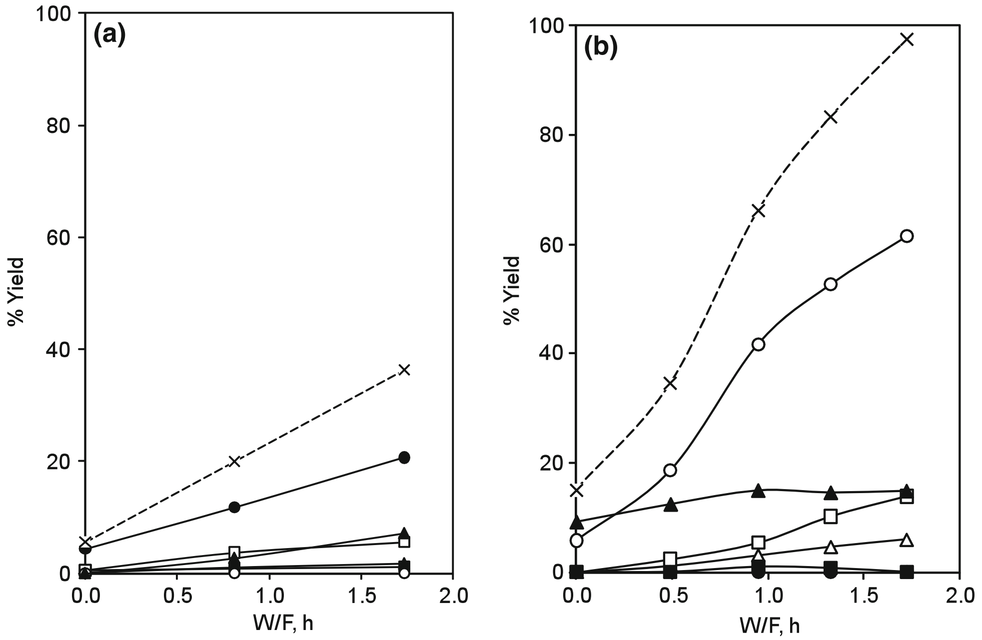


Fig. 3 Product yields from the reaction of **a** 1-tetralone and **b** 2-tetralone as a function of space time (W/F) at 300 °C over HY. Reaction conditions: 1 atm H_2, TOS = 0.5 h. Tetralin (*open triangle*), dihydronaphthalene (*filled square*), naphthalene (*open square*), 1-naphthol (*filled circle*), 2-naphthol (*open circle*), heavies (*filled triangle*), and conversion (*times*)

the corresponding naphthols are the major products for both 1- and 2-tetralone, with no evidence of isomerization. Also, at low temperatures, deoxygenated products, naphthalene and tetralin only appear in relatively small amounts.

As shown in Fig. 4, during the reaction of 1-tetralone over HY at 500 °C, while the overall conversion continuously increases with W/F, the yield of 1-naphthol goes through a maximum and then decreases at high W/F. This decrease in 1-naphthol is accompanied by a rapid increase in concentration of coupling products and 2-naphthol. While it is clear that secondary isomerization of 1-naphthol to 2-naphthol is an important reaction occurring at high temperature and W/F, formation of coupling products it also seems to be a secondary reaction. As shown in Fig. 4, the first derivative of their concentration near zero W/F is approximately to zero. The experiment conducted with 1-naphthol as a feed (Table 2) indicates that this molecule can undergo coupling over HY.

3.3 Reaction Pathways

The significant difference in reactivity of the two isomers can be explained from the higher stability of 1-tetralone due to the conjugation of the carbonyl group and the π system of the aromatic ring. In addition, the presence of a benzylic α-carbon (adjacent to both the C=O and the aromatic ring) in 2-tetralone leads to a more stable reaction intermediate [4], and consequently lower activation energy and higher rate for the thermal reaction. Conversely, 1-tetralone is expected to form a less stable intermediate with cross-conjugated double bonds. At the same time, a higher probability of formation of the free radical intermediate in 2-tetralone can explain the higher rate of

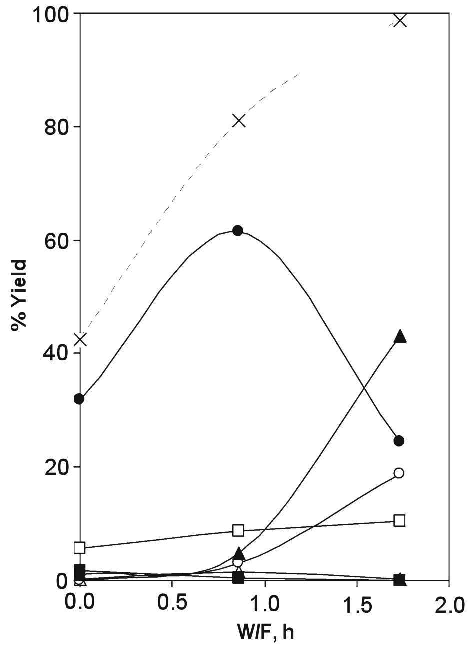


Fig. 4 Product yields from the reaction of 1-tetralone as a function of space time (W/F) at 500 °C. Reaction conditions: 1 atm H_2, TOS = 0.5 h. Tetralin (*open triangle*), dihydronaphthalene (*filled square*), naphthalene (*open square*), 1-naphthol (*filled circle*), 2-naphthol (*open circle*), heavies (*filled triangle*), and conversion (*times*). The values at zero W/F correspond to those obtained in the blank reactor (thermal)

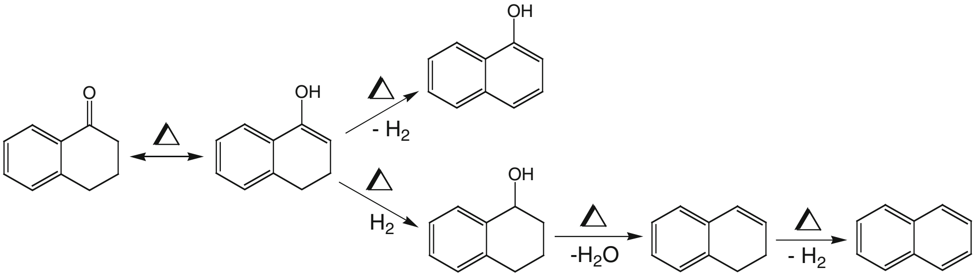
Table 2 Reactions of tetralin, tetralones and 1-naphthol catalyzed by HY zeolite

Feed:	Tetralin	1-Tetralone	2-Tetralone	1-Naphthol	
Catalyst:	HY	HY	HY	Blank	HY
Conversion (%)	11.5	98.7	99.9	0.0	36.4
Product yields (wt%)					
RO	0.0	0.8	0.5	0.0	0.0
RC	0.0	1.2	1.6	0.0	0.0
Tetralin	88.5	0.2	0.4	0.0	0.0
Dihydronaphthalene	0.0	0.0	0.0	0.0	0.0
Naphthalene	11.5	10.4	3.3	0.0	0.0
Tetralone	0.0	1.3	0.1	0.0	0.0
Tetralol	0.0	0.0	0.0	0.0	0.0
1-Naphthol	0.0	24.3	12.8	100.0	63.6
2-Naphthol	0.0	18.8	34.3	0.0	27.5
Heavies	0.0	43.1	47.1	0.0	8.9

Reaction conditions: 500 °C, 1 atm H_2, TOS 0.5 h

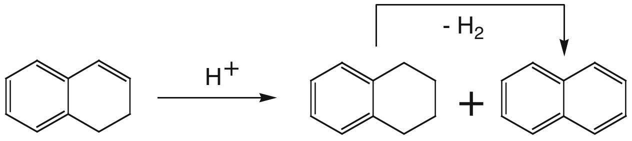
formation of coupling products observed with 2-tetralone, but not with 1-tetralone, which does not have any benzylic α-carbon.

In parallel, dehydrogenation via C–H thermal cracking forming aromatic rings [13] will be favored at high temperatures. This dehydrogenation would lead to the formation of the corresponding naphthols. As hydrogen would be produced in stoichiometric amounts during the dehydrogenation of 1-tetralone to 1-naphthol, a significant hydrogen transfer to fresh 1-tetralone can be expected. It is known that ketones are good hydrogen acceptors [14], leading to the formation of tetralol. This, in turn, can be readily dehydrated and subsequently dehydrogenated to produce stable naphthalene, as shown below.



This reaction path is confirmed by the experiment done with 1-tetralol as a feed (see Table 3), which shows the production of dihydronaphthalene and naphthalene, as proposed. However, thermal conversion of tetralones favors dehydrogenation over deoxygenation (i.e. hydrogenation then dehydration). Consequently, the production of the corresponding naphthol is dominant over naphthalene (Table 1).

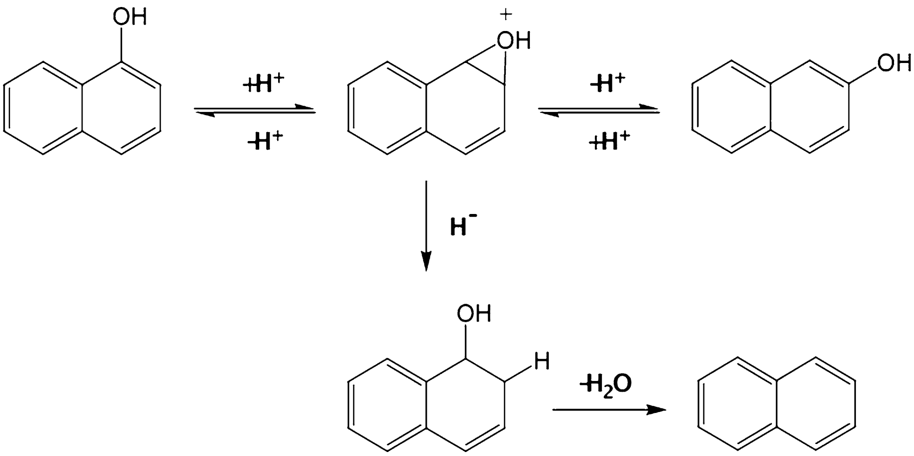
The situation is somewhat different in the presence of HY, in which conversion of the tetralones result from a combination of thermal and acid-catalyzed reactions. The presence of acid HY zeolite enhances the rate of the hydrogen transfer [9–11]. Hence, both the overall conversion and formation of naphthol are enhanced. However, the parallel reaction, i.e. hydrogen transfer to form tetralol that produces dihydronaphthalene and naphthalene, is greatly enhanced. Moreover, dihydronaphthalene is readily disproportionated (i.e. intermolecular hydride transfer) producing naphthalene and tetralin [15, 16], as shown below.



As shown in Table 3, this disproportionation is largely observed in the acid-catalyzed reaction of 1-tetralol, but not in its thermal reaction. Naphthalene, at high temperatures, can also derive from tetralin dehydrogenation [17, 18], which may explain the slight decrease in tetralin/naphthalene ratio observed at higher W/F.

Thermal transformation of 1-naphthol to naphthalene could occur at high hydrogen pressures [19] or high temperatures [20]. However, this reaction did not occur under the conditions of this study.

The observed isomerization and deoxygenation of 1-naphthol to 2-naphthol and naphthalene over HY zeolite at high temperatures can be explained as follows. Protonation of 1-naphthol by a Brønsted site of the HY zeolite leads to the formation of naphthalene-1,2-oxide intermediate [21–23]. Ring opening of this intermediate results in the formation of 2-naphthol. In a parallel path, acid-site assisted hydrogen transfer from carbon deposits or heavies can form a 1-hydroxy-1,2-dihydronaphthalene intermediate [21, 24]. This species can be readily dehydrated over the Brønsted sites to form naphthalene. The two parallel paths are illustrated in the following scheme.



Since heavy products derive mainly from thermal coupling of oxygenated aromatic intermediates [5], the formation of heavies would be suppressed under rapid hydrogen transfer. Accordingly, a similar product distribution was obtained from both 1- and 2-tetralone reactions over the acid catalyst despite the higher conversion obtained for 2-tetralone.

Table 3 Reactions of 1-tetralol

Feed:	1-Tetralol	
catalyst:	Blank	HY
Product yields (wt%)		
RO	0.0	0.0
RC	0.0	0.0
Tetralin	4.8	42.6
Dihydronaphthalene	59.5	0.0
Naphthalene	35.7	57.4
Tetralone	0.0	0.0
Tetralol	0.0	0.0
1-Naphthol	0.0	0.0
2-Naphthol	0.0	0.0
Heavies	0.0	0.0

Reaction conditions: 300 °C, 1 atm H_2, TOS 0.5 h

4 Conclusion

Among the two isomers, 2-tetralone is the most active for both thermal activation and acid-catalyzed reactions. The lower reactivity of 1-tetralone is due to the conjugation of the double bond of the carbonyl group with the aromatic ring, which makes the molecule more stable. Hydrogen transfer during the reaction pathway has a significant effect on product distribution. Dehydrogenation of each tetralone to its corresponding naphthol is the major pathway. The hydrogen transfer promoted by the acid catalyst leads to the formation of deoxygenated products, namely naphthalene and trace amounts of dihydronaphthalene, which is an intermediate product. Heavy coupling products, formed by coupling of the free radical intermediates, can be readily suppressed over acid-catalyzed reaction at relatively lower temperatures by hydrogen transfer.

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References

1. International Energy Outlook (2009) DOE report DOE/EIA-0484
2. World Energy Council (2004) Encyclopedia of energy. World Energy Council, London, pp 731–737
3. Dupain X, Gamas ED, Madon R, Kelkar CP, Makkee M, Moulijn JA (2003) Fuel 82:1559
4. Bruckner B (2002) Adv Org Chem 1
5. Kjærsbo T, Daasbjerg K, Pedersen SU (2003) Electrochim Acta 48:1807
6. Behar F, Pelet R (1988) Energy Fuels 2:259
7. Bezouhanova CP (2002) Appl Catal A 229:127

8. Lei X, Turro NJ (1992) J Photochem Photobiol A 69:53
9. Puente G, Sedran U (2000) Chem Eng Sci 55:759
10. Pajak J, Krebs V, Marêché JF, Furdin G (1996) Fuel Process Technol 48:73
11. Suarez W, Cheng W-C, Rajagopalan K, Peters AW (1990) Chem Eng Sci 45:2581
12. Santikunaporn M, Alvarez WE, Resasco DE (2007) Appl Catal A 325:175
13. Xu B, Sievers C, Hong SB, Prins R, van Bokhoven JA (2006) J Catal 244:163
14. Rattanasumrit A, Ruangpornvisuti V (2005) J Mol Catal A 239:68
15. Corma A, Gonzalez-Alfaro V, Orchilles DV (2001) J Catal 200:34
16. Santikunaporn M, Herrera JE, Jongpatiwut S, Resasco DE, Alvarez WE, Sughrue EL (2004) J Catal 228:100
17. Townsend AT, Abbot J (1992) Appl Catal A 90:97
18. Townsend AT, Abbot J (1993) Appl Catal A 95:221
19. Schlosberg RH, Kurs A (1984) J Org Chem 49:3032
20. Cypres R (1981) Prepr Pap Am Chem Soc Div Fuel Chem 26
21. Brandt P, Jia ZS, Thibblin A (2002) J Org Chem 67:7676
22. Rao SN, More O'Ferrall RA, Kelly SC, Boyd DR, Agarwal R (1993) J Am Chem Soc 115:5458
23. Kasperek GJ, Bruice TC (1972) J Am Chem Soc 94:198
24. Pirinccioglu N, Thibblin A (1998) J Am Chem Soc 120:6512