Study of Dibenzothiophene Adsorption Over Carbon Nanotube Supported CoMo HDS Catalysts

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Abstract: Adsorption properties of dibenzothiophene (DBT) on a CNT (carbon nanotube) support as well as on CoMoS/CNT and CoMoO/CNT catalysts have been studied. Consecutive desorption of adsorbates was measured by TGA. The commonly used carriers AC (activated carbon), \(\gamma\)-Al\(_2\)O\(_3\), and their supported catalysts (CoMoO/AC, CoMoS/AC, CoMoO/\(\gamma\)-Al\(_2\)O\(_3\), CoMoS/\(\gamma\)-Al\(_2\)O\(_3\)) were also subjected to analysis for comparison. The acidic properties of the samples were characterized using the NH\(_3\)-TPD technique. Correlation between the adsorption of DBT and the acidic properties of the catalysts has been established. It was found that the Co-Mo catalysts in the sulfide state adsorbed much more DBT molecules than the corresponding Co-Mo catalysts in the oxide state. The CoMoS/CNT catalyst exhibited very high HDS activity and selectivity, as compared with the CoMoS/\(\gamma\)-Al\(_2\)O\(_3\) catalysts. Based on the BET data of the high hydrogenolysis/hydrogenation selectivity of the CoMoS/CNT, it was deduced that more than 90% of the DBT molecules adsorbed on the CoMoS/CNT with an end-on mode, and the surface of the CoMoS/CNT catalyst was almost fully covered with DBT molecules. Although the AC support had very high surface area and high loading ability, the AC supported CoMoS catalyst showed lower HDS activity, as compared with the CoMoS/\(\gamma\)-Al\(_2\)O\(_3\) catalyst.

Key words: carbon nanotubes, adsorption properties, dibenzothiophene, hydrodesulfurization, network

1. Introduction

In heterogeneous catalysis systems, catalytic reactions proceed on the surface of the catalysts. Therefore, adsorption properties, especially the chemical adsorption of reactants on the surface of the catalysts, play an important role in the process of catalysis. Hydrodesulfurization (HDS) is a critical process in the production of clean oils \([1,2]\). Thiophene, dibenzothiophene (DBT) and its alkyl derivatives are the most common sulfur containing organic molecules existing in the petroleum-derived feed-stocks. The difficulty in removing the sulfur from DBT is derived from the strong stability of the aromatic ring (about 85 kJ/mol for thiophene). Thus, the key point in the reaction would be the weakening of the aromatic \(\pi\) bonding upon adsorption on the metal surface of the catalyst. A great deal of efforts have been made to try to elucidate the adsorption state of the organic sulfur containing molecules on the surface of the catalysts. St. Clair \textit{et al} \([3]\) studied the adsorption and reaction of thiophene on \(\alpha\)-Mo\(_2\)C (0001). It was found

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that thiophene can adsorb both reversibly and irreversibly on α-MoO₃ (0001). The irreversible adsorption resulted in a decomposition to surface C, surface S and gaseous H₂. The chemical states of the carbon and sulfur, as identified by X-ray photoelectron spectroscopy, were carbidic and sulfidic, respectively, and this implied that the surface decomposition products were bound to the metal sites. Terada et al [4] studied thiophene adsorption on Pd(111) and Pd(100) surfaces by the total reflection S K-edge X-ray adsorption fine structure technique. Thiophene was found to lie flat, accompanied by slightly elongated S-C bonds due to the charge transfer of 1.1–1.2 electrons from the Pd valence bands to the π* orbital. The S atom in the thiophene adsorbate located at an intermediate position between bridge and atop sites. Rodriguez et al [5] used synchrotron-based resolution photoemission to study the adsorption and decomposition of thiophene on clean Mo(110) and carbide- or sulfide-modified molybdenum. It was found that thiophene adsorbed molecularly on Mo(110) at 110 K. At lower than 180 K, upon the desorption of the thiophene multilayer, chemisorbed thiophene and its decomposition products (S and CₓHₓ fragments) co-existed on the Mo(110) surface. At 250 K, no C-S bonds were left. There was a continuous transformation of the CₓHₓ species into atomic C at temperatures between 300 K and 600 K. All these results show that thiophene is easily decomposed at low temperatures during the desorption process.

Compared with thiophene, dibenzothiophene (DBT) and alkyl DBT are difficult to be removed from the feedstocks even at high temperatures and pressures [6]. Farag [7] studied the adsorption of DBT on carbon supported CoMo catalysts and conducted some surface characterizations by adsorption and desorption techniques. He also used the thermal gravimetric technique to get useful information on the nature of dispersion of the catalysts on the support. Xu et al [8] studied the dispersion as well as adsorption of dibenzothiophene on the commonly used CoMo/γ-Al₂O₃ catalyst surface. It was suggested that the adsorption of DBT on the surface of CoMo/γ-Al₂O₃ might include two states, one was the end on mode through the adsorbed sulfur atom, and the other was the flat mode through the π electrons of the DBT molecule, which was the main adsorption state. Larrubia et al [9] studied the adsorption of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethylbenzothiophene (4,6-DBT) on supports such as alumina, zirconia and magnetia by IR spectroscopy. The main adsorption process was due to adsorption on Lewis sites or on acid-base pairs. On the alumina support, the adsorption was the strongest, and desorption was not observed even above 723 K. Adsorption of 4,6-DBT was limited in extent, very likely due to a steric hindrance. The results showed that DBT and 4,6-DBT did not undergo decomposition during desorption due to the stability of the aromatic rings. Up to now, few studies have been done on the adsorption states of DBT on carbon nanotube as well as carbon nanotube supported oxide and sulfide CoMo catalysts.

In this paper, the acidities of the catalysts were investigated by using the NH₃-TPD technique. The adsorption characteristics of DBT on carbon nanotube (CNT) support and on oxide and sulfide Co-Mo catalysts were also studied by using the TGA technique. The supported CoMo catalysts are prepared by a pore volume impregnation method, and the dispersion of the active phases was studied by the XRD technique. Alumina, activated carbon (AC) and their corresponding supported catalysts were also subjected to studies for comparison. The hydro-desulfurization (HDS) activities of the sulfide catalysts were measured using DBT as the model compound in a solution of toluene, and the results were correlated with their corresponding DBT adsorption properties. As a novel catalytic support, some fundamental work has been done on the carbon nanotube, together with the carbon nanotube supported CoMo catalytic system.

2. Experimental

2.1. Preparation of catalysts

A kind of multi-wall carbon nanotube (CNT) supplied by Tsinghua University is used as-received, and a pillar type activated carbon (AC, 20–40 mesh) was provided by the Beijing Institute of Coal Science and used as-received. Catalysts with 10wt%MoO₃ loading and Co/Mo atomic ratio of 0.35 were prepared by a pore volume impregnation method using aqueous solutions of (NH₄)₆Mo₇O₂₄.24H₂O and Co(NO₃)₂·6H₂O (both A.R.). The Mo phase is introduced first and dried in air at 110 °C for 12 h, then the Co precursor was introduced by pore volume impregnation, followed by drying at 110 °C for 12 h. Finally the bimetallic catalysts were heat-treated at 500 °C for 4 h in a flow of nitrogen. The CNT supported oxide state catalyst is designated as Co-MoO/CNT and the AC supported oxide state cata-
lyst as CoMoO/AC. The alumina supported CoMo catalyst was prepared with the same method as the CoMoO/CNT, except it was calcined at 500 °C in air. The γ-Al2O3 supported oxide state catalyst is designated as CoMoO/γ-Al2O3.

In the preparation of the sulfide state CoMo catalyst, the sulfided Mo phase was obtained via ammonium tetrathiomolybdate (ATTM) [10], followed by the impregnation of Co(NO3)2·6H2O, dried at 110 °C for 24 h, and finally heat-treated at 500 °C in a flow of N2 for 4 h. In the case of alumina, the catalyst was calcined in air. The sulfide catalysts are designated as CoMoS/CNT, CoMoS/AC, and CoMoS/γ-Al2O3, respectively. In some cases, the catalysts are labelled as CoMoX/support, where X denotes the O or S atoms, while the supports are denoted as AC, CNT and γ-Al2O3, respectively.

2.2. Adsorption of DBT

A solution of 1wt% DBT in toluene was used in the adsorption experiments. 0.05 g adsorbent was immersed in 15 g of the 1wt% DBT in toluene solution, and the mixture was stirred under ultrasonic condition for 2 h. Finally, the samples were filtered under suction till almost dry.

2.3. Thermal gravimetric analyses

The sample after filtration is investigated using a DuPont 952 thermo-gravimetric apparatus with a thermo-balance, and with a computer control unit for the recording of TG. Before recording the curves, the sample is treated in a flow of N2 for 1 h at 100 °C in order to remove traces of toluene and physically adsorbed DBT molecules. Then, the runs were carried out in a continuous flowing N2 gas and the TGA curves of the samples were recorded from 100 to 600 °C at a rate of 10 °C/min for all runs.

2.4. X-ray diffraction (XRD)

XRD patterns were recorded at ambient temperature on a D/Max-III type spectrometer with Cu Kα radiation, the voltage was 40 kV and the electrical current 40 mA.

2.5. Temperature programmed desorption (TPD)

Temperature programmed desorption experiments are conducted on a LCD-I type TPD/TPR combined apparatus. About 0.1 g sample was placed in a stainless tubular reactor with inner diameter of 6 mm. The sample was treated in a flow of ultra-pure nitrogen with a flow rate of 30 ml/min at 150 °C for 2 h to remove impurities adsorbed on the surface of the samples. The reactor was cooled down to 50 °C and then NH3 was pulsed into the system until saturation was reached at this temperature. The flow of nitrogen was kept for another 2 h at 50 °C in order to obtain a satisfactory baseline. Finally, the reactor was heated from 50 to 600 °C at a rate of 8 °C/min, then held at 600 °C for 10 min. The gas evolved during each TPD run was detected with a thermal conductivity detector (TCD) and recorded by a computer.

2.6. BET measurements

BET surface areas, average pore diameters and total pore volumes of the supports as well as the catalysts were determined by nitrogen adsorption-desorption isotherms at 77.35 K in an ASAP2010 adsorption apparatus. The physical properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>189.6</td>
<td>0.47</td>
<td>8.9</td>
</tr>
<tr>
<td>CoMoO/CNT</td>
<td>163.7</td>
<td>0.43</td>
<td>8.1</td>
</tr>
<tr>
<td>CoMoS/CNT</td>
<td>107.0</td>
<td>0.37</td>
<td>7.8</td>
</tr>
<tr>
<td>AC</td>
<td>1006.0</td>
<td>0.37</td>
<td>4.8</td>
</tr>
<tr>
<td>CoMoO/AC</td>
<td>860.0</td>
<td>0.31</td>
<td>3.9</td>
</tr>
<tr>
<td>CoMoS/AC</td>
<td>920.0</td>
<td>0.34</td>
<td>4.2</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>216.0</td>
<td>0.51</td>
<td>7.1</td>
</tr>
<tr>
<td>CoMoO/γ-Al2O3</td>
<td>174.7</td>
<td>0.27</td>
<td>6.1</td>
</tr>
<tr>
<td>CoMoS/γ-Al2O3</td>
<td>193.0</td>
<td>0.50</td>
<td>6.8</td>
</tr>
</tbody>
</table>
2.7. Calculation method for the adsorption amount of DBT

According to the known method for surface area calculation [9], the following equation was applied to calculate the surface areas of adsorbed DBT, based on the assumption that DBT molecules were in a side-on mode on the surface of catalyst:

\[ A = \frac{m_1/M \times 6.02 \times 10^{23} \times 66.5 \times 10^{-20}}{m - m_1} \]  

(1)

where \( A \) is the total specific area (m\(^2\)/g) of adsorbed DBT, \( M \) is the molar weight (g/mol) of DBT, \( m \) represents the total weight (mg) of the sample after the adsorption of DBT, \( m_1 \) represents the amount of the weight loss of DBT during the DTA process. 66.5 \( \times 10^{-20} \) is the surface area of DBT per molecule, m\(^2\).

The adsorption ratio of DBT can be obtained from the following equation:

\[ R = \frac{m_1}{m - m_1} \]  

(2)

where \( R \) is the adsorption ratio (mg/g) of DBT, \( m \) and \( m_1 \) are the same as in Equation 1.

2.8. HDS activity measurements

The HDS experiments were carried out in a high pressure flow micro-reactor, using DBT as the model compound and toluene as the solvent. Reaction temperature \( T=280 \) °C, \( H_2 \) pressure \( p=2 \) MPa, and LHSV=6 h\(^{-1}\).

3. Results

3.1. XRD

Powder X-ray diffraction patterns of the carbon nanotube, CoMoO/CNT and CoMoS/CNT are presented in Figure 1(a). For the CNT, a strong peak at a 2\( \theta \) value of 26.05° can be observed, representing the (002) graphitic basal plane. In addition, a weaker broad peak near 2\( \theta \) of 43.0° also can be found. In the XRD pattern of the oxide CoMoO/CNT, new diffraction peaks are clearly observed at the 2\( \theta \) values of 36.9° and 53.49°, respectively. These peaks are characteristics of MoO\(_2\), but not those of the expected MoO\(_3\) [11], indicating that the main active phase on the surface of CNT is the low valence state Mo, and the active phase conglomerates into crystallites.
In the XRD pattern of the sulfide CoMoS/CNT, no obvious peaks of MoS$_2$ and CoMoS are found, indicating that the active phases are well dispersed on the support. It should be emphasized that no diffraction peaks of the DBT are found. A broad and weak peak, representing the diffraction of MoO$_2$, is found in the XRD pattern of the CoMoO/AC (Figure 1(b)), indicating that a large part of the Mo phase is also reduced from Mo$^{6+}$ to the low valence Mo$^{4+}$, and that the active phase is dispersed better on the AC carrier than on the CNT. Similarly, no diffractions of DBT are detected on the XRD. As for the sulfide CoMoS/AC, all of the active phases are well dispersed, and no peaks belonging to MoS$_2$ and CoMoS are detected. DBT diffraction patterns are not found, indicating that DBT molecules are well dispersed on the AC and the AC supported catalysts.

There are no obvious differences in the XRD patterns between CoMoO/$\gamma$-Al$_2$O$_3$ and CoMoS/$\gamma$-Al$_2$O$_3$, indicating that all the active phases are smaller than 2 nm and could not be detected. Again, DBT diffractions are not detected, giving the evidence that the DBT is well dispersed on the $\gamma$-Al$_2$O$_3$ and on the supported catalysts.

### 3.2. NH$_3$-TPD

The NH$_3$-TPD profiles for supports, supported oxide CoMo catalysts and supported sulfide CoMo catalysts are presented in Figure 2, respectively.

It was reported [13] that the acid sites could be classified into three types: weak ($T_{des} < 300$ °C), medium (300 °C < $T_{des} < 450$ °C) and strong (450 °C < $T_{des} < 550$ °C) according to the adsorption temperatures on the NH$_3$-TPD profiles. It can be seen that the relative amount of the acid sites of the CoMoS/CNT is greater than those of the CoMoO/CNT, and this is also the case with the CoMoS/$\gamma$-Al$_2$O$_3$. In addition, new strong acidic sites are produced for the CoMoS/$\gamma$-Al$_2$O$_3$ and the CoMoS/CNT, as compared with the corresponding support and the oxide CoMo catalysts. It is interesting that the strength and relative amount of the acid sites decreased greatly after loading with the oxide CoMo active phase or the sulfide active phase on the AC support, and that the CoMoS/AC had the weakest acidity.
3.3. TGA

The TG curves of DBT desorption on various carriers and catalysts are presented in Figure 3. The specific surface areas of the DBT adsorbed on the supports and catalysts calculated according to formula (1) are listed in Table 2, the adsorption ratios of DBT on the supports and catalysts are also given in Table 2.

![Figure 3. TG desorption curves of supports (a), and CoMoO (b), CoMoS (c) supported catalyst](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorption ratio of DBT (mg/g)</th>
<th>Specific surface area of DBT absorbed on samples (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>2.47</td>
<td>53.56</td>
</tr>
<tr>
<td>AC</td>
<td>3.13</td>
<td>67.91</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>2.01</td>
<td>43.59</td>
</tr>
<tr>
<td>CoMoO/CNT</td>
<td>2.15</td>
<td>46.69</td>
</tr>
<tr>
<td>CoMoO/AC</td>
<td>7.81</td>
<td>169.63</td>
</tr>
<tr>
<td>CoMoO/γ-Al₂O₃</td>
<td>1.71</td>
<td>37.08</td>
</tr>
<tr>
<td>CoMoS/CNT</td>
<td>4.97</td>
<td>107.92</td>
</tr>
<tr>
<td>CoMoS/AC</td>
<td>8.11</td>
<td>176.18</td>
</tr>
<tr>
<td>CoMoS/γ-Al₂O₃</td>
<td>6.91</td>
<td>150.22</td>
</tr>
</tbody>
</table>

The adsorption amount of DBT on the CoMoO/CNT is smaller than on the CNT carrier alone, but the adsorption amount on the CoMoS/CNT is twice as great as on the CNT. Similarly, more DBT molecules are adsorbed on the γ-Al₂O₃ than on the CoMoO/γ-Al₂O₃ catalyst, whilst the CoMoS/γ-Al₂O₃ catalyst has a strong adsorption ability for DBT, about 3–4 times greater than that of the γ-Al₂O₃. As for the AC and AC supported catalysts, the CoMoO/AC and CoMoS/AC have almost the same adsorption ability for the DBT molecules, but they are much more stronger in adsorption ability than the AC carrier, namely, about 2.5 times greater. In general, the sulfide catalyst adsorbs much more DBT molecules than the corresponding oxide catalyst. AC has the strongest adsorption ability for DBT molecules among CNT, AC and γ-Al₂O₃. Similarly, among the three oxide catalysts, the CoMo/AC has the highest adsorption ratio towards DBT.

4. Discussion

The reason for the high loading ability of AC may be due to its large surface area and surface oxygen-containing groups [14,15], and the oxide state and sulfide state CoMo active phases are well dispersed on AC, so that no diffraction peaks are detected. As for the CNT, the active phases are poorly dispersed, and the reason is probably that the surface of the CNT is hydrophobic [16], so that few oxygen groups exist on the surface of the CNT. Therefore, the interaction between the active phases and the CNT is weak, and mobilization and conglomeration of the active phases may occur during the process of heat-treatment at 500
In addition, the low valence MoO$_2$ is produced during heat-treatment at 500 °C because of the reduction ability of the carbon materials [17]. In case of the alumina supported catalyst systems, the active phases strongly interact with the —OH groups on the support and result in a high dispersion.

The adsorption states of DBT on the catalysts are supposed to be in two ways, one is the end-on mode and the other is the side-on mode [18]. DBT molecules can adsorb on acidic sites and/or transition metals with vacant orbits which can accept electrons. According to the BET data, the specific surface area of CNT (189.6 m$^2$/g) is much larger than the surface area (53.56 m$^2$/g) of the DBT molecules which adsorbed on the CNT, it can be deduced that the DBT molecules adsorb on the support in the manner of monolayer adsorption, and the surface of the CNT is not thoroughly covered by DBT molecules. It is also the case with the CoMoO/CNT. As for the CoMoS/CNT, its specific surface area is equal to the surface area of the DBT molecules adsorbed. The low ability of the CNT for the adsorption of DBT molecules is due to its weak acidity and small number of acidic sites. On the other hand, the great increase in DBT adsorption on the CoMoS/CNT is attributed to the newly produced acidic centers which may due to the anion vacancies of the active phase, since the number of acidic sites and the acid strength increased greatly after loading with the sulfide active phases, in light of the TPD results. The HDS activity and selectivity results of the catalysts are listed in Table 3, and the relationship between the adsorption modes of DBT over the HDS catalysts and the HDS pathway or product distributions is shown in Figure 4.

### Table 3. HDS measurements of catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity$^a$ (wt%)</th>
<th>Desulfurization ratio$^b$ (wt%)</th>
<th>Selectivity$^c$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMoS/γ-Al$_2$O$_3$</td>
<td>83.61</td>
<td>83.00</td>
<td>4.35</td>
</tr>
<tr>
<td>CoMoS/CNT</td>
<td>97.23</td>
<td>96.71</td>
<td>16.48</td>
</tr>
<tr>
<td>CoMoS/AC</td>
<td>49.51</td>
<td>39.78</td>
<td>4.91</td>
</tr>
</tbody>
</table>

$^a$: Activity = (total amount of DBT-unreacted amount of DBT)/total amount of DBT  
$^b$: Desulfurization ratio = (product of diphenyl+product of cyclohexylbenzene)/ total amount of DBT  
$^c$: Selectivity = product of hydrogenolysis / product of hydrogenation

In the distribution of products, BPN denotes biphenyl, CHB denotes cyclohexylbenzene, 4H-DBT represents tetrahydrodibenzothiophene, and DBT represents dibenzothiophene. In dealing with the experimental data, conversion ratio (wt%) represents total amount of DBT subtracts un-reacted amount of DBT/total amount of DBT, and selectivity is defined as the amount of BPN/amount of BPN plus the amount of CHB. It can be seen that the CoMoS/CNT exhibits the highest activity and hydrogenolysis/hydrogenation selectivity. By taking the HDS, DBT adsorption and TPD results into account, it can be concluded that the DBT molecules adsorb on the active sites of the CoMoS/CNT in an end-on mode over the HDS catalysts and the HDS pathway or product distributions is shown in Figure 4.
mode, mainly owing to its very high hydrogenolysis selectivity. One reason for the very high activity of the CoMoS/CNT may be that there are a number of anion vacancies in the active phases, in spite that the active phases are not well dispersed on the support. Another reason for the high activity of the CoMoS/CNT may be due to a combination of the electron donor effect of the carbon nanotube and the so-called nano-size effect [19,20].

Although the adsorption ratio is high for the AC, the surface area of the adsorbed DBT molecules is merely 67.91 m²/g, which is very small compared with the surface area of AC (1006 m²/g), and is far from a full coverage even in a manner of flat adsorption, and this indicates that a large part of the surface is uncovered. The relative large number of DBT molecules adsorbed on the AC is attributed to the large surface area, as well as the broad acid distribution of the AC. It is also the case with the CoMoO/AC and CoMoS/AC. In general, the DBT molecules are well dispersed on the catalysts in the manner of monolayer coverage. After loading with the active phases, the acidity becomes weaker for the oxide and sulfide catalysts, especially for the CoMoS/AC, but the adsorption of DBT increases for the CoMoS/AC, indicating that the transition metals act as adsorption sites. The TPD results show that the CoMoS/AC catalyst has very low activity and selectivity. Taking the results of TPD, adsorption and HDS measurements into account, it can be concluded that part of the DBT molecules adsorbs on the CoMoS/AC is in the end-on manner, while the others are in a so-called side-on manner.

As for the γ-Al₂O₃ and the CoMoO/γ-Al₂O₃, the surface areas of adsorbed DBT molecules are merely 43.59 and 38.07 m²/g, respectively. The adsorbed DBT molecules could not cover the surface of the γ-Al₂O₃ (216 m²/g) and the CoMoO/γ-Al₂O₃ (174.7 m²/g) even in a manner of monolayer coverage. On the contrary, the DBT molecules adsorbed (155.22 m²/g) on the CoMoS/γ-Al₂O₃ can almost cover entirely the surface of the sulfide catalyst (193 m²/g). The adsorption property of the CoMoS/γ-Al₂O₃ for DBT is similar to that of the CoMoS/CNT in this sense, but differs from that of the CoMoS/AC catalyst. The TPD results show that the acidity increases greatly after loading with the CoMoS phases, indicating that anion vacancies may be produced in the process of CoMoS/γ-Al₂O₃ preparation. The reason for the decrease in acidity after the loading of the oxide phases, as compared with the γ-Al₂O₃, may be due to the fact that part of the acid sites is covered by the oxide phases. The adsorption abilities for DBT molecules follow the same sequence of the acidity distributions, namely, γ-Al₂O₃, CoMoO/γ-Al₂O₃ and CoMoS/γ-Al₂O₃. Thus, the acidic sites play an important role in the process of DBT adsorption, but the transition metal sites could not be ruled out as well. According to the results of HDS measurements, the higher HDS activity of the CoMoS/γ-Al₂O₃ catalyst compared with the CoMoS/AC may be related to its good adsorption ability for DBT. The CoMoS/γ-Al₂O₃ catalyst exhibits much lower selectivity compared with the CoMoS/CNT, indicating that a portion of the DBT molecules may adsorb on the CoMoS/γ-Al₂O₃ in the end-on mode, producing the hydrogenolysis product of biphenyl, while about 20%-30% of the DBT molecules adsorb on the catalyst are in the flat manner, resulting in the hydrogenation product of cyclohexylbenene.

5. Conclusions

Sulfide CoMoS/CNT, CoMoS/AC and CoMoS/γ-Al₂O₃ have higher adsorption abilities towards DBT molecules than their corresponding oxide catalysts.

CoMoS/CNT exhibits very high HDS activity compared with CoMoS/γ-Al₂O₃ and CoMoS/AC. Based on the high selectivity of the CoMoS/CNT, it can be deduced that almost more than 90% of the DBT molecules adsorb on CoMoS/CNT are in an end-on manner, and the surface of the CoMoS/CNT is fully covered.

Although the AC support has very high surface area and high loading ability, the AC supported CoMoS catalyst shows very lower HDS activity compared with CoMoS/γ-Al₂O₃ and CoMoS/AC. The surface area of the DBT molecules adsorbed on CoMoS/AC is merely 176.18 m²/g, that is, only 19.1% of the surface area of CoMoS/AC (920 m²/g) is covered by DBT molecules.

The high HDS activity of CoMoS/γ-Al₂O₃ (193 m²/g) is related to its good adsorption ability towards DBT molecules. The low selectivity of CoMoS/γ-Al₂O₃ may be that a part of the DBT molecules adsorbed on the active sites is in the end-on manner, thus producing hydrogenolysis products, while another part of the DBT molecules adsorbed on active sites is in the flat manner, hence producing hydrogenation products.
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References