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# Water as an additive to enhance the ring opening of naphthalene

Qian Wang, Honglei Fan, Suxiang Wu, Zhaofu Zhang, Peng Zhang and Buxing Han\*

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Use of water as a reaction medium or additive to enhance reaction efficiency is an important topic in green chemistry, and ring opening and contraction reactions of aromatics are crucial for upgrading diesels. In this work, we investigated the effect of water on the yields of ring opening and contraction reactions of naphthalene. A series of catalysts, such as  $Rh_2O_3/HY$  zeolite, Mo–Ni oxide and their physical mixtures, were used as the catalysts. The influences of the amount of water, hydrogen pressure, reaction temperature and reaction time on the yields of the ring opening and contraction products (ROCP) were studied. It was found that  $Rh_2O_3/HY$  and Mo–Ni oxide showed an excellent synergistic effect for catalyzing the reaction, and water could be used as a green and efficient additive for enhancing the yield of the ROCP. At the optimized conditions, the yield of the ROCP could be as high as 63.3%. The mechanism for the effect of water on the basis of control experiments.

# Introduction

Currently, consumption of diesel is fast growing because of its higher energy content and less greenhouse gas emission than gasoline. The light cycle oil (LCO) with low cetane number (CN) and high content of aromatics needs to be upgraded to obtain high quality diesel. A high aromatic content reduces the CN and contributes significantly to the formation of environmentally harmful emissions.<sup>1,2</sup> To meet the increasingly rigorous environmental regulation and fuel specifications, it is necessary to reduce the content of aromatics and increase CN. Several methods have been used to improve CN, such as adding cetane additives,<sup>3</sup> blending with biodiesel,<sup>4</sup> hydrotreating<sup>5</sup> and selective ring opening (SRO).<sup>6</sup> Among the methods used, SRO improves CN efficiently without losing the total mass, and the CN increases from 5 to about 50 by converting aromatics to alkylaromatics or alkylhexanes, and the CN just locates in the range of 45-55 that is the best for the ignition of diesel engines.<sup>7</sup> The most efficient CN-improving products of SRO are ring opening/ contraction products (ROCP), including ring-opening products (ROP) which are one-ring compounds of high CN and ring-contraction products (RCP) that are multi-ring compounds with at least one five-membered naphthenic ring.<sup>8,9</sup>

LCO consists largely of two-fused six member rings, such as naphthalene, tetralin, and decalins, which are often used as model compounds in the SRO studies of LCOs.<sup>10–13</sup> Compared with tetralin and decalin, naphthalene is more representative of LCO for its higher aromatic content. Meanwhile, naphthalene is more difficult to achieve high ROCP yield because the reaction pathway is more complex. In the literature, the maximum yield of ROCP of decalin and tetralin is about 70%,<sup>14,15</sup> while that of

naphthalene is only 47.9%.<sup>16</sup> So, obtaining a high yield of ROCP from naphthalene is of great significance, but is challenging.

Ring opening of aromatics can be catalyzed by Brønsted acids such as solid acids<sup>10</sup> and bifunctional catalysts for hydrocracking.<sup>8,17</sup> The yields of ROCP catalyzed by solid acids are usually low due to the large extent of overcracking and fast catalyst deactivation. Bifunctional catalysts, which consist of highly dispersed metal for hydrogenation and acidic support for cracking, are usually more effective. Transition metals and noble metals have been widely used as the metal components, and different acidic supports such as zeolites have been used as the supports. Many bifunctional catalysts have been developed, such as NiW/Al<sub>2</sub>O<sub>3</sub>-USY,<sup>10</sup> NiMo/zeolite,<sup>18</sup> Ir/beta,<sup>13</sup> Mo<sub>2</sub>C/HY,<sup>19</sup> Pt-Ir/HY,<sup>20</sup> Pt/ MCM-41,<sup>21</sup> Rh/Al<sub>2</sub>O<sub>3</sub>,<sup>22,23</sup> Ru/Al<sub>2</sub>O<sub>3</sub>,<sup>24</sup> Pt-Rh/Al<sub>2</sub>O<sub>3</sub>,<sup>25</sup> Rh-Ag/ TiO<sub>2</sub><sup>26</sup> and Rh-Ge/Al<sub>2</sub>O<sub>3</sub>.<sup>27</sup> Generally, the catalysts with transition metals are cheaper, but the activity is lower. While the supported noble metal catalysts are more effective, they are more expensive.

Supercritical or near-critical water is an excellent solvent for organic compounds, and the dissociation of water generates a sufficiently high H<sup>+</sup> concentration.<sup>28,29</sup> Recently, supercritical or near-critical water have attracted much attention as environmentally benign media for chemical reactions,<sup>30–38</sup> including some reactions in near-critical water under microwave irradiation.<sup>39,40</sup> It has been reported that water influences the catalytic behavior of zeolites.<sup>41,42</sup> At low water coverage, water reduces the density of the Lewis acid sites and favors the formation of new Brønsted acid sites.<sup>43–45</sup> Water can change the distribution of Brønsted and Lewis acid sites and inhibit the carbon deposition on zeolites.<sup>46</sup> It can also enhance the selectivity to tetralin in the naphthalene hydrogenation and inhibit coke formation.<sup>47</sup>

There is no doubt that the study of the effect of water as an additive on the selective ring opening of aromatics is an very interesting topic. In this work, we studied the effect of water on

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P.R. China. E-mail: hanbx@iccas.ac.cn; Fax: (+86) 10 6255 9373; Tel: (+86) 10 6256 2821

the selective ring opening reaction of naphthalene, and the physical mixture of  $Rh_2O_3/HY$  zeolite (denoted as HY hereafter) and Mo–Ni oxide (denoted as Mo–Ni hereafter) was used as the catalyst. The influences of reaction parameters, such as amount of water, hydrogen pressure, reaction temperature and reaction time on the reaction were studied. Interestingly, it was found that  $Rh_2O_3/HY$  and Mo–Ni had excellent synergistic catalytic properties for the reaction and water was an efficient additive to enhance the yield of the ROCP, and the yield could reach 63.3% at suitable conditions. The mechanism for the effect of water on the reactions was studied on the basis of control experiments.

## **Experimental**

Naphthalene was purchased from Shantou Xilong Chemical Factory (Guangdong, China). Sulfur powder, rhodium chloride and n-hexane were obtained from Beijing Chemical Reagent Company. All the above chemicals were of analytical grade and used without further purification. The HY zeolite was provided by Zibo Taixing Chemicals Co. Ltd (Shandong, China). The Mo–Ni catalyst used was the same as that used previously.<sup>42</sup> The Rh<sub>2</sub>O<sub>3</sub>/HY catalyst with 2 wt% Rh<sub>2</sub>O<sub>3</sub> was prepared by an impregnation method using RhCl<sub>3</sub> solution followed by calcination at 823 K. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK $\alpha$  radiation. The base pressure was 3 × 10<sup>-9</sup> mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

The reaction was carried out in a high-pressure cylindricalshaped 316 stainless reactor of 6 mL. In a typical experiment, a desired amount of naphthalene, catalysts, S powder (S is commonly used to activate the transition metal catalyst in oil refineries), and water were added into the reactor. The reactor was purged with hydrogen three times to remove the air and then pressurized to the desired pressure. The loaded reactor was placed into a preheated isothermal furnace. After a desired reaction time, the reactor was taken out of the furnace and cooled in a water bath to quench the reaction quickly. The cooled reactor was then opened and the reaction mixture was transferred into a 10 mL vial. The reactor was then rinsed with n-hexane and the washings were added to the above vial. Then an internal standard, biphenyl, was added into the vial for analysis. The reaction products were analyzed by an Agilent 4890D gas chromatograph equipped with an SUPELCOWAX-10 capillary column (30 m) and an FID detector. GC-MS analysis of the compounds was performed on a SHIMADZU-QP2010.

The products include mainly hydrogenation products (tetralin and decalin), ring opening/contracting products (ROCP) (*e.g.*, alkyl-benzene, alkyl-hexane, methyl-indans and decalin skeletal isomers), cracking products (less than 10 carbon atoms), and heavy compounds (HC) (more than 11 carbon atoms). Naphthalene conversion was calculated from  $(M_{\text{initial}} - M_{\text{un}})/M_{\text{initial}}$ , where  $M_{\text{initial}}$  is the initial mass of naphthalene, and  $M_{\text{un}}$  is the mass of naphthalene unreacted. The yield to product *i* ( $Y_i$ ) is defined as  $M_i/M_{\text{initial}}$ , where  $M_i$  is the mass of product *i*. For hydrogenation products and naphthalene, GC calibration factors were obtained using pure reference compounds. For the other compounds the calculated average GC factors were adopted, which is a commonly used method.  $^{12,48}\,$ 

### **Results and discussion**

#### Performance of different catalysts without and with added water

Different catalysts were tested for the ring opening reaction of naphthalene, and the results are provided in Table 1.

For the catalyst Rh<sub>2</sub>O<sub>3</sub>/HY, hydrogenation was the dominant reaction, and decalin was the main product (entry 1). When HY + Mo-Ni was used as the catalyst, hydrogenation also dominated the reaction (entry 3), but the yield of decalin was much lower than that catalyzed by Rh<sub>2</sub>O<sub>3</sub>/HY, indicating that Rh is more active for hydrogenation than the Mo-Ni catalyst. When sulfur was added, the catalysts Rh<sub>2</sub>O<sub>3</sub>/HY and HY + Mo-Ni showed the similar product distribution (entries 5 and 7). Entries 1 and 5 indicate that sulfur reduced the activity of Rh<sub>2</sub>O<sub>3</sub>/HY for the hydrogenation reaction. But the yield of the ROCP catalyzed by HY + Mo-Ni was improved by adding sulfur (entries 3 and 7), mainly because sulfur can improve the hydrogenation activity of Mo-Ni and promote the cleavage of C-C bonds.<sup>49</sup> All the results demonstrate that high yield of ROCP could not be reached using Rh<sub>2</sub>O<sub>3</sub>/HY or HY + Mo-Ni. However, when they were combined, a higher yield of the ROCP could be achieved (entries 9, 11, 13, 15, 17 and 19), especially when the mass ratio of Rh<sub>2</sub>O<sub>3</sub>/HY and Mo-Ni was 1:0.3. Generally, the ring opening reaction of a six-member ring is much easier after isomerization to a five-member ring. Therefore, the catalysts with the functions of isomerization and cracking simultaneously should be highly efficient for ring-opening reaction. It was reported that MoO<sub>2</sub> from the hydrogenation reduction and MoS<sub>2</sub> possess the ability of catalyzing isomerization and ring opening by the formation of Brønsted Mo-OH and Mo-SH acidic group (s) on the surface,  ${}^{50,51}$  and the hydrogenation activity of Rh will not be affected by Mo-Ni.50 Therefore, we can deduce that the Rh and Mo-Ni catalyzed hydrogenation, and HY and Mo-Ni promoted the isomerization and ring opening reactions.

The influence of water added on the performances of different catalysts was studied. Using Rh<sub>2</sub>O<sub>3</sub>/HY as the catalyst, the ROCP yield increased from 21.5% to 26.3% and the yield of HC was reduced from 15.2% to zero with the addition of water (entries 1 and 2). The water on the zeolite can form new Brønsted acid sites, <sup>43–46,52</sup> which may enhance the ring opening reaction and therefore the ROCP yield can be higher. At the same time, the water molecules adsorbed on the HY zeolite competed with reactants and inhibited bimolecular reactions, which reduced the yield of HC. The influence of water on the yield of ROCP catalyzed by Mo-Ni + HY was not considerable, both the ROCP yields with and without water were about 11% (entries 3 and 4). The tetralin yield decreased, and decalin and ROCP yields increased after adding water for Rh<sub>2</sub>O<sub>3</sub>/HY + S (entries 5 and 6) and Mo–Ni + S + HY (entries 7 and 8), indicating that water improved the hydrogenation activity of the metallic components and enhanced the acidity of the HY zeolite. The yield of ROCP was increased considerably when Mo-Ni and Rh<sub>2</sub>O<sub>3</sub>/HY were combined (Rh<sub>2</sub>O<sub>3</sub>/HY + Mo-Ni), and water could also improve the yield of ROCP (entries 9 to 14).

Entry	Catalyst	Water (mg)	Conv. (%)	Yield (%)			
				Decalin	Tetralin	ROCP	HC
1	Rh <sub>2</sub> O <sub>3</sub> /HY	0	100	57.6	0.4	21.5	15.2
2	Rh <sub>2</sub> O <sub>3</sub> /HY	2	100	67.4	0.2	26.3	0
3	HY + Mo - Ni(1:0.3)	0	99.6	41.5	42.3	11.4	1.2
4	HY + Mo - Ni(1:0.3)	2	100	42.2	41.0	11.6	0
5	$Rh_2O_3/HY + S$	0	99.6	24.3	30.2	23.4	14.6
6	$Rh_2O_3/HY + S$	2	99.7	36.3	19.1	28.9	1.7
7	HY + Mo - Ni(1:0.3) + S	0	99.7	35.0	27.3	19.5	11.8
8	HY + Mo - Ni(1:0.3) + S	2	99.8	38.5	21.1	28.3	1.3
9	$Rh_2O_3/HY + Mo-Ni(1:0.1)$	0	100	18.9	0	38.8	19.4
10	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.1)$	2	100	24.2	0	44.8	11.2
11	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.3)$	0	100	10.4	0	47.4	27.3
12	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.3)$	2	100	16.7	0	53.1	14.5
13	$Rh_{2}O_{3}/HY + Mo-Ni(1:1.2)$	0	100	10.1	23.1	36.9	22.1
14	$Rh_{2}O_{3}/HY + Mo-Ni(1:1.2)$	2	100	13.1	26.8	39.2	14.8
15	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.1) + S$	0	99.7	37.2	0	43.9	10.2
16	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.1) + S$	2	100	37.4	0	50.8	1.6
17	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.3) + S$	0	100	17.9	0.4	50.7	12.3
18	$Rh_{2}O_{3}/HY + Mo-Ni(1:0.3) + S$	2	100	24.3	0	63.3	0
19	$Rh_{2}O_{3}/HY + Mo-Ni(1:1.2) + S$	0	100	6.7	28.0	42.2	13.9
20	$Rh_{2}O_{3}/HY + Mo-Ni(1:1.2) + S$	2	99.5	10.1	31.2	47.5	1.7

Table 1 Selective ring opening of naphthalene with different catalysts with and without water

*Reaction conditions*: naphthalene 6 mg, H<sub>2</sub> 5 MPa, 613 K, 4 h, Rh<sub>2</sub>O<sub>3</sub>/HY contains 2 wt% Rh<sub>2</sub>O<sub>3</sub>, Si/Al = 4.6 in HY, total mass of the catalyst 6.5 mg, S 3 mg, the ratios in the second column from the right are the mass ratio of Rh<sub>2</sub>O<sub>3</sub>/HY : Mo–Ni or HY : Mo–Ni, the volume of the reactor was 6 mL.

 Table 2
 Selective ring opening of naphthalene with different amounts of water

			Yield (%)				
Entry	Water (mg)	Conv. (%)	Decalin	Tetralin	ROCP	HC	
1	0	100	17.9	0	50.7	12.3	
2	2	100	24.3	0	63.3	0	
3	6	100	21.3	4.9	55.6	0	
4	10	100	50.9	4.6	49.2	0	
5	50	99.1	55.0	22.3	16.1	0	
6	100	97.8	13.7	79.2	0.4	0	
7	400	59.6	2.6	51.6	0	0	

*Reaction conditions*: naphthalene 6 mg,  $H_2$  5 MPa, 613 K, 4 h,  $Rh_2O_3$ /HY contains 2 wt%  $Rh_2O_3$ , Si/Al = 4.6 in HY, total mass of the catalyst 6.5 mg; S 3 mg,  $Rh_2O_3$ /HY: Mo–Ni 1:0.3, the volume of the reactor was 6 mL.

When Rh<sub>2</sub>O<sub>3</sub>/HY + Mo–Ni + S was used as the catalyst, the yield of the ROCP was 50.7% (entry 17). After adding water, the maximum ROCP yield was as high as 63.3% (entry 18), which was considerably higher than the yield reported in the literature (47.9%).<sup>16</sup> In addition, water could also inhibit the formation of the HC.

### Effect of the amount of added water on the reaction

The effect of the amount of added water on the reaction catalyzed by  $Rh_2O_3/HY + Mo-Ni + S$  was studied and the results are presented in Table 2. Addition of 2 mg water could reduce the yield of HC significantly and increase the yield of ROCP considerably because of the formation of Brønsted acid sites on the surface of the catalysts.<sup>53</sup> But the yield of ROCP decreased

and that of the hydrogenated compounds increased with further increasing the amount of water added. The reason may be that some acidic sites for cracking reaction were covered by water. As the water added exceeded 100 mg, no ROCP could be detected, and conversion of naphthalene and the yields of the hydrogenated compounds decreased significantly, indicating that addition of too much water reduced the activity of the catalyst for all the reactions by covering the surface of the catalyst.

### Effect of temperature on the reaction

The effect of the temperature on the reaction is shown in Fig. 1. At the lower temperature, the hydrogenation products, decalin and tetralin, were mainly produced, and their yields decreased with increasing temperature. The ROCP yield increased with increasing temperature and reached a maximum at 613 K, and then decreased with further increasing temperature. The main reason was that at the lower temperature the reaction rate of the hydrogenation was much faster than the ring opening reaction, and the ring opening reaction became faster as the temperature was raised, which was favorable to yielding the ROCP. As the temperature was too high, significant overcracking occurred and the yield of the ROCP decreased.

#### Influence of hydrogen pressure on the reaction

The influence of hydrogen pressure on the yields of different products is illustrated in Fig. 2. Both the yields of ROCP and decalin increased with hydrogen pressure at the beginning and then decreased after about 5 MPa. This is understandable because hydrogenation is necessary for the ring open cracking and contraction reactions. At the lower hydrogen pressure, the



**Fig. 1** Effect of temperature on the yield of different products; ROCP,  $\bullet$  tetralin,  $\blacktriangle$  decalin. Reaction conditions: naphthalene 6 mg, H<sub>2</sub> 5 MPa, water 2 mg, 4 h, Rh<sub>2</sub>O<sub>3</sub>/HY contains 2 wt% Rh<sub>2</sub>O<sub>3</sub>, Si/Al = 4.6 in HY, total mass of the catalyst 6.5 mg, S 3 mg, Rh<sub>2</sub>O<sub>3</sub>/HY: Mo–Ni 1:0.3, the volume of the reactor was 6 mL.



**Fig. 2** The effect of hydrogen pressure on the yield of different products; **I** ROCP, **•** tetralin, **A** decalin. Reaction conditions: naphthalene 6 mg, 613 K, water 2 mg, 4 h, Rh<sub>2</sub>O<sub>3</sub>/HY contains 2 wt% Rh<sub>2</sub>O<sub>3</sub>, Si/Al = 4.6 in HY, total mass of the catalyst 6.5 mg, S 3 mg, Rh<sub>2</sub>O<sub>3</sub>/HY: Mo–Ni 1:0.3, the volume of the reactor was 6 mL.

concentration of hydrogen on the catalyst surface was low, and therefore the yields of the ROCP and decalin increased with pressure. However, the overcracking was more significant at the higher pressure, and the yields decreased with increasing pressure. As expected, the yield of tetralin, the partially hydrogenated compound, decreased monotonously with pressure.

#### Effect of reaction time on the reaction

The effect of reaction time on the distribution of the products is shown in Fig. 3. Tetralin was the main product at 1 h and its yield decreased with increasing reaction time. The yields of ROCP and decalin increased with time up to 4 h, and the yields decreased with further increasing reaction time. This is consistent with the argument that the hydrogenation rate of naphthalene to tetralin is much higher than that of tetralin to decalin due to the strong adsorption of naphthalene on the metal surface.<sup>53</sup> At



Fig. 3 The effect of reaction time on product distribution of naphthalene hydrocracking;  $\blacksquare$  ROCP,  $\bullet$  tetralin,  $\blacktriangle$  decalin. Reaction conditions: naphthalene 6 mg, H<sub>2</sub> 5 MPa, 613 K, water 2 mg, Rh<sub>2</sub>O<sub>3</sub>/HY contains 2 wt% Rh<sub>2</sub>O<sub>3</sub>, Si/Al = 4.6 in HY, total mass of the catalyst 6.5 mg, S 3 mg, Rh<sub>2</sub>O<sub>3</sub>/HY: Mo–Ni 1:0.3, the volume of the reactor was 6 mL.

the beginning, the main product was tetralin. With increasing time, more tetralin was converted to decalin and ROCP. After that, extending the reaction time would result in more overcracking. Therefore, both the yields of decalin and ROCP decreased, as shown in Fig. 3.

### Characterization of the catalysts

The Rh<sub>2</sub>O<sub>3</sub>/HY + Mo-Ni catalysts with and without sulfur (entries 12 and 18 of Table 1) were characterized before and after the reaction by XPS. The results with and without sulfur are shown in the left and right columns of Fig. 4, respectively. Fig. 4(a) shows that Mo<sup>6+</sup> (232.5 eV) was fully converted to MoS<sub>2</sub> (228.9 eV) with addition of sulfur after the reaction, while Fig. 4(d) illustrates that Mo<sup>6+</sup> was partly reduced to Mo<sup>4+</sup> (229.2 eV) after the reaction without sulfur. Therefore, in the reaction, the Mo in the reaction system existed as MoS<sub>2</sub> in the presence of sulfur, and as MoO<sub>3</sub> and MoO<sub>2</sub> without sulfur. MoO<sub>3</sub> dissociated hydrogen into H atoms, and the bonding of H to surface O atoms led to the formation of Brønsted acidic Mo-OH groups on the MoO<sub>2</sub> surface. In the sulfide catalyst, the dissociated H atoms form the Mo-SH group on MoS2 surface. The acidity of  $MoS_2$  is weaker than  $MoO_2$ .<sup>51</sup> But  $MoS_2$  is more active for hydrogenation than  $MoO_2$ .<sup>52</sup> So the acidity of the oxide system is higher than that of the sulfide system. Too high acidity usually causes overcracking and condensation, which produces HC.54 This can explain in part why the yield of HC is much lower when the sulfide catalyst was used.

There are four peaks at 307.95 eV, 308.55 eV, 309.8 eV and 310.5 eV in Rh 3d figures Fig. 4(b) and 4(e), and they are assigned to Rh,  $Rh^{2+}$ ,  $Rh^{3+}$  and Rh sulfide, respectively. In the presence of sulfur, a part of  $Rh^{3+}$  was reduced to Rh, and part was converted to Rh sulfide that is inactive for hydrogenation. Without sulfur, Rh oxide was reduced to Rh after reaction, which is active for the hydrogenation. So the Rh was less active in the sulfide catalyst than the oxide catalyst. The decalin yield of entry 5 is lower than that of entry 1 in Table 1 because the hydrogenation activity of Rh is reduced by sulfur. However,



Fig. 4 X-ray photoelectron spectra for the catalysts with and without sulfur before and after the reaction: (a) and (d) Mo 3d level, (b) and (e) Rh 3d level, (c) and (f) Ni 2p level. The left column is for the  $Rh_2O_3/HY + Mo-Ni + S$ , the right column is for the  $Rh_2O_3/HY + Mo-Ni$ .

when Rh was combined with Mo–Ni, the hydrogenation activity reduction of Rh can be compensated by the enhanced activity of Mo–Ni sulfide, as can be known by the comparison of entries 12 and 18 in the table.

Fig. 4(c) and 4(f) show the Ni 2p level XPS spectrum. In the presence of sulfur, there was a very weak peak for Ni sulfide (852.7 eV), and a strong peak for Ni oxide (855.5 eV), indicating that the Ni existed mainly in the form of Ni oxide. Without sulfur, the peak for the Ni oxide increased to 856.1 eV. The Ni oxide was not reduced to Ni (852 eV) by hydrogen in the reaction. In the presence of sulfur, a small part of Ni was sulfided and Ni also existed mainly in the form of Ni oxide. In our experimental conditions, the main form of Ni in the catalysts was Ni oxide with and without S. So the effect of sulfur on the function of Ni should be very limited.

Based on our results and the related work in the literature, the reaction pathway for the selective ring opening reaction of naphthalene catalyzed by a bifunctional catalyst can be illustrated by Scheme 1.<sup>8,55</sup> On the bifunctional catalysts, the selective ring opening reaction is accompanied by hydrogenation, isomerization and cracking. Naphthalene is first converted to tetralin and decalin with the aid of the hydrogenation catalyst. The acidic support promotes the isomerization and ring opening reaction. The overcracking reaction can yield some small molecules. HC is produced by condensation reactions, forming the precursors of coke. In this work, the Rh and Mo-Ni sulfide are active for the hydrogenation, and the HY and Mo-Ni sulfide promote the isomerization and cracking. Some new Brønsted acid sites were formed on the HY and Mo-Ni sulfide in the presence of water, which enhances the isomerization and cracking. Besides, the water molecules adsorbed on the zeolite inhibited the condensation reaction, which reduced the probability to form the HC. All the factors were favorable to achieving a higher yield of ROCP.



Scheme 1 The possible reaction pathway of naphthalene hydrocracking.

# Conclusions

We have studied the effect of water on the ring opening and contraction reactions of naphthalene promoted by different catalysts. The results indicate that Rh<sub>2</sub>O<sub>3</sub>/HY and Mo-Ni + S can catalyze the reaction synergistically. The best ratio of Rh<sub>2</sub>O<sub>3</sub>/HY and Mo-Ni is 1:0.3 for the reaction. In the reaction, Rh and Mo-Ni sulfide are active for the hydrogenation, and the HY and Mo-Ni sulfide provide acid sites for isomerization and cracking reactions. Water can be used as an effective green additive for enhancing the yield of the ROCP catalyzed by Rh<sub>2</sub>O<sub>3</sub>/HY + Mo-Ni + S because it can improve the hydrogenation activity of the catalyst, produce new Brønsted acid sites on the HY and Mo-Ni sulfide, which enhances the isomerization and cracking. In addition, the water molecules adsorbed on the zeolite can prevent the condensation reaction, which inhibits the formation of heavy compounds. All the factors are favorable to achieving higher yield of ROCP. This work provides new and useful knowledge for improving the CN of diesel in a greener and efficient way. We believe that water as green additive has great potential for promoting some other chemical reactions.

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