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Effect of water on HDS of DBT over a dispersed Mo catalyst using in situ generated hydrogen

Roy Z. Lee, Flora T.T. Ng *

Department of Chemical Engineering, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

Abstract

A novel process was developed for the bitumen emulsion upgrading, wherein emulsion breaking and upgrading occurred in the same reactor using H_2 generated in situ from the water in the emulsion via the water gas shift reaction (WGSR). In this study, dibenzothiophene (DBT) was chosen as a model compound to investigate the effect of water and in situ H_2 on hydrodesulfurization (HDS). All the experiments were performed in a 1-L autoclave reactor at temperatures between 300 and 380 °C using in situ H_2 and ex situ H_2 (externally supplied H_2) over a dispersed Mo catalyst formed from phosphomolybdic acid (PMA). At very low water content, water was found to promote the HDS reaction in the ex situ H_2 run probably because it facilitates the formation of more active dispersed MoS_x species. At higher water content, however, water inhibits every individual reaction in the reaction network in the HDS of DBT, blocking the hydrogenation pathway more than the hydrogenolysis pathway. The relative reactivity of the in situ and ex situ H_2 depends on the water content present in the reaction system. At an optimized mole ratio of H_2O:CO (1.35), higher HDS activity was observed in the in situ H_2 run compared to ex situ H_2 run, and particularly, the hydrogenation pathway was promoted in the in situ H_2 run.

Keywords: Hydrodesulfurization; HDS; Dibenzothiophene; DBT; Phosphomolybdic acid; PMA; Water gas shift reaction; WGSR; In situ H_2; Water effect

1. Introduction

Canada's bitumen is very sour with sulfur contents in the range of 2–6 wt% [1]. The sulfur content increases progressively with the boiling point of the fraction with the majority of the sulfur being contained in the heavy fraction of the oils. Sulfur removal is one of the most important tasks in the upgrading of heavy oils for two main reasons: to control the air pollution and to avoid catalyst poisoning. Much of the sulfur in gas oil fed to an FCC unit may be found in the coke deposit, the sulfur content of which is converted to sulfur dioxide in the regenerator and emitted to the atmosphere in the combustion gases. Sulfur compounds in the feed are fatal to catalytic reforming catalysts and hydrocracking catalysts. Sulfur in transportation fuels (diesel and gasoline) are emitted into the air as sulfur oxides after combustion in the engines of automobiles. Extremely low sulfur levels are necessary for future NO_x tailpipe conversion systems and for particulate filter systems [2]. The reduction of sulfur content also reduces corrosion during refining and handling, and improves the odor of the products. Recent stricter environmental regulations require a significant reduction of sulfur contents in gasoline and diesel to 10 ppm by the year 2010. If most of the sulfur in bitumen could be removed in the preliminary upgrading process, the burden of sulfur removal in the downstream treatments would be alleviated greatly.

A novel one-stage bitumen emulsion upgrading process has been developed in our laboratory [3], wherein emulsion breaking and bitumen upgrading take place in one reactor, and hydrogen used for upgrading is generated from the water in the emulsion via water gas shift reaction. It was observed that the upgraded bitumen via this novel upgrading process meets Canadian pipeline specifications and the quality of the upgraded bitumen was improved significantly [4].

In this study, dibenzothiophene (DBT) was chosen as a model compound to investigate the hydrodesulfurization (HDS) using in situ generated H_2 via the water gas shift reaction (WGSR). As shown in Fig. 1, there are two reaction pathways for HDS of DBT: (1) hydrogenolysis or the direct removal of sulfur through C–S bond cleavage with simultaneous hydrogenation and (2)

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* Corresponding author. Tel.: +1 519 888 4567; fax: +1 519 746 4979.
E-mail address: fttng@cape.uwaterloo.ca (F.T.T. Ng).

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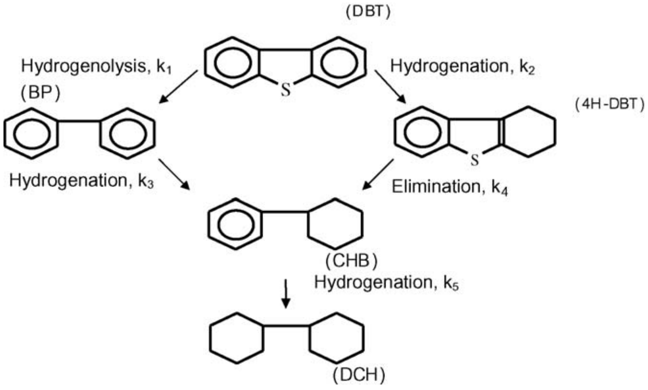

Fig. 1. Reaction network for HDS of DBT.

hydrogenation of thiophenic ring of DBT to destabilize the molecule followed by elimination of sulfur. It is generally considered that the main reaction pathway for HDS of DBT is hydrogenolysis [5]. It was found that the in situ generated H_2 possesses relatively higher hydrogenation activity in the hydrogenation of naphthalene [6]. Therefore, in situ H_2 might promote the HDS of DBT via accelerating the hydrogenation/elimination pathway. In this paper, the role of water and the comparison of in situ H_2 and ex situ H_2 on HDS will be discussed.

2. Experimental

The catalysts used in this work were dispersed Mo-based catalysts, which were prepared in situ via decomposition, reduction, and sulfidation of the precursor. The catalyst precursor used in this study was phosphomolybdic acid (PMA), purchased from Aldrich. The experiments of HDS of DBT were performed in a 1000 ml Autoclave Engineers batch reactor.

When the catalysts were prepared in situ, the catalyst preparation and HDS reaction took place in the same reactor. The catalyst precursors were dissolved in a certain amount of water, and then added into the reactor together with a certain amount of a solution of DBT in toluene. After the reactor was sealed and leak tested, it was purged three times with the reactant gases (H_2 or CO). When CO was used as the reactant gas, in situ H_2 was generated via the water gas shift reaction. The reactor was then charged with 400–600 psi of H_2 or CO. After that, the reactor was heated up gradually to a designated temperature at a rate of 2–3 °C/min and stirred at 1200 rpm. Once the reactor reached the designated temperature, both liquid and gas samples were taken every half hour. The reaction was terminated after 2 h at the designated temperature. The gas samples were analyzed immediately by a GC with TCD; the liquid samples were analyzed by a GC with a FID.

The gas samples were analyzed by GC–TCD (Perkin-Elmer 8500). The inlet system was composed of two columns in series: the first column was packed with 80/100 mesh Hayesep C (1.52 m × 3.12 mm O.D.), and the second column packed with 80/100 mesh 5A molecular sieve (2 m × 3 mm O.D.). The carrier gas was helium containing 8.5% hydrogen. The gases, H_2, O_2, N_2 and CO, were separated in the 5A molecular sieve column, whereas CO_2 and H_2S were separated in the Hayesep C column, because CO_2 and H_2S poison the molecular sieve. The gases were switched between the two columns by a 10-port valve. The liquid products were filtered to remove the solids, analyzed via GC–MS (Trio-1S) to identify their compositions with the aid of the standard compounds, and quantified by GC–FID (Perkin-Elmer Autosystem) with a DB-1701 fused silica column coated with 0.25 μm 7% cyanopropylphenyl silicone (30 m × 0.25 mm O.D.). The carrier gas was helium.

The X-ray diffraction (XRD) measurements were performed on a Siemens D500 Powder X-ray diffractometer with a Cu X-ray source. The wave length (λ) was 0.15405 nm. The survey measurement was scanned from 20° to 80° with 0.05° per step. The specific peak measurement was scanned from 55° to 68° with 0.02° per step. The calculation of the rate constants in HDS of DBT is based on the pseudo-first-order assumption. The calculation was performed using Matcad software.

3. Results and discussions

3.1. Characterization of the catalysts

The XRD spectrum of the catalysts was compared with the standard XRD spectra of MoS_2, MoS_3, MoO_2, and MoO_3, which are provided by the software of the XRD machine. It is found that the spectrum is close to that of the MoS_2 crystal, as shown in Fig. 2. It is well known that the width of the peaks in the XRD spectra increases with a decrease of the crystal size according to the Scherrer equation. Compared with the peaks of the standard MoS_2 crystal, the peaks of the measured sample are much wider and overlapped; no single peaks were detected because of the small size of the particles. It was found that the XRD spectra of the spent catalyst obtained at the end of the reaction is almost the same as that of the fresh catalyst which was isolated at the beginning of the HDS reaction, suggesting that the bulk structure of the dispersed catalyst does not change during the reaction.

3.2. Effect of sulfur and nitrogen compounds on WGSR

In the bitumen emulsion upgrading process many reactions, such as HDS, hydrodenitrogenation (HDN) and hydrogenation,

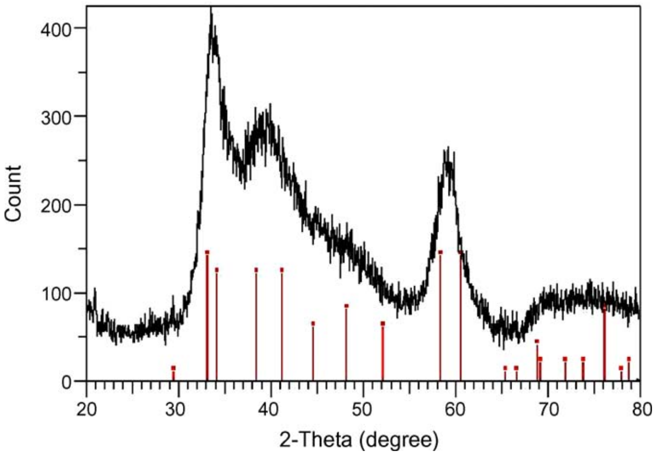

Fig. 2. XRD spectra of the catalyst and the standard MoS_2 crystal.

take place together with the WGSR. The sulfur and nitrogen compounds in bitumen may affect the WGSR due to the competitive adsorption on the active sites. The objective of this study is to investigate the effect of sulfur and nitrogen compounds on WGSR. Dibenzothiophene (DBT) is chosen as the model sulfur compound and quinoline as the model nitrogen compound. Diesel, which contains a variety of sulfur and nitrogen compounds, is selected to study the mixed effect of S and N compounds. For the purpose of comparison, the weight percentage of sulfur in the DBT run is the same as that of nitrogen in the quinoline run, and the total sulfur content in the diesel run is equal to that of the DBT run.

As shown in Fig. 3, when the reaction time is less than about 1.5 h, CO conversion increases as follows: quinoline run $<$ diesel run $<$ DBT run $<$ reference run (without added DBT and quinoline), suggesting that sulfur and nitrogen compounds inhibit the WGSR activity of the catalyst possibly due to the poisoning of the active sites. It is well known that nitrogen compounds adsorb much more strongly than sulfur compounds on Mo-based catalysts [7]. Quinoline has an obviously stronger inhibiting effect for the WGSR than DBT. The inhibiting effect in the diesel run was stronger than in the DBT run, and weaker than in the quinoline run. The sulfur content of the diesel run was similar to that in the DBT run, however, the nitrogen content of the diesel run was much lower than that of the quinoline run.

It is very interesting to note that the CO conversion in the DBT run is higher than the reference run beyond 1 h at 340 °C, and the diesel and nitrogen run did not exhibit such a trend. For the HDS of DBT, the main products are biphenyl, cyclohexylbenzene and bicyclohexyl. Compared to DBT, these hydrocarbon products have much weaker inhibiting effects because of their relatively weak adsorption on the catalysts. Therefore, in the progress of the reactions, the inhibition from sulfur compounds lessens because of the decrease of DBT content. The consumption of H_2 in HDS would promote WGSR. The formation of H_2S in HDS could increase the H_2S concentration in the gas phase. H_2S could keep the catalysts in sulfided form, which is the active state for WGSR [8]. Ng and Milad [9] reported that the rate constant of the WGSR in the presence of benzothiophene (BT) was almost twice as high as that of a reference run without BT. BT is more reactive in HDS than DBT and is thus consumed much faster than the latter in HDS. Therefore, the promoting effect of BT attributed to the consumption of hydrogen and production of hydrogen sulfide was greater than its inhibiting effect, which is quickly lessened due to the fast conversion of BT.

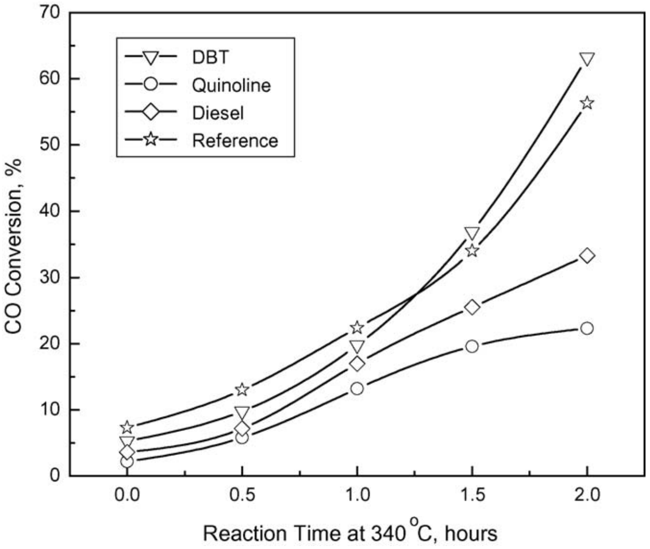

Fig. 3. Conversion of WGSR in presence of DBT, quinoline and diesel over a dispersed MoS_2 catalyst at 340 °C.

In HDN of quinoline at 340 °C, the main products are 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, *o*-propylaniline, and very small amounts of hydrocarbons [7]. During HDN, the quinoline concentration decreases, but the total content of nitrogen compounds does not change significantly. These nitrogen-containing intermediates also have inhibiting effect. Therefore, the inhibiting effect of nitrogen compounds on WGSR does not change much in the quinoline run.

In the initial stage of the diesel run the inhibiting effect came from both sulfur and nitrogen compounds. However, the inhibiting effects from the sulfur compounds decreased with the progress of HDS reaction because most of the sulfur compounds were converted to hydrocarbon via HDS, whereas the effect from nitrogen compounds remained approximately the same because the total nitrogen removal was low at this temperature.

3.3. Effect of temperature on HDS of DBT

HDS of DBT was carried out at 300, 340 and 380 °C for 2 h using in situ H_2 with about 20 wt%. water initially loaded. The DBT conversions were 21.2% at 300 °C, 58.8% at 340 °C and 84.6% at 380 °C. Based on the concentrations of the biphenyl (BP) and tetrahydrodibenzothiophene (4H-DBT) determined as a function of time, the rate constants for hydrogenolysis (k_1) and hydrogenation (k_2) as defined in Fig. 1 were calculated and shown in Table 1. It can be seen that the overall rate constants ($k_1 + k_2$) of HDS of DBT using in situ H_2 increase from $2.0 \times 10^{-5}\ s^{-1}$ at 300 °C to $1.01 \times 10^{-4}\ s^{-1}$ at 340 °C, and further still to $1.69 \times 10^{-4}\ s^{-1}$ at 380 °C. When the temperature was increased from 300 to 340 °C, the rate constant was enhanced by 400%; the rate constant increased only by 68% when the temperature was further increased from 340 to 380 °C. According to the Arrhenius equation, ln(k) versus 1/T is

Table 1
Rate constants at different temperatures over a dispersed Mo catalyst using in situ H_2

Temperature (°C)	Rate constant, $\times 10^5$ (s^{-1})						k_1/k_2
	k^*	k_1	k_2	k_3	k_4	k_5	
300	2.0	1.3	0.7	0.33	15.7	0.23	1.86
340	10.1	7.6	2.5	0.66	30.5	0.61	3.02
380	16.9	13.8	3.1	0.92	35.7	1.0	4.45

$k^* = k_1 + k_2$.

plotted and an obvious linear relationship is observed with a correlation coefficient of 0.9987. The apparent activation energy obtained from the correlation equation is 37.8 kcal/mol. The activation energies for HDS of DBT reported in the literature range from 28 to 39 kcal/mol and the activation energy of HDS of DBT using in situ H_2 over Co–Mo/Al_2O_3 was reported to be 36.9 kcal/mol [10]. Therefore, similar HDS mechanisms likely occur for both the dispersed Mo catalyst and Co–Mo/Al_2O_3 catalyst. The activation energy of HDS of benzothiophene (BT) using in situ H_2 over Mo-based dispersed catalysts was 72.4 kJ/mol (17.30 kcal/mol) [9], revealing that sulfur removal from DBT is much more difficult than that from BT.

As shown in Table 1, k_1 is always higher than k_2 regardless of the reaction temperature, indicating that the main reaction pathway is hydrogenolysis. This is consistent with the results reported in literature [5,11]. Every reaction in the network of HDS of DBT is accelerated with increased temperatures. However, the increase of the rate constants with the increase in temperatures is different for the two reaction pathways. The increase of the k_1/k_2 ratio with temperature indicates that the hydrogenolysis rate increases faster than the hydrogenation rate with increasing temperature.

3.4. Effect of water on HDS of DBT

Compared to the conventional HDS process, there is water present in the HDS reaction in the bitumen emulsion upgrading process. Therefore, it is very important to investigate the role of water in HDS to gain an understanding of the complexities of the in situ upgrading process. The involvement of CO in the WGSR adds complexity to the process. Therefore, for simplicity, externally supplied H_2 (ex situ H_2) was used in these experiments. The experiments were carried out using in situ generated Mo-based catalyst and ex situ H_2 at 340 and 380 °C, respectively.

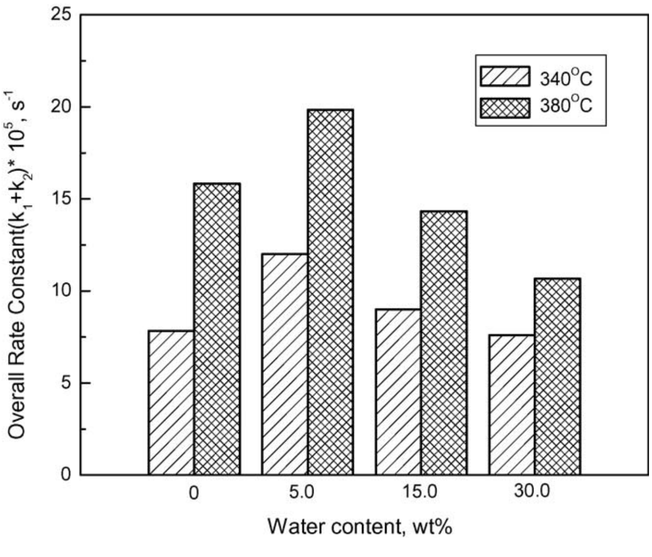

Fig. 4. Effect of water on HDS of DBT at 340 and 380 °C using ex situ H_2 over a Mo-based dispersed catalyst.

Table 2
Rate constants of HDS of DBT at different water contents at 340 °C using externally supplied H_2 over a dispersed Mo catalyst

Water content (wt%)	Pseudo-first-order rate constants, $\times 10^5$ (s^{-1})					k_1/k_2
	k_1	k_2	k_3	k_4	k_5	
0.0	5.9	1.7	1.1	22.3	0.9	3.4
0.05	9.7	2.3	1.3	23.0	1.1	4.2
0.15	7.6	1.4	1.0	21.1	0.8	5.4
0.3	6.5	1.1	0.7	18.1	0.5	5.9

As shown in Fig. 4, there is considerable conversion of DBT in the absence of water. The overall pseudo-first-order rate constants are 7.81×10^{-5} s^{-1} at 340 °C and 1.58×10^{-4} s^{-1} at 380 °C. The introduction of a small amount of water into the system (5%) promotes HDS of DBT, and the rate constants increase to 1.20×10^{-4} s^{-1} at 340 °C and 1.98×10^{-4} s^{-1} at 380 °C. However, upon introduction of more water into the system, HDS of DBT is inhibited. When 15% water is present, the rate constants decreased to 9.0×10^{-5} s^{-1} at 340 °C and 1.43×10^{-4} s^{-1} at 380 °C, respectively. A further decrease of the rate constants to 7.6×10^{-5} s^{-1} at 340 °C and 1.07×10^{-4} s^{-1} at 380 °C is observed when 30% water is introduced.

Takemura et al. [12] performed HDS of the residual oil using in situ H_2 at 400 °C for 1 h over the Co–Mo/Al_2O_3 catalyst in a 146 ml autoclave with different water contents. It was reported that when only 2.5 ml water was present with a mole ratio of H_2O:CO at 0.72, the sulfur removal was 40.8%. When 5.0 ml water was present, sulfur removal was increased to 48.4%. This increase was attributed to the generation of more in situ hydrogen when more water was introduced. When 10 and 20 ml water were present, the sulfur removal was decreased to 31.0 and 14.2%, respectively. Our result is consistent with that reported by Takemura et al. [12].

The rate constants of each step in the reaction network at different water content are listed in Tables 2 and 3 for reactions at 340 and 380 °C, respectively. When the water content increases from 0.0 to 5%, every step is promoted in the HDS reaction (Fig. 1) is promoted. Song et al. [13] found that addition of water promotes the formation of MoS_2 with a higher surface area from the decomposition of ammonia tetrathiomolybdate. Therefore, the increase of reaction rate with adding a small amount of water may be due to the formation of a more active dispersed catalyst with a higher surface area.

When the water content is increased further from 5 to 15% and 30%, k_1, k_2, k_3, k_4 and k_5 started to decrease, indicating that

Table 3
Rate constants of HDS of DBT at different water contents at 380 °C using externally supplied H_2 over a dispersed Mo catalyst

Water content (wt%)	Pseudo-first-order rate constants, $\times 10^5$ (s^{-1})					k_1/k_2
	k_1	k_2	k_3	k_4	k_5	
0.0	12.7	3.1	1.5	26.9	1.4	4.1
0.05	16.3	3.5	2.1	28.8	1.9	4.7
0.15	12.2	2.1	1.3	26.1	1.4	5.8
0.3	9.3	1.4	0.9	24.4	0.8	6.6

water inhibits every reaction in the network, including hydrogenolysis of DBT, hydrogenation of DBT, BP and CHB. However, the sensitivities of every step to water are different. The increase of k_1/k_2 ratio with water content suggests that water inhibits hydrogenation more significantly than hydrogenolysis. At the same water content, the k_1/k_2 ratio at 380 °C is higher than that at 340 °C, suggesting that the hydrogenolysis reaction is preferred at a higher temperature or that water probably inhibit the hydrogenation reaction more strongly at higher temperature.

3.5. *In situ H_2 versus ex situ H_2 in HDS of DBT*

In the literature, there are contradicting reports about the comparison of in situ H_2 and ex situ H_2 on HDS. It was reported that in situ H_2 was superior to ex situ H_2 in HDS of BT [9] and in the HDS of DBT [11]; Takemura et al. [12] reported that in situ H_2 was inferior to ex situ H_2 in HDS of Khafji residual oil over Co–Mo/Al_2O_3 catalysts. Kumar et al. [14] and Hook and Akgerman [10] observed that in situ H_2 was as efficient and effective as ex situ H_2 in HDS of BT and DBT over the commercial Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts in a trickle bed reactor.

Our results show that it is likely the proportion of water that causes these contradicting claims. Water inhibits the HDS reaction; however, it promotes formation of more active dispersed catalysts. It should be noted that in the case of using in situ H_2 for HDS, water is a reactant to generate H_2. The water concentration in the system also has a significant effect on the rate of WGSR.

In this study, the dispersed catalysts were prepared in situ during the heating time and HDS of DBT was performed at 340 and 380 °C with different water contents using in situ H_2 and ex situ H_2. The results are presented in Figs. 5 and 6.

In the absence of water, in situ H_2 could not be generated via the WGSR; therefore, HDS of DBT could not take place. However, HDS of DBT under ex situ H_2 could take place considerably in the absence of water. When a small amount of water ($H_2O:H_2) = 0.65$ (mol/mol)) is introduced into the system, ex situ H_2 exhibits the highest HDS activity. The rate constants using in situ H_2 for HDS of DBT are $1.20 \times 10^{-4}\ s^{-1}$ at 340 °C and $1.98 \times 10^{-4}\ s^{-1}$ at 380 °C. Compared to ex situ H_2, in situ H_2 has much lower HDS activity at the ratio of H_2O:CO(or $H_2) = 0.65$, and the rate constants are $3.2 \times 10^{-5}\ s^{-1}$ at 340 °C and $5.4 \times 10^{-5}\ s^{-1}$ at 380 °C.

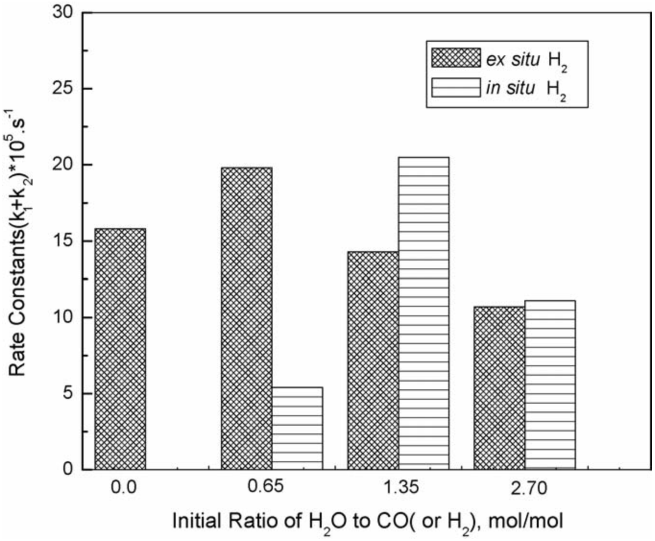

Fig. 6. Comparison of in situ H_2 and ex situ H_2 in HDS of DBT in the presence of different amounts of water at 380 °C over a dispersed Mo catalyst.

Figs. 7 and 8 show the results of the WGSR, which occurs during the HDS of DBT. As the system temperature reaches 340 °C, CO conversion is 43.9%, indicating that WGSR has begun some time during the heating time. At the end of the 2 h period at which the reactor is kept at 340 °C, CO conversion has increased to 58.5%. The initial H_2 or CO loading into the

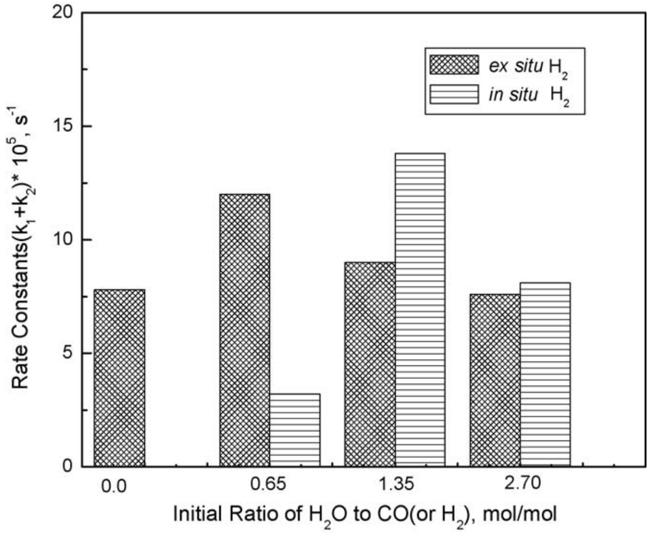

Fig. 5. Comparison of in situ H_2 and ex situ H_2 in HDS of DBT in the presence of different amounts of water at 340 °C over a dispersed Mo catalyst.

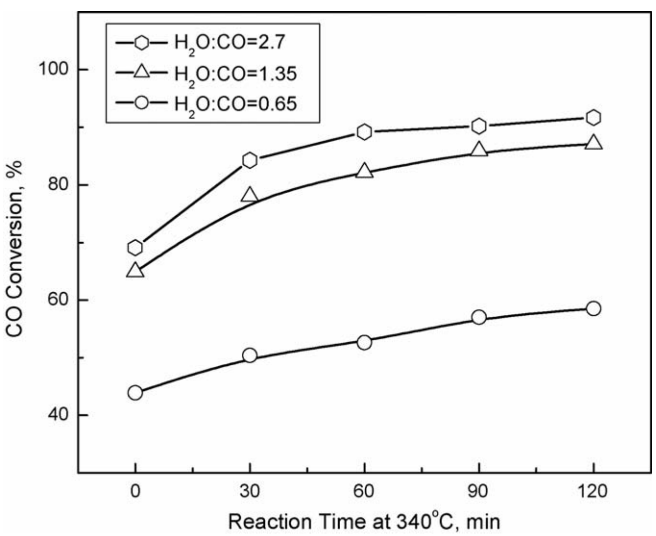

Fig. 7. WGSR at different water contents at 340 °C over a dispersed Mo catalyst.

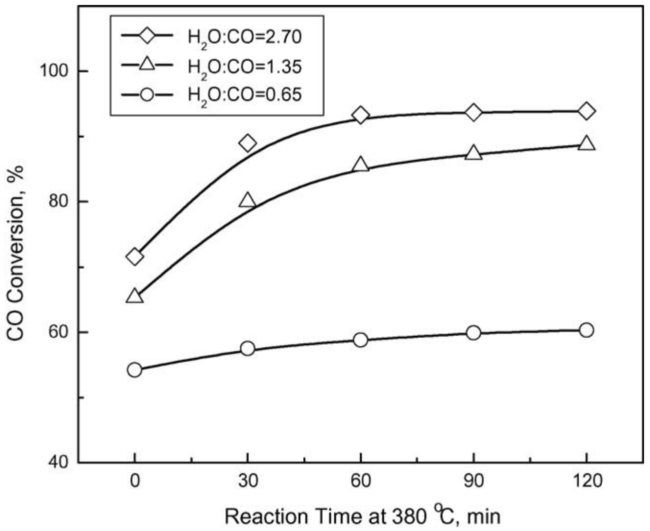

Fig. 8. WGSR at different water contents at 380 °C over a dispersed Mo catalyst.

reactor is the same (i.e., 400 psi) in all the experiments. In the WGSR, 1 mol CO is converted to 1 mol H_2. Therefore, in the in situ H_2 run at 340 °C and at the mole ratio of H_2O:CO = 0.65, the H_2 level is only 40–58% of that in the corresponding ex situ H_2 run. Similarly, the H_2 level in the in situ H_2 run at 380 °C and at the mole ratio of H_2O:CO = 0.65 is about 54–60% of that in the corresponding ex situ H_2 run. Therefore, there is not enough water in the in situ runs to generate a comparable amount of the in situ H_2. Hence, the in situ H_2 runs exhibit much lower HDS activity than the ex situ H_2 runs that have much more H_2 present in the gas phase.

When more water is put into the system (H_2O:CO(or H_2) = 1.35 mol/mol), the HDS activity of the ex situ H_2 runs start to decrease due to the inhibiting effect of water, as discussed previously. For the in situ H_2 run, the rate of HDS increases significantly at H_2O:CO mole ratio of 1.35, both at 340 °C and 380 °C. This increase in HDS activity coincides with a significant increase in CO conversion as shown in Figs. 7 and 8. Hou et al. [8] proposed the Langmuir-Hinshelwood mechanism for the WGSR over Mo-based catalysts and the rate of WGSR is proportional to water content when the ratio of H_2O:CO is low (i.e., less than 1). When the mole ratio of H_2O:CO is increased from 0.65 to 1.35, the range of CO conversion increases from 65 to 87.7% at 340 °C, and from 65 to 89% at 380 °C. Although the H_2 level in the in situ H_2 run remained about 10–35% lower than in the ex situ H_2 run, the HDS activity in the in situ runs is still higher than that in the ex situ H_2 runs by 59.2% at 340 °C, and higher by 48.6% at 380 °C. The greater activity in the in situ runs as compared to the ex situ runs at the mole ratio of H_2O:CO of 1.35 could be attributed to one or more of the following reasons: (1) in situ H_2 is more reactive than the ex situ H_2 in HDS; (2) the catalysts formed under CO and under in situ H_2 are more active than those formed under the ex situ H_2; (3) consumption of water via WGSR in the in situ H_2 run reduces the inhibiting effect of water on HDS. The highest HDS activity of in situ H_2 runs at H_2O:CO mole ratio of 1.35 is slightly higher than or comparable to the highest HDS activity of ex situ H_2 runs at H_2O:H_2 = 0.65. Ng and Milad [9] studied HDS of BT over a Mo-based dispersed catalyst using in situ H_2 and ex situ H_2 at 340 °C with a mole ratio of H_2O:CO (or H_2) at 4:1. It was reported that in situ H_2 was about seven times more active than the ex situ H_2 in the hydrogenation of BT. Hook and Akgerman [10] performed HDS of DBT over Co–Mo/Al_2O_3 at 344 °C using in situ H_2 with a mole ratio of H_2O:CO at about 1:1, and reported a pseudo-first-order rate constant of about $3.05 \times 10^{-2}\ s^{-1}$, which is about 10 times faster than the results reported in the literature for ex situ H_2 under similar conditions. Liu and Ng [11] studied the HDS of DBT using PMA and MA as catalyst precursors at 340 °C with an initial mole ratio of H_2O to CO (or H_2) at 2.8:1 and found that the in situ H_2 was about 40% more active than ex situ H_2 for the conversion of DBT.

Table 4
Rate constants of HDS of DBT using in situ H_2 and ex situ H_2 at 340 °C over a dispersed Mo catalyst

Mole ratio of H_2O:CO(H_2)	Rate constants, 10^5 (s^{-1})							
	In situ H_2				Ex situ H_2			
	k^*	k_1	k_2	k_1/k_2	k^*	k_1	k_2	k_1/k_2
1.35	13.8	11.1	2.7	4.1	9.0	7.6	1.4	5.4
2.70	8.1	6.8	1.3	5.2	7.6	6.5	1.1	5.9

$k^* = k_1 + k_2$.

When the water content in our reaction system is increased further to H_2O:CO(or H_2) = 2.70, much more excess water is present in the system. Although CO conversion increases slightly, the inhibiting effect of the excess water is dominant, and HDS activity of both in situ and ex situ H_2 runs decrease dramatically.

Tables 4 and 5 show the rate constants for HDS in the in situ H_2 and ex situ H_2 runs. At the H_2O:CO(or H_2) mole ratio of 1.35 and at 340 °C, the rate constant of the in situ H_2 run is $1.38 \times 10^{-4}\ s^{-1}$, which is higher than that of the ex situ H_2 run, $9.0 \times 10^{-5}\ s^{-1}$. The k_1/k_2 ratio of the in situ H_2 run is 4.1, which is lower than that of the ex situ H_2 run, 5.4. At the H_2O:CO(or H_2) mole ratio of 2.70 and at 340 °C, the rate constants of HDS in the in situ H_2 run decrease and is only slightly higher than that of the ex situ H_2 run which has also decreased somewhat. The k_1/k_2 ratio of the in situ H_2 run is 5.2, which is still lower than that of the ex situ H_2 run, 5.9. Similar results are observed in the runs at 380 °C, as shown in Table 5.

Table 5
Rate constants of HDS of DBT using in situ H_2 and ex situ H_2 at 380 °C over a dispersed Mo catalyst

Mole ratio of H_2O:CO(H_2)	Rate constants, 10^5 (s^{-1})							
	In situ H_2				Ex situ H_2			
	k^*	k_1	k_2	k_1/k_2	k^*	k_1	k_2	k_1/k_2
1.35	20.5	16.9	3.6	4.7	14.3	12.2	2.1	5.8
2.70	11.1	9.5	1.6	6.0	10.7	9.3	1.4	6.6

$k^* = k_1 + k_2$.

The relatively lower ratio k_1/k_2 in the in situ runs suggests that the in situ H_2 possesses higher hydrogenation activity, which promotes the hydrogenation/elimination pathway over hydrogenolysis in the HDS of DBT.

It should be also noted that although the initial water loadings are the same in the in situ and the ex situ H_2 runs, there was less water present in the in situ H_2 run during the HDS of DBT due to the conversion of water in the WGSR. As discussed in the previous section, water inhibits the HDS of DBT, particularly the hydrogenation pathway. Therefore, the relatively lower k_1/k_2 ratio in the in situ run may also have resulted from the relatively lower water content.

4. Conclusions

The effect of water and in situ H_2 on the HDS of DBT was studied in a water/toluene solution using dispersed Mo catalyst. The DBT conversions were 21.2% at 300 °C, 58.8% at 340 °C and 84.6% at 380 °C when in situ H_2 was used with about 20 wt% water loaded. At very low water content (5 wt%), water is found to promote the HDS reaction in the ex situ H_2 run probably due to the formation of more active dispersed MoS_x species. At higher water content, water inhibits every individual reaction in the reaction network in the HDS of DBT, blocking the hydrogenation pathway more than the hydrogenolysis pathway. At an optimized mole ratio of H_2O:CO (1.35), higher HDS activity was observed in the in situ H_2 run than the ex situ H_2 run. The hydrogenation/elimination pathway for the HDS of DBT was also promoted in the in situ H_2 run.

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