Deep Desulfurization of Gasoline by Selective Adsorption over Nickel-Based Adsorbent for Fuel Cell Applications

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Adsorptive desulfurization of model gasoline fuels and a real gasoline over a nickel-based adsorbent Ni−Al was conducted in a flowing adsorption system at a temperature range of 25−200 °C under ambient pressure without using H_2 gas in order to evaluate the desulfurization performance of the adsorbent for producing ultra-low-sulfur gasoline for fuel cell applications. Adsorptive capacity and selectivity of the Ni−Al adsorbent for various sulfur compounds and the effects of coexisting olefin in gasoline as well as adsorptive conditions on the adsorptive performance were examined. It was found that the nickel-based adsorbent shows high capacity and selectivity for the adsorptive desulfurization of gasoline. Olefins in gasoline have a strong inhibiting effect on the desulfurization performance of the nickel-based adsorbent at room temperature. Increasing the temperature to 200 °C can significantly improve the desulfurization performance of the nickel-based adsorbent for real gasoline. The adsorption mechanism and selectivity are discussed on the basis of the experimental results and computational analysis. The adsorption of sulfur compounds on the nickel surface involves C−S bond cleavage, as evidenced by the formation of ethylbenzene from benzothiophene in the absence of H_2 gas in the flow adsorption system.

1. Introduction

Ultradeep removal of sulfur from transportation fuels has become more and more important in research and development worldwide, not only because of the heightened interest for cleaner air and environmental protection but also due to the great need for making ultra-low-sulfur fuels for use in fuel cells.[1−4] Fuel cells are attractive for electric power generation because significantly higher efficiencies can be achieved in a more environmentally friendly way than in combustion engines. For the automotive fuel cells and the portable fuel cells, liquid hydrocarbon fuels are candidate fuels due to their higher energy density and safety for transportation and storage. Among liquid hydrocarbon fuels, gasoline is a promising fuel for the new systems based on the proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC), especially for the fuel cell auxiliary power unit for automobile, because it is readily available and the existing infrastructure in production, delivery, and storage can be used. However, the current commercial gasoline usually contains significant amounts of sulfur, up to 350 ppmw.[1] The sulfur compounds in gasoline and H_2S produced from these sulfur compounds in the hydrocarbon reforming process are poisonous to the reforming and shift catalysts in the fuel processor and the electrode catalysts in fuel cell stacks.[5,6] Consequently, for fuel cell applications, the sulfur concentration in gasoline must be reduced to less than 0.1 ppmw for PEMFC and less than 10 ppmw for SOFC. However, even with the future EPA regulation for low-sulfur gasoline at refinery to have an average of 30 ppmw with a per-gallon cap of 80 ppmw effective in 2006,[1] the sulfur contents in the gasoline will still be too high for fuel cell applications.

In terms of technology availability, the current hydrodesulfurization (HDS) process is not very efficient for reducing the sulfur content in gasoline to less than 10 ppmw, because the deep removal of the remaining thiophenic compounds in current commercial gasoline is inhibited significantly by the coexisting olefins, and H_2S produced in the HDS process adds into the olefins to form new mercaptans. On the other hand, the conventional hydrodesulfurization processes need to work at higher temperature and higher hydrogen pressure, which is not suitable for onboard or on-site desulfurization for fuel cell applications. Consequently, development of a new ultradeep desulfurization process of gasoline becomes an important research subject in hydrocarbon fuel processing for the gasoline-based fuel cell applications. Recently, Conoco Phillips Petroleum Co. developed a new S-Zorb process for the production of low-sulfur gasoline by reactive adsorption of sulfur compounds over a solid sorbent.[7] The process uses a fluidized-bed reactor in the temperature range between 377 and 502 °C under H_2 pressures in the range of 7.1−21.1 kg/cm^2. The Research Triangle Institute (RTI) reported a TReND process for adsorptive desulfurization of gasoline over a metal oxide sorbent around 400 °C in H_2 atmosphere.[8] Tawara et al. reported an "adsorptive catalyst" (Ni/ZnO) for removing sulfur in kerosene to less than 0.1 ppmw in the temperature range between 270 and 300 °C in H_2 atmosphere under a pressure of 0.60 MPa.[9] However, for fuel cell applications, a desulfurization process on board or on site at low temperatures without using H_2 gas would be preferred. As a consequence, considerable attention has been paid to developing an adsorptive process for ultradeep desulfurization of gasoline under ambient conditions without using H_2 gas for the gasoline-based fuel cell systems.[1−4] As is well-known, gasoline not only contains saturated

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hydrocarbons but also a large amount of unsaturated hydrocarbons, such as aromatics and olefins with concentration even up to 40 and 20 wt %, respectively, especially in FCC gasoline. The molar concentration of these coexisting unsaturated hydrocarbons is up to about 300−600 times higher than that of the sulfur compounds in commercial gasoline. Consequently, the challenge in the development of an adsorptive process is to develop an adsorbent that has higher adsorptive selectivity and capacity for the sulfur compounds.

Yang and co-workers reported the adsorptive desulfurization of transportation fuels over Cu(I)−Y zeolite under ambient conditions, and they indicated π-complexation as the adsorption mechanism.[10−12] We recently proposed and have been exploring at The Pennsylvania State University the selective adsorption for removing sulfur (PSU-SARS) over various adsorbents including metals, metal sulfides, metal oxides, and zeolite-based adsorbents under ambient conditions without using H_2 gas for fuel cell and refinery applications.[1,3,13−19] The PSU-SARS approach aims at removing sulfur compounds in gasoline, jet fuels, and diesel fuels selectively by a direct sulfur−adsorbent interaction.[1,13,17] Among several types of adsorbents explored, we found that Ni-based adsorbent exhibited better performance for removing thiophenic sulfur compounds from liquid hydrocarbon fuels.[14] It should be mentioned that nickel was used for the reductive removal of thiophene for purifying benzene and toluene more than half a century ago.[20] The Ni-based adsorbent was also widely used for removing sulfur in preparative organic chemistry at room or elevated temperature up to 60−80 °C.[21−24] In 1987, Bailey and Swan filed a patent about using nickel adsorbents for sulfur removal from hydrocarbon reformer feeds.[25] Recently, International Fuel Cell[26,27] and UTC Fuel Cell[28,29] filed some patents relating to a method for desulfurizing gasoline or diesel fuel over nickel adsorbents for use in a fuel cell power plant. According to the breakthrough curves for adsorptive desulfurization of an additive-free gasoline with 21 ppmw of sulfur, as shown in their patent,[29] the estimated capacity is around 0.8 mg of sulfur/g of adsorbent (mg/g) at a breakthrough sulfur level of 10 ppmw. Fukunaga et al. reported the removal of sulfur in a kerosene fuel from 48 ppmw in the fuel to less than 0.05 ppmw using a Ni-based adsorbent, but they did not report the quantitative capacity of their adsorbent.[30] The information about adsorptive desulfurization of liquid hydrocarbon fuels over the Ni-based adsorbents, involving adsorptive capacity, selectivity, and mechanism, is still very limited in the scientific literature. To develop high selectivity and capacity of the Ni-based adsorbents, it is essential to understand the adsorption mechanism of Ni-based adsorbent and to clarify effects of the coexisting species in the fuel and adsorption conditions on adsorptive performance.

In the present study, adsorptive desulfurization of model gasoline fuels and a real gasoline was conducted in a fixed bed system to evaluate the performance of the Ni-based adsorbent and to understand the fundamental adsorption mechanism. Adsorptive selectivity for various sulfur compounds and effects of the coexisting olefins as well as adsorption conditions on the adsorptive performance were examined. The adsorptive mechanism and selectivity will be discussed on the basis of the experimental and computational approaches.

Table 1. Composition of Model Gasoline Samples

		MG-I		MG-II	
no.	name	concn, wt %	S concn, ppmw	concn, wt %	S concn, ppmw
		Sulfur Compounds			
1	thiophene	0.0531	202	0.0535	203
2	benzothiophene	0.0829	198	0.0830	198
	total	0.1360	400	0.1360	401
		Paraffins			
3	*n*-hexane	39.9		40.1	
4	*n*-decane	51.9		46.6	
	total	91.8		86.7	
		Aromatics			
5	toluene	8.0		8.0	
		Olefins			
6	1-octene	no		5.1	

Table 2. Composition of MG-III

no.	name	concn, wt %	S concn, ppmw	molar concn, mmol/L
		Sulfur Compounds		
1	thiophene	0.0263	100	2.23
2	2-MT	0.0307	100	2.23
3	3-MT	0.0307	100	2.23
4	2,5-DMT	0.0354	101	2.25
5	benzothiophene	0.0419	100	2.23
	total		501	
		Paraffins		
6	*n*-hexane	45.03		
7	*n*-decane	46.71		
	total	91.75		
		Aromatics		
8	toluene	8.02		
		Olefins		
9	1-octene	0.0350		2.22

2. Experimental Section

2.1. Model Gasoline Fuels. The compositions of three model gasoline fuels (MG-I, MG-II, and MG-III) used in the present work are listed in Tables 1 and 2. Both MG-I and MG-II contained 202 ppmw sulfur as thiophene (T) and 198 ppmw sulfur as benzothiophene (BT) as well as 8.0 wt % of toluene as aromatic. The major difference between MG-I and MG-II is that MG-II contained 5.1 wt % of 1-octene as olefin. MG-III contained five sulfur compounds [T, 2-methylthiophene (2-MT), 3-methylthiophene (3-MT), 2,5-dimethylthiophene (2,5-DMT) and BT] and 1-octene with total sulfur content of 502 ppmw. These six compounds have the same molar concentration (~2.23 mmol/L) in the fuel. All the sulfur compounds and hydrocarbon compounds used for preparing the model fuels were purchased from Aldrich and used as such without further purification.

2.2. Real Gasoline. A commercial gasoline was purchased from a local Exxon gasoline station in State College, Pennsylvania. The total sulfur concentration in the gasoline was 210 ppmw according to our analysis using an Antek 9000S total sulfur analyzer. The major sulfur compounds existing in the commercial gasoline of the present study are T, 2-MT, 3-MT, 2,4-DMDBT, and BT. A GC−PFPD chromatogram of the gasoline with identification of major peaks is shown in Figure 1.

2.3. Adsorbent. A nickel-based adsorbent was used in the present study, which contained 88 wt % of nickel in metallic state with the remainder made up of aluminum metal. The adsorbent is denoted as A-2. It

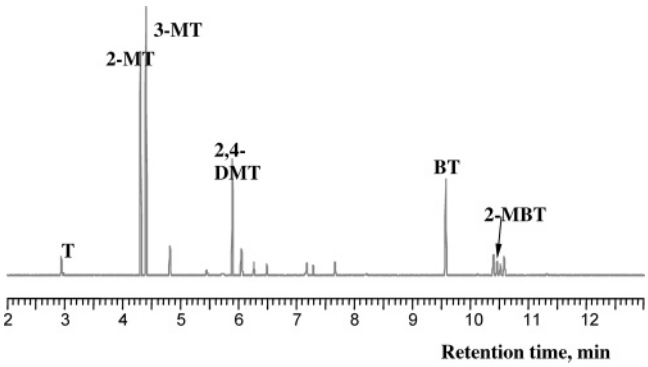

Figure 1. GC−PFPD chromatogram of commercial gasoline.

has a BET surface area of ~80 m^2/g, and its particle size is around 40 μm. The general procedure for the adsorbent preparation and pretreatment has been described elsewhere.[15]

2.4. Fixed-Bed Adsorption Experiments. Adsorption experiments were performed at a temperature range from 25 to 200 °C under ambient pressure without using H_2 gas. About 4.5 g of the adsorbent was packed in a stainless steel column having a bed dimension of 4.6 mm i.d. and 150 mm length. The packed column was placed in a multichannel convection oven designed in our laboratory for the adsorption experiments. Before introducing the fuel into the adsorbent bed, the adsorbent bed was pretreated with H_2 gas at a flow rate of 100 mL/min under ambient pressure, heated to 200 °C, and kept at this temperature for about 1 h in a H_2 flow. After the pretreatment, the oven temperature was decreased to the desired adsorption temperature. The fuel was then sent into the adsorbent column by a HPLC pump, flowed up through the adsorbent bed. The effluent from the adsorbent bed was collected periodically for analysis.

2.5. GC−FID/PFPD Analysis. A Hewlett Packard 5890 series II gas chromatograph with a capillary column (XTI-5, Restek, bonded 5%, 30 m × 0.25 mm i.d. × 0.25 μm film thickness) and a split mode injector (ratio: 100:1) was used with ultrahigh-purity helium as a carrier gas. The injector temperature was kept at 290 °C. A flame ionization detector (FID) was used for quantitative analysis of the model gasoline samples. The relative error in the GC−FID analysis was within 5%. A plus flame photometric detector (PFPD, O.I. Analytical 5380) was used for identification and qualification of the treated real gasoline samples. For analysis of the gasoline samples, the column temperature program was set at 50 °C for 3 min, 20 °C/min from 50 to 290 °C, and the injection volume was 1 μL.

2.6. Total Sulfur Analysis. The total sulfur concentrations in the commercial gasoline and desulfurized gasoline were determined using an Antek 9000S total sulfur analyzer. The instrument was calibrated to at least four different sulfur concentration ranges using standard samples, and linear calibration curves were obtained for each calibration range.[17] The sulfur detection limit of the total sulfur analyzer in the normal working range is 0.5 ppmw sulfur.

3. Computational Method

Calculations of bond order and electron density of some sulfur compounds and hydrocarbon compounds were conducted using a semiempirical quantum chemistry method, MOPAC-PM3, in CAChe (version 6.1.1).

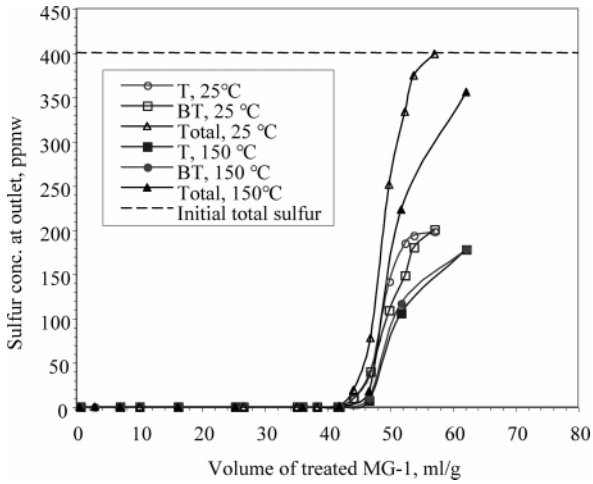

Figure 2. Breakthrough curves of MG-I over A-2 at 25 and 150 °C, LHSV 24 h^{-1}, feed MG-1, 400 ppmw S.

The PM3 method determines both the optimum geometry and electronic properties of molecules by solving the Schrödinger equation using the PM3 semiempirical Hamiltonians developed by Stewart.[31,32] The computational method was described in detail in the previous papers.[33,34]

4. Results and Discussion

4.1. Model Gasoline. 4.1.1. Adsorptive Performance. Adsorptive desulfurization of MG-I over Ni−Al (A-2) was conducted at ambient temperature (25 °C), ambient pressure, and liquid hourly space velocity (LHSV) of 24 h^{-1}. The sulfur concentration in the treated MG-I as a function of the effluent volume (mL/g, milliliter of the treated MG-I per gram of adsorbent) is shown in Figure 2. No detectable sulfur was found in the effluent when the effluent volume was less than 42 mL/g, indicating that all sulfur in MG-I was removed by the selective adsorption. Within this region, the sulfur concentration in the treated MG-I was less than 1 ppmw. The adsorptive capacity corresponding to the breakthrough volume (42 mL/g) was 12.3 mg/g (milligram of sulfur per gram of the adsorbent). After the breakthrough, the total sulfur concentration in the effluent increased sharply with the increasing volume of the effluent. When the volume increased to around 57 mL/g, the adsorbent was saturated by sulfur. The adsorptive capacity corresponding to the saturate point was 14.2 mg/g. Although MG-I contained 8 wt % of toluene as aromatics, the molar concentration being about 70 times higher than that of the total sulfur compounds, Ni−Al (A-2) exhibited high adsorptive capacity for sulfur compounds. This indicates that the adsorbent has much higher adsorptive selectivity for the sulfur compounds in comparison with aromatics. The adsorptive desulfurization of MG-I was also conducted at 150 °C, and the corresponding breakthrough curves are also shown in Figure 2. By comparison with the adsorptive performance at the room temperature, it is shown that the higher temperature improves only slightly the adsorptive capacity of Ni−Al (A-2) for MG-I.

4.1.2. Effect of Olefin. Effect of olefin on the adsorptive desulfurization over A-2 was examined by using a model gasoline, MG-II, which contained 5.1 wt % of 1-octene. The adsorptive desulfurization of MG-II over A-2 was performed at 25 °C, LHSV 24 h^{-1}. The breakthrough curves are shown in Figure 3 in compari-

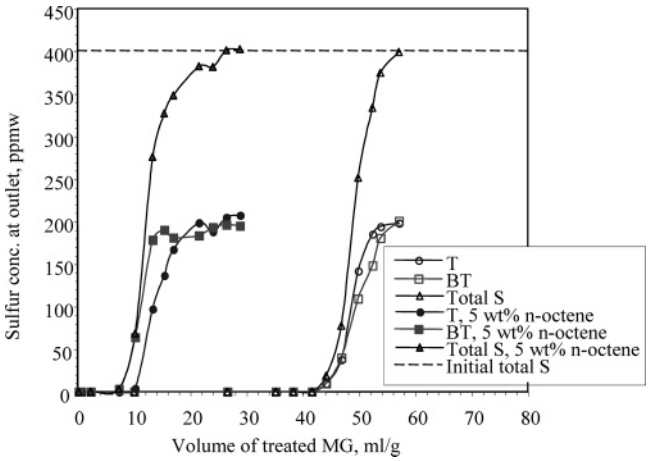

Figure 3. Effect of olefin on adsorptive desulfurization, breakthrough curves of MG-I and MG-II over A-2 at 25 °C, LHSV 24 h^{-1}.

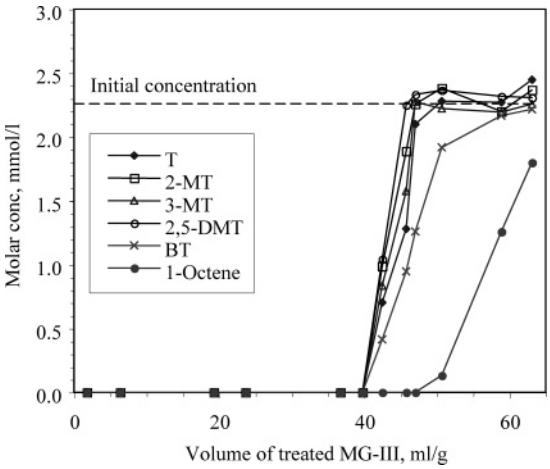

Figure 4. Breakthrough curves of MG-III over A-2 at 25 °C, LHSV 24 h^{-1}.

son with the adsorptive desulfurization of MG-I under the same conditions. The breakthrough volume decreased significantly from 42 mL/g for MG-I to 7.5 mL/g and the corresponding capacity was only 2.0 mg/g. This adsorptive capacity is about 6 times less than that in the absence of 1-octene, indicating that the olefin coexisting in commercial gasoline decreases the desulfurization capacity of A-2 substantially.

By comparing the breakthrough curves for thiophene and BT in the presence of 5 wt % 1-octene, it is shown that the effluent volume corresponding to the BT breakthrough point was significant less than that corresponding to the thiophene breakthrough point, while in the absence of 1-octene the breakthrough volume of thiophene and BT was almost the same and after the breakthrough point the concentration of thiophene in the effluent was even slightly higher than that of benzothiophenes. This implies that the olefin has a slightly stronger effect on the adsorption of BT than thiophene.

4.1.3. Adsorptive Selectivity. The commercial gasoline contains various sulfur compounds and olefins. To examine the adsorptive selectivity of A-2 for various sulfur compounds as well as olefin, the adsorptive desulfurization of MG-III over A-2 at 25 °C, LHSV 4.8 h^{-1}, was conducted. The breakthrough curves for each compound are shown in Figure 4. When the effluent volume was less than 40 mL/g, no sulfur compounds were detected. The breakthrough point for the five

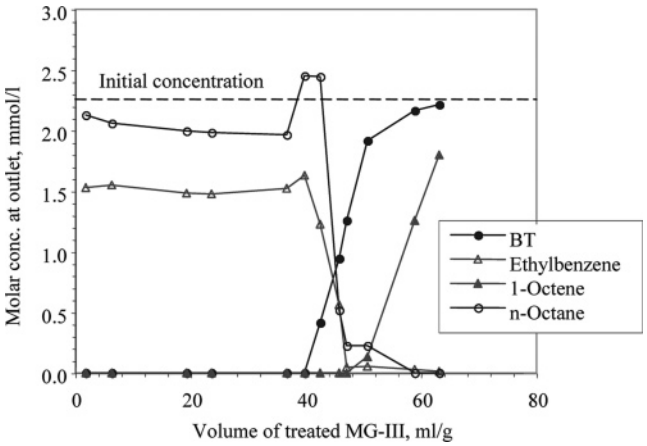

Figure 5. Concentration of BT, 1-octene, and their products vs volume of treated MG-III, at 25 °C, LHSV 24^{-1}.

sulfur compounds was almost the same, being 40 mL/g. After this point, the concentration for the sulfur compounds increased rapidly with increasing effluent volume. The saturate point for the five sulfur compounds was slightly different, being 45.8, 47.1, 47.4, 50.0, and 64.0 mL/g for 2,5-DMT, 2-MT, 3-MT, T, and BT, respectively. The breakthrough volume for 1-octene was 47.1 mL/g, indicating that A-2 exhibits a higher adsorptive selectivity for 1-octene than for the five sulfur compounds. By comparison of the adsorption profiles for various compounds, we can find that the adsorptive selectivity of A-2 at 25 °C increases in the order of 2,5-DMT < 2-MT ≈ 3-MT < T < BT ≪ 1-octene, implying that 1-octene might inhibit the adsorption of the sulfur compounds on the A-2 surface at 25 °C through a competitive adsorption on the active sites. This is in agreement with the observation of the effect of 1-octene on the adsorptive desulfurization of MG-II (see Figure 3).

4.2. Adsorption Mechanism. In the GC−FID/PFPD analysis of the MG-III samples treated over A-2 at 25 °C, LHSV 24 h^{-1}, it was found that there was *n*-octane and ethylbenzene but no detectable styrene or other intermediate sulfur compounds in the effluent. The concentrations of BT, 1-octene, ethylbenzene, and *n*-octane as a function of the effluent volume are shown in Figure 5. The molar concentration of *n*-octane in the first collected effluent sample was about 2.1 mmol/mL, close to the molar concentration of 1-octene in the initial MG-III. With increasing effluent volume, the molar concentration of *n*-octane in the effluent was kept at this value until 1-octene broke through at 45 mL/g, and then it decreased sharply to near zero, while the concentration of 1-octene increased to 1.9 mmol/L at the effluent volume of 63 mL/g. This pattern suggests that 1-octene was hydrogenated and converted to *n*-octane in the process, although there was no hydrogen gas in the system. Ethylbenzene was also detected in the effluent. The molar concentration of ethylbenzene was kept at about 1.5 mmol/L (less than the molar concentration of BT in MG-III) before BT broke through at 40 mL/g. After the breakthrough point, the concentration of ethylbenzene decreased to zero, when the concentration of BT increased to the initial concentration. This pattern also indicates that ethylbenzene is a product from hydrogenolysis of BT, although not all of BT was converted into ethylbenzene according to ethylbenzene concentration in the effluent. The results demonstrate that adsorptive desulfurization over A-2 at room temperature involves not only a chemical adsorption but

Table 3. Bond Order and Electron Density on the Sulfur Atom on the Basis of Semiempirical Calculations

	compound							
	1-octene	BT	2-MBT	T	3-MT	2-MT	2,5-DMT	toluene
bond order[a]	1.973	1.769	1.747	1.689	1.699	1.692	1.673	1.434
electron density on S		5.739	5.748	1.689	5.697	5.706	5.716	

[a] For the bond with the largest bond order in the molecule.

also a C−S bond hydrogenolysis to form nickel sulfides. The adsorptive sites covered by 1-octene can be recovered during the process by hydrogenating 1-octene and then releasing the formed *n*-octane. However, the adsorption of sulfur compounds on the active sites results in the formation of nickel sulfides on the surface, and these bound sulfur atoms cannot be removed under the adsorption conditions. As a consequence, the process is irreversible, as reported in the literature.[22] The experimental data in the literature are in favor of a radical mechanism for desulfurization of sulfur compounds over a nickel surface.[20,24] Following the adsorption of a sulfur compound on the surface, the cleavage of C−S bonds takes place, resulting in the formation of strongly bound sulfur and hydrocarbon radicals. These radicals are further saturated by hydrogen existing on the nickel surface or by radical dimerization or disproportionation in the absence of surface hydrogen.[21] Such radical reactions in the absence of surface hydrogen may result in carbon deposit on the surface, as observed by Lesieur and his colleagues.[29] In view of this point, the amount of active hydrogen atoms on the surface might play a very important role in improvement of the desulfurization capacity. On the other hand, as olefins are also saturated by hydrogen in the process, the effect of olefins on the adsorptive desulfurization may also be ascribed to that the saturation of olefins scrambles for the activated hydrogen on the surface with the hydrocarbon radicals from the C−S bond hydrogenolysis.

In a mechanismic study of sulfur poisoning of metal catalysts, many approaches have been made for measuring the adsorption stoichiometry of sulfur over different single-crystal faces of nickel.[37] Interestedly, it was found that the amount of sulfur adsorbed per unit of surface area of Ni at saturation coverage by sulfur is almost the same, being $\sim 44.2 \times 10^{-2}$ mg of S/m^2, although the number of the sulfur atoms adsorbed per surface Ni atom is quite different on different crystal faces, from 0.48 S atom/Ni atom for Ni(111) crystal face to 1.09 S atom/Ni atom for Ni(210) crystal face.[38] If assuming that the ratio of surface Ni area to surface Al area is equal to the ratio of their volumes in bulk, the surface Ni area of the present Ni adsorbent (A-2) can be estimated, being about 67 m^2/g. The adsorption capacity of the Ni adsorbent at the saturation coverage, thus, should be about 30 mg of S/g of A, theoretically. However, the maximum saturation capacity observed in the present study is only 14.2 mg/g for A-2, much lower than the estimated value. This result indicates that about a half of the Ni surface was not covered by sulfur, but probably covered by other species, such as the adsorbed sulfur compound molecules, hydrogenolysis products, and/or others, which block the way of the following sulfur compounds in the liquid phase to approach the nickel surface. One of the experimental evidences to support this point is that the molar concentration of ethylbenzene in the effluent before BT breakthrough was only two-thirds of the molar concentration of BT in the initial feed (see Figure 5), implying that BT molecules and/or their hydrogenolysis products are still stayed on the adsorbent surface. As discussed above, the absence of active hydrogen atoms on the Ni surface should be one of the major reasons, which is further supported by the experimental data that introduction of hydrogen gas into the Ni adsorbent bed increased the adsorption capacity of the Ni adsorbent significantly.[29]

To understand further the adsorption mechanism, molecular simulation of some sulfur compounds as well as 1-octene was conducted. The calculated bond order and electron density on the sulfur atom are tabulated in Table 3. For the unsaturated bond, the higher bond order indicates the higher π-electron density of the bond. By comparing the largest bond order in the molecules with their adsorptive selectivity, it shows that the higher the largest bond order is, the higher the adsorptive selectivity, except for 2-MT and 3-MT, where the methyl group at the 2 and 3 positions might somewhat inhibit the adsorption sterically. This result suggests that the interaction between adsorbate and nickel through π-electron might play a role in the competitive adsorption, which explains why the presence of 1-octene decreases significantly the adsorptive capacity for sulfur compounds. On the other hand, it also shows that the adsorptive selectivity increases with increasing electron density on the sulfur atom (except for 2-MT and 2,5-DMT, which can be contributed to the steric hindrance of methyl group against the approach of the sulfur atom to nickel on the surface). It indicates that the surface reaction (hydrogenolysis) rate of the adsorbed sulfur compounds with the surface nickel is related to the electron density on the sulfur atom in the sulfur compounds, which is agreement with the previous observation during hydrogenolysis of sulfur compounds.[33] We believe that the electron density on the sulfur atom might play a more important role than the π-electron density in the adsorptive desulfurization over the nickel-based adsorbent, since the abstraction of the sulfur atom from the adsorbed sulfur compounds by the surface nickel is irreversible, while the adsorption of the unsaturate molecules through the π-electrons is reversible or recoverable. This point is further evidenced by the results shown in Figure 3 that even the molar concentration of 1-octene is about 70 times higher than that of thiophene or BT in the liquid phase and the largest bond order of 1-octene (1.973) is much higher than that of both thiophene (1.689) and BT (1.769), A-2 still showed a considerable desulfurization capacity (2.0 mg/g).

4.3. Adsorptive Desulfurization of Real Gasoline. Adsorptive desulfurization of a real gasoline with a sulfur concentration of 210 ppmw was performed at 25 °C, LHVS 4.8 h^{-1}. The results are shown in Figure 6. The breakthrough volume was 1.3 mL/g, and the corresponding capacity was only 0.3 mg/g. After the breakthrough the sulfur concentration at the outlet increased gradually with increasing effluent volume. When the effluent volume reached 19.5 mL/g, the sulfur concentration increased to 180 ppmw and the corresponding capacity was 1.7 mg/g, as shown in Figure 7.

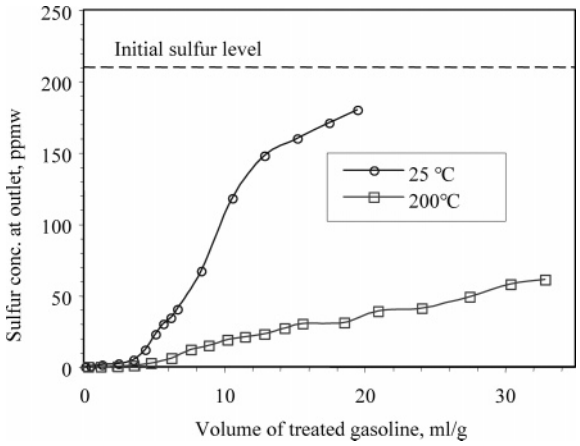

Figure 6. Breakthrough curves of real gasoline over A-2 at 25 and 200 °C, LHSV 4.8 h^{-1}.

This adsorptive capacity is much lower than that using MG-I. We think one of the major reasons is that the real gasoline contains much more olefins, which reduces the desulfurization capacity by a competitive adsorption on the nickel surface or a competitive consumption of the activated hydrogen on the surface. It should be pointed out that most commercial gasolines contain oxygenates such as MTBE and ethanol, which might affect the adsorption performance of the nickel-based adsorbents. When the adsorptive desulfurization temperature was increased to 200 °C, the desulfurization performance was dramatically improved, as shown in Figure 6. The breakthrough volume increased to 3.6 mL/g, and the corresponding capacity was 0.62 mg/g. Of more interest is that when the breakthrough volume increased continuously after breakthrough point, the sulfur concentration at the outlet increased slowly. When the effluent volume reached 33.0 mL/g, the sulfur concentration increased to 61 ppmw, corresponding to 23% of the initial sulfur concentration, and the adsorptive capacity was 4.4 mg/g. The results indicate that the elevated temperature is in favor of the adsorptive desulfurization of real gasoline over the nickel-based adsorbent. The dramatic improvement of desulfurization performance at high temperature can be attributed to that the increase in temperature reduces the adsorption of olefin on the Ni surface, restrains thermodynamically the hydrogenation of olefin, and/or accelerates kinetically the surface reaction rate of the adsorbed sulfur compounds with the nickel. This phenomenon further supports that the adsorption of sulfur compounds on the nickel surface involves a surface reaction, while the adsorption of olefin on the nickel surface is reversible or recoverable.

Figure 7 shows the GC−PFPD chromatograms of some gasoline samples desulfurized over A-2 at 200 °C, LHSV 4.8 h^{-1}. As the GC−PFPD signal is nonlinear and suffers the quenching effect due to the coeluted hydrocarbons,[35,36] here we only qualitatively compare the adsorptive selectivity of various sulfur compounds on

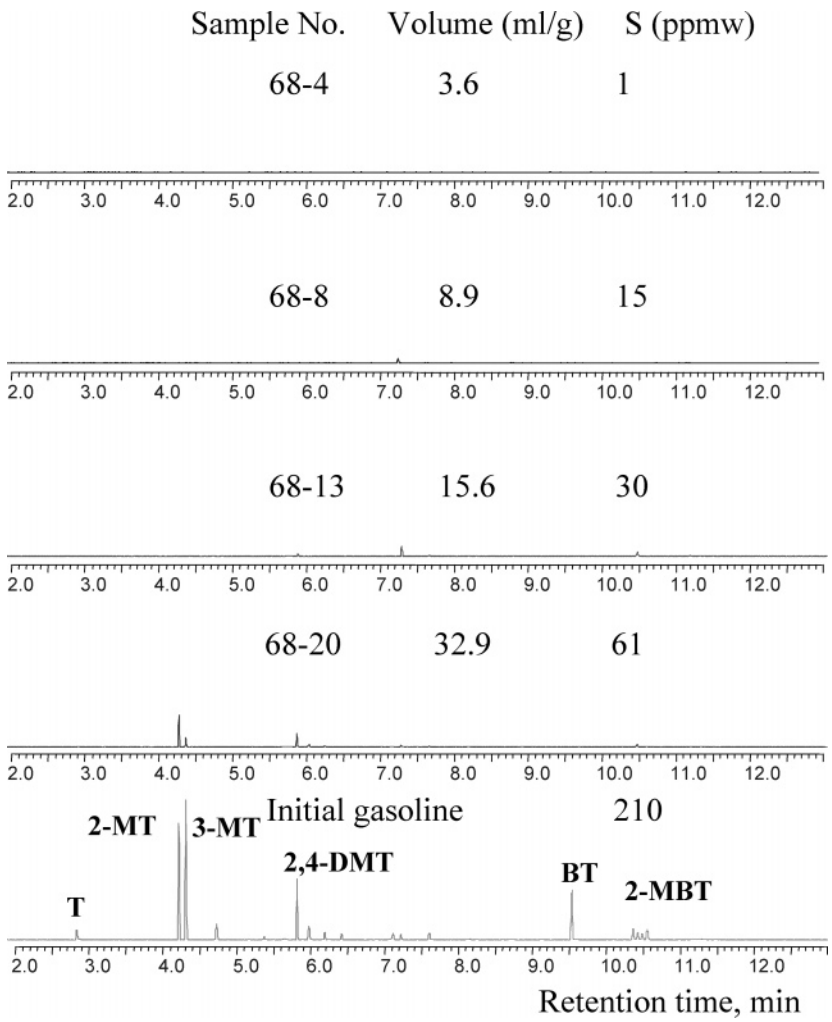

Figure 7. GC−PFPD chromatograms of initial gasoline and the effluent gasoline samples treated at 200 °C, LHSV 4.8 h^{-1} over A-2.

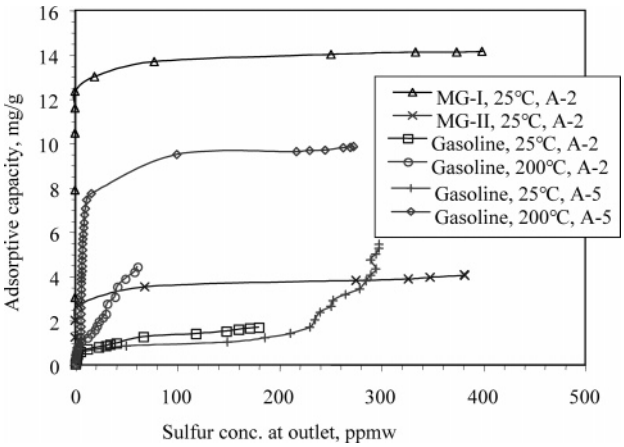

Figure 8. Adsorptive capacity of adsorbents as a function of sulfur concentration at outlet.

the basis of the GC−PFPD chromatograms. As can be seen, the first breakthrough sulfur compound is the one with retention time at 7.3 min, the second one is 2-methylbenzothiophene (2-MBT), and then 2,4-DMT, 2-MT, 3-MT, and others. The results indicate that the adsorptive selectivity increases in the order of 2-MBT < 2,4-DMT < 2-MT < 3-MT < T ∼ BT, which is in agreement with that observed in the adsorptive desulfurization of MG-III. The low selectivity for 2-MBT is probably due to the steric hindrance of the methyl group at the 2 position, which blocks the way for the sulfur atom to approach to the active site.

The desulfurization capacity of A-2 for the model gasoline fuels and the real gasoline as a function of the sulfur concentration at the outlet are shown in Figure 8. To facilitate discussion, the data for adsorptive desulfurization of a real gasoline over a supported nickel adsorbent (A-5), which was reported in one of our previous papers,[36] are also shown in Figure 8. By comparing the adsorptive capacity curves for various fuels at different temperatures, it is clearly shown that (1) the presence of olefins in gasoline reduces substantially the adsorptive capacity of the nickel-based adsorbents and (2) the increase in the adsorption temperature improves significantly the adsorptive capacity of both A-2 and A-5. By comparing the adsorptive capacity curves for A-2 and A-5 at 200 °C, we can find that the desulfurization performance of A-5 is much better than that of A-2. This is probably because A-5 has much higher surface area (157 m^2/g) than that (∼80 m^2/g) of A-2, suggesting that it is possible to improve the performance of the nickel-based adsorbent by increasing the surface area of nickel.

Finally, it should be noted that *reduced nickel metal is often pyrophoric and should be handled with proper treatment before exposure to air. It should be stored in the presence of a solvent.* The A-2 adsorbent used in this work can be stored in water or in an organic solvent such as dodecane.

5. Conclusions

To evaluate the performance of the nickel-based adsorbent and to fundamentally understand the adsorption mechanism, adsorptive desulfurization of model gasoline and real gasoline fuels over A-2 was conducted in a flowing adsorption system at a temperature range of 25−200 °C under ambient pressure without using H_2 gas. Adsorption selectivity and capacity of the adsorbents for various sulfur compounds and effects of olefins coexisting in gasoline as well as adsorption temperature on the adsorptive performance were examined. On the basis of the experimental and computational results, the following conclusions can be made:

(1) The nickel-based adsorbents show high selectivity and considerable capacity for the adsorptive desulfurization of real gasoline.

(2) The adsorption of sulfur compounds on the nickel surface involves C−S bond cleavage, as evidenced by the formation of ethylbenzene from benzothiophene in the absence of H_2 gas in the flow adsorption system. The results suggest the hydrogenolysis of the C−S bond in the adsorbed sulfur compounds to form nickel sulfides on the surface. Such an adsorption is irreversible under the usual adsorption conditions.

(3) Olefins in gasoline have a strong effect on the desulfurization performance of the nickel-based adsorbent, probably by a competitive adsorption via the π-electron and/or a competitive scramble for the activated hydrogen on the surface.

(4) Increasing the temperature significantly improves the adsorption performance of the nickel-based adsorbents for real gasoline, probably through thermodynamically restraining the adsorption and hydrogenation of olefins and/or kinetically accelerating the surface reaction rate of the adsorbed sulfur compounds with the surface of the nickel.

(5) The present study indicates that the adsorption capacity of the nickel-based adsorbents can be improved by increasing the Ni surface area and by introducing the active hydrogen atoms into the Ni surface.

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