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Adsorptive Removal of Nitrogen-Containing Compounds from Fuel

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The feasibility of using microporous and mesoporous materials as adsorbents to remove nitrogen-containing compounds (NCCs) in fuel, such as pyridine, quinoline, pyrrole, and indole, was explored. A mesoporous molecular sieve Ti−HMS was chosen as the optimum adsorbent for the adsorptive denitrogenation (ADN) of fuel. Effect of adsorption time, temperature, and ratio of adsorbent to oil (A/O) on the removal of NCCs was investigated. Meanwhile, the adsorption isotherms and adsorption thermodynamics were studied. The thermodynamic functions show that the adsorption of NCCs on Ti−HMS is an exothermic, irregularity decreased, spontaneous physical process. Furthermore, the adsorption process primarily occurs in the pores of Ti−HMS, which is confirmed by comparing the adsorptive denitrogenation performance of Ti−HMS with uncalcined Ti−HMS.

1. Introduction

With increasingly stringent environmental regulations, the removal of sulfur and nitrogen compounds from fuel has become a more and more important research subject.[1−11] Nowadays, refiners are facing the inevitable reality to produce clean fuels with lower sulfur and nitrogen levels. Traditional desulfurization technology has received the most attention all over the world for many years due to the higher sulfur concentration relative to nitrogen-containing compounds and other oxygen-containing compounds in the fuel oils. However, denitrogenation is usually more difficult than desulfurization because most organonitrogen compounds are much less reactive than organosulfur compounds.[12−15]

Nitrogen-containing compounds (NCCs) in the oil consist of two groups. One is a neutral group with a pyrrole ring, such as pyrroles, indoles, carbazoles, and benzocarbazoles. The other is a basic group with a pyridine ring, such as pyridines, tetrahydroquinolines, quinolines, and acridines. It is necessary for refiners to monitor neutral and basic nitrogen species during the refining process. On one hand, neutral NCCs tend to build gums by polymerization leading to the plugging of burners and injectors of petroleum processing units. On the other hand, basic NCCs are known to have an inhibiting effect on catalysts currently used in catalytic converters for reducing CO and SO_x.[16] Moreover, the combustion of NCCs generates NO_x which are responsible for acid rain. Owing to these reasons, there is a strong need for nitrogen removal from fuels. It is well-known that nitrogen removal from FCC naphtha can be achieved by catalytic hydrodenitrogenation (HDN), but conventional HDN requires higher temperatures, higher pressures, large reactor volumes, and more active catalysts.[17] Meanwhile, the octane number of gasoline may decrease due to the saturation of olefins. Therefore, new approaches, such as adsorptive denitrogenation (ADN), oxidative denitrogenation (ODN), and acid extractive denitrogenation are alternatively proposed. Among the above methods, ADN using solid material can remove N-containing compounds effectively on mild conditions and without using hydrogen. It is a cheap, simple, and environmentally friendly process to remove N-containing compounds from fuel. Meanwhile, solid adsorbents will not deteriorate the quality of the fuel. Therefore, ADN using solid material as the absorbent arouses economic interest and has been intensively studied. The reported adsorbents include reduced metals,[18−21] metal oxides,[22,23] zeolite-based materials,[24−28] and carbon materials.[29−32] Bae et al.[33] have reported that N-containing compounds in light gas oil could be adsorbed by a silica−zirconia Cogel, and the adsorption behavior was significantly affected by kinetic as well as thermodynamics factors.

In this paper, denitrogenation of model fuel containing NCCs was studied using Ti−HMS, etc. as the adsorbents. The adsorption thermodynamic functions of NCCs over Ti−HMS were measured, as will be useful for the further design of the adsorption process in the denitrogenation of fuel.

2. Experimental Section

2.1. Materials. Basic nitrogen-containing compounds pyridine (Analytical Reagent) and quinoline (Analytical Reagent) were purchased from Guangxi Chemical Co. Neutral nitrogen-containing compounds pyrrole (Analytical Reagent) and indole (Chemically Pure) were purchased from the Sinopharm Chemical Reagent Co. *N*-Octane was purchased from the Tianjin Bodi Chemical Co. No. 0 commercial diesel was purchased from CNPC. All of the materials were used without any pretreatment. The adsorbent acidic Al_2O_3 with a surface area of 152.1 $m^2 \cdot g^{-1}$ and average pore size of 5 nm was purchased from the Shanghai Ludu Chemical Co. β-Zeolite with a surface area of 550 $m^2 \cdot g^{-1}$ and average pore size of 0.65 nm was prepared according to the literature.[34] Ti−HMS possessing a surface area of 800 $m^2 \cdot g^{-1}$ and average pore size of 2.3 nm was prepared according to the literature.[35] HZSM-5 was prepared according to the literature,[36] which had a surface area of 350 $m^2 \cdot g^{-1}$ and average pore size of 0.55 nm.

2.2. Adsorption. NCCs (pyridine, quinoline, pyrrole, or indole) were dissolved in *n*-octane as the model fuel, in which the concentration of the nitrogen element was 200 $\mu g \cdot g^{-1}$. The

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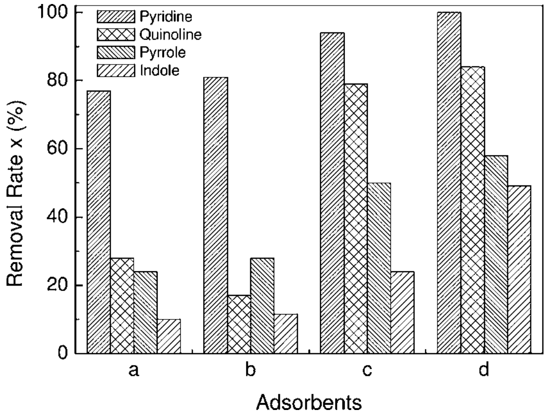

Figure 1. Adsorptive removal of pyridine, quinoline, indole, and pyrrole over (a) acidic Al_2O_3, (b) HZSM-5, (c) β-zeolite, and (d) Ti−HMS at 293 K for 1 h.

adsorption process was carried out in a flask with a water-bathed jacket and a condenser. In a typical adsorption process, 0.1 g of the adsorbent and 10 mL of model fuel were added into the reactor and stirred at a speed of 700 $r\cdot min^{-1}$. The adsorption process was carried out at 293 K∼333 K. The adsorbent was regenerated by washing using ethanol at ambient temperature. The oil phase was analyzed using KY-3000N (Keyuan Inc. Co. China) equipped with a nitrogen-chemiluminescence detector with a "flameless burner". FT-IR spectra were recorded on a Bruker EQUINOX55 spectrometer, using the KBr pellet technique.

The adsorption amount q and removal rate x can be obtained by the following functions

$$q = \frac{(C_0 - C_e)}{M\cdot a}\cdot 10^{-3} \qquad (1)$$

$$x = \frac{(C_0 - C_t)}{C_0}\cdot 100\ \% \qquad (2)$$

q is adsorption amount ($mmol\cdot g^{-1}$); C_0 is initial concentration ($\mu g\cdot g^{-1}$); C_e is equilibrium concentration ($\mu g\cdot g^{-1}$); M is nitrogen-containing compound molecular weight ($g\cdot mol^{-1}$); a is the ratio of adsorbent to oil ($g\cdot g^{-1}$); x is the removal rate (%); and C_t is concentration after t (min) ($\mu g\cdot g^{-1}$).

3. Results and Discussion

3.1. Effect of Adsorbents. The adsorption performance of adsorbents usually depends on their surface chemical characteristic and physical properties, such as active sites, surface area, and pore size and distribution. In this section, the NCCs (pyridine, quinoline, pyrrole, or indole) in the model fuel were removed using different adsorbents at ambient temperature and pressure. As shown in Figure 1, the metal oxide acidic Al_2O_3, microporous zeolites HZSM-5, or beta and mesoporous material Ti−HMS all showed better adsorptive capacities for the smaller basic molecule pyridine. For the bigger basic molecule quinoline, the removal rate was lower than that of pyridine. The pore sizes of the adsorbents will be enough for the kinetic diameters or molecular sizes of the applied NCCs. According to the results in Figure 1, the adsorption trends correspond to the surface area of the adsorbents. It can be seen that with the surface area increasing of the adsorbent the removal rate is enhanced. However, other chemical characteristics of the adsorbents, such as acidity, also have some effect. Basic N-containing compounds pyridine and quinoline are more easily adsorbed on the acid sites of the adsorbents than the neutual ones.[37−39] For most adsorbents, the removal rate of NCCs follows the order: pyridine > quinoline > pyrrole > indole. That is, the neutral NCCs with larger molecule size are most refractory in adsorptive denitrogenation. In the end, Ti−HMS was chosen as the optimal adsorbent to remove the typical NCCs from model fuel in this paper.

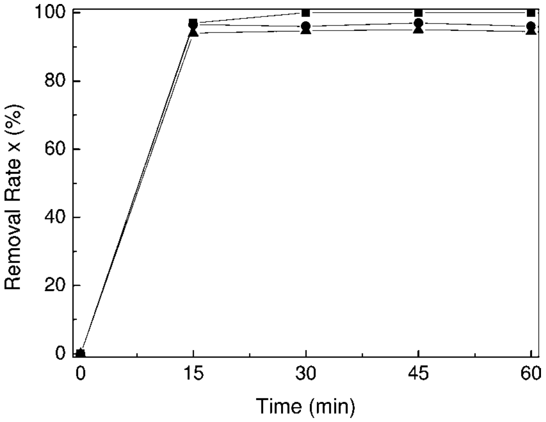

Figure 2. Effect of temperature on the adsorptive removal of pyridine over Ti−HMS. Temperature: ■, 293 K; ●, 313 K; ▲, 333 K.

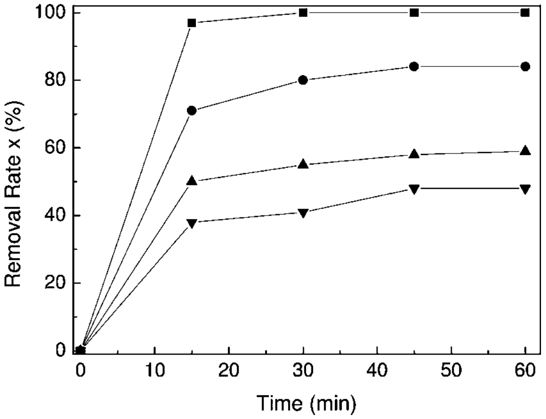

Figure 3. Effect of adsorption time on the removal of NCCs over Ti−HMS at 293 K. Nitrogen-containing compounds: ■, pyridine; ●, quinoline; ▲, pyrrole; ▼, indole.

3.2. Effect of Adsorption Conditions. 3.2.1. Effect of Temperature. The removal of pyridine from model fuel using Ti−HMS as the adsorbent at different temperatures is shown in Figure 2. The removal rate decreased with an increase of temperature, which could be explained as an exothermic process for adsorption of pyridine on Ti−HMS. High temperature is adverse to the adsorption process. The above laws on temperature also fit for quinoline, pyrrole, and indole over Ti−HMS. Generally, the suitable adsorption temperature is 293 K or ambient temperature.

3.2.2. Effect of Time. As shown in Figure 3, the removal rate of pyridine over Ti−HMS increased constantly and achieved over 90 % in the first 15 min, then became stable as the adsorption time was prolonged. It may have achieved equilibrium adsorption. Similar behavior was also found for the other NCCs, but the maximum adsorption amount of the different NCCs follows the order: pyridine > quinoline > pyrrole > indole. From the results in Figure 3, it can be concluded that the maximum adsorption amount can be achieved in 45 min.

3.2.3. Effect of Ratio of Adsorbent to Oil (A/O). The ratio of adsorbent to oil is a considerable factor on batch conditions. Figure 4 presents the effect of the A/O on denitrogenation at 293 K. As shown in Figure 4, the removal rates of pyridine, quinoline, pyrrole, and indole over Ti−HMS all decreased

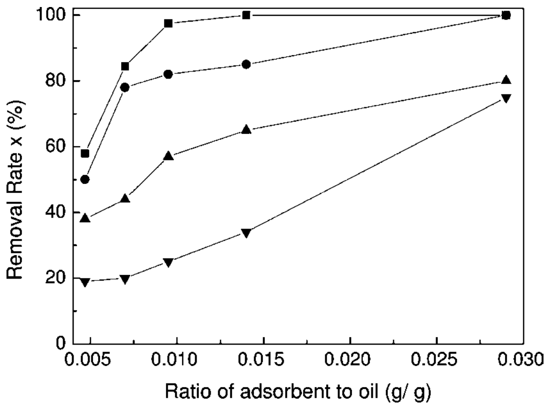

Figure 4. Effect of ratio of adsorbent to oil on denitrogenation at 293 K for 45 min. Nitrogen-containing compounds: ■, pyridine; ●, quinoline; ▲, pyrrole; ▼, indole.

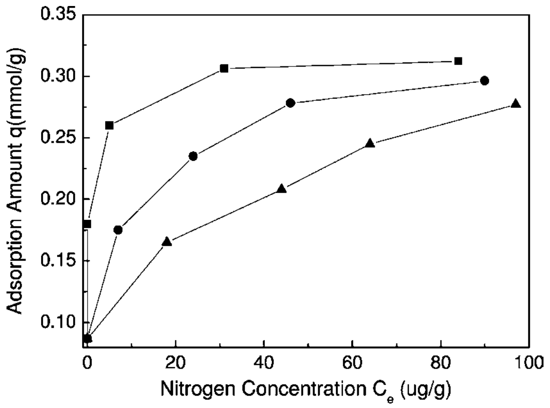

Figure 5. Adsorption isotherms of pyridine over Ti−HMS at different temperatures. Temperature: ■, 293 K; ●, 313 K; ▲, 333 K.

constantly with a decrease of the A/O. For pyridine, the removal rate decreased to 58 % as the A/O reduced to 0.0047 $g \cdot g^{-1}$. However, the higher A/O leads to a decrease in the processing capacity of the unit mass. Considering the adsorption performance and economic factors, 0.014 $g \cdot g^{-1}$ is assumed to be the optimal ratio of adsorbent to oil for pyridine. For quinoline, pyrrole, and indole, the maximum removal rates are obtained at the ratio of adsorbent to oil of 0.029 $g \cdot g^{-1}$. This shows that the adsorption of different nitrogen compounds over Ti−HMS requires a different amount of adsorbent. Using the same amount of adsorbents, the adsorptive removal rate of neutral NCCs pyrrole and indole is far lower than that of basic compounds pyridine and quinoline. So the adsorptive denitrogenation of the neutral NCCs is more difficult than the basic ones.

3.3. Adsorption Isotherm and Adsorption Thermodynamics.

3.3.1. Adsorption Isotherm. Figure 5 showed the adsorption isotherms of pyridine on Ti−HMS at different temperatures. They are typical curves of the L type.[40] The adsorption isotherms of quinoline, pyrrole, and indole at different temperatures are displayed in Figures 6 to 8. The curves of quinoline are also typical of the L type. Those of pyrrole and indole are all typical of the S type.[40] In fact, with a decrease of temperature, the adsorption performance of all these NCCs is improved.

Before reaching equilibrium adsorption, the adsorption amount of pyridine on Ti−HMS increased with an increase of the adsorbent dosage. The adsorption isotherms of pyridine on Ti−HMS fit the Freundlich model and equation satisfactorily. The Freundlich model is listed as follows

$$q = K' \cdot C_e^{\,n} \tag{3}$$

K' and n are Freundlich constants.

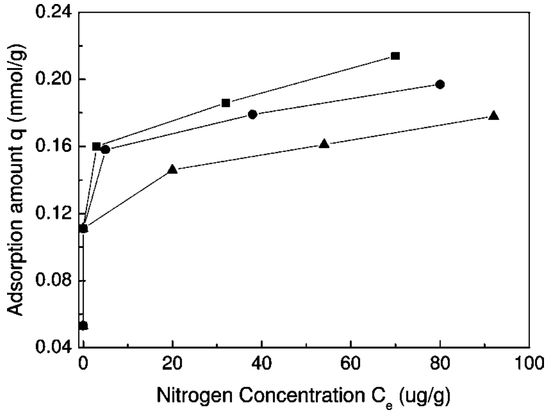

Figure 6. Adsorption isotherms of quinoline over Ti−HMS at different temperatures. Temperature: ■, 293 K; ●, 313 K; ▲, 333 K.

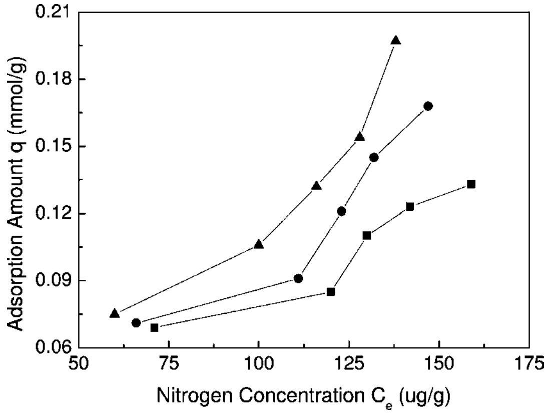

Figure 7. Adsorption isotherms of pyrrole over Ti−HMS at different temperatures. Temperature: ■, 293 K; ●, 313 K; ▲, 333 K.

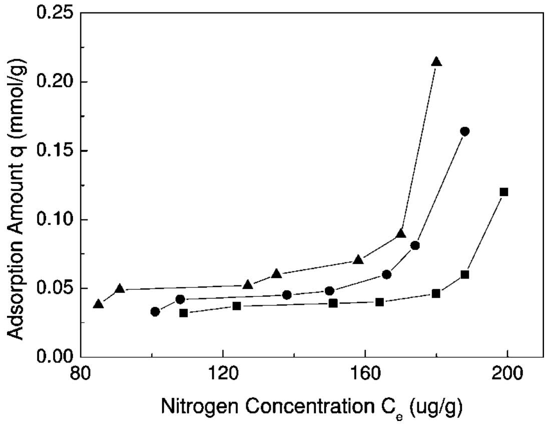

Figure 8. Adsorption isotherms of indole over Ti−HMS at different temperatures. Temperature: ■, 293 K; ●, 313 K; ▲, 333 K.

The adsorption process was easy to carry out, when the constant n was between 0.1 and 0.5.[40] Values for the Freundlich constants K' and n of the NCCs (pyridine, quinoline, pyrrole, and indole) are displayed in Table 1.

3.3.2. Adsorption Thermodynamics. The adsorption data are frequently quantified via theoretical or empirical isotherm equations. Gibbs energy (ΔG), adsorption enthalpy (ΔH), and adsorption entropy (ΔS) can be calculated by Gibbs, van't Hoff, and Gibbs−Helmholtz formulas.[41] The calculation formulas are listed as follows

$$\Delta G = -RT \ln K \tag{4}$$

$$\ln K_3(T_3) - \ln K_1(T_1) = -\frac{\Delta H}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{5}$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{6}$$

K, K_1, and K_3 are equilibrium constants; R is the molar gas constant, 8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T, T_1, and T_3 are adsorption temperatures, in K; ΔH is adsorption enthalpy, in $\text{kJ}\cdot\text{mol}^{-1}$; ΔG is Gibbs energy, in $\text{kJ}\cdot\text{mol}^{-1}$; and ΔS is adsorption entropy, in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

The above adsorption equilibrium constants K, K_1, and K_3 were determined from the intercept of the $q-\ln(q/C_e)$ function.[42] The calculation results of the thermodynamic functions are shown in Table 2. By analyzing the thermodynamic functions, it can be concluded that the adsorptions of pyridine, quinoline, and indole over Ti−HMS are all exothermic, irregularity decreased, and spontaneous processes. As shown in Table 2, the enthalpies evolved during adsorption were less than 40 $\text{KJ}\cdot\text{mol}^{-1}$, which was accorded with the observed physical adsorption.[40] This was also supported by the fact that the adsorbates on the spent adsorbents could be desorbed completely. More than 91 % of the pyridine can be desorbed and recovered from the spent Ti−HMS using *n*-octane solvent at ambient temperature and pressure. It could be concluded that the adsorption of pydine over Ti−HMS is mainly a physical process. The results of the other NCCs were similar to that of pyridine.

The Gibbs energies (ΔG) for adsorption processes are negative, which confirms these processes will happen spontaneously. However, it is unimaginable that in Table 2 the Gibbs energy (ΔG) for the adsorption of pyrrole is positive. So the adsorption of pyrrole was performed at 293 K in the presence of nitrogen as a shielding gas instead of air or oxygen. A ΔG value of −1.22 $\text{kJ}\cdot\text{mol}^{-1}$ was obtained in the presence of nitrogen. Some pyrrole can be oxidized by the oxygen in air, which will disturb the adsorption process.

In addition, the negative values of the enthalpies for the above typical NCCs increased in the order of indole < quinoline < pyridine, which indicated that the adsorption of pyridine over Ti−HMS was stronger than that of quinoline or indole. So the adsorptive capacities of NCCs over Ti−HMS increase in the following order: indole < quinoline < pyridine.

Table 1. Regression Equation of the Adsorption of Pyridine, Quinoline, Pyrrole, and Indole

T/K	293	313	333
pyridine	$q = 0.0080\cdot C_e^{0.102}$	$q = 0.0094\cdot C_e^{0.224}$	$q = 0.0046\cdot C_e^{0.304}$
R	0.9031	0.9692	0.9318
quinoline	$q = 0.00048\cdot C_e^{0.087}$	$q = 0.00039\cdot C_e^{0.075}$	$q = 0.00058\cdot C_e^{0.127}$
R	0.9472	0.9718	0.9799
pyrrole	$q = 46.00\cdot C_e^{1.40}$	$q = 0.127\cdot C_e^{0.79}$	$q = 0.012\cdot C_e^{0.56}$
R	0.8655	0.9602	0.7955
indole	$q = 75.19\cdot C_e^{1.55}$	$q = 32.45\cdot C_e^{2.009}$	$q = 29.08\cdot C_e^{1.51}$
R	0.8509	0.8386	0.7694

Table 2. Thermodynamic Parameter Values of NCCs Adsorption over Ti−HMS

NCCs	T/K	K_0	$\ln K_0$	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	ΔG $\text{kJ}\cdot\text{mol}^{-1}$	ΔS $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
pyridine	293	17.19	2.85	−31.30	−6.92	−83.21
	313	5.99	1.79	−31.30	−4.66	−85.13
	333	3.79	1.33	−31.30	−3.68	−82.91
quinoline	293	17.08	2.83	−16.01	−6.91	−31.11
	313	10.35	2.34	−16.01	−6.08	−31.72
	333	7.90	2.07	−16.01	−5.72	−30.91
indole	293	1.17	0.16	−9.60	−0.39	−31.41
	313	1.48	0.39	−9.60	−1.01	−27.42
	333	1.86	0.62	−9.60	−1.72	−23.72
pyrrole	293	0.19	−1.66	-	4.04	-
	313	0.46	−0.78	-	2.03	-
	333	0.75	−0.28	-	0.78	-

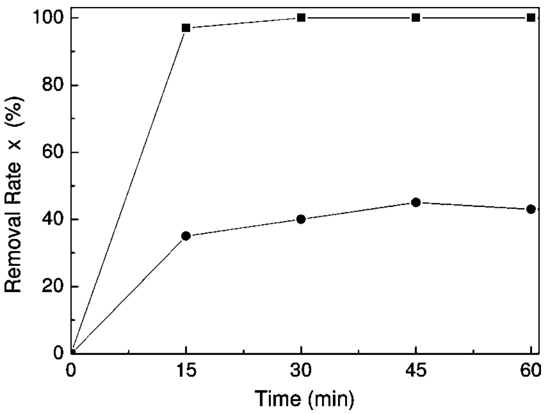

Figure 9. Adsorption of pyridine over calcined (■) and uncalcined Ti−HMS (●).

Table 3. Removal Rate of Quinoline over the Fresh and Regenerated Ti−HMS

regeneration times	fresh	1	2	3	4	5	6	7
removal rate %	84	79	78	80	77	79	82	80

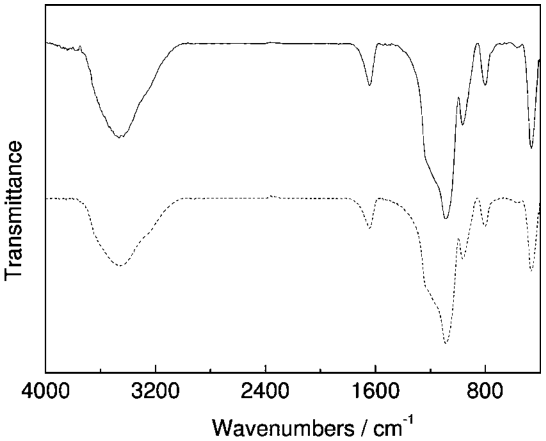

Figure 10. FT-IR spectra of Ti−HMS (---) and regenerative Ti−HMS (—).

3.4. Adsorption Sites of NCCs over Ti−HMS. The contrast of adsorption performance between calcined and uncalcined Ti−HMS is shown in Figure 9. The removal rate of pyridine using the uncalcined Ti−HMS as the adsorbent, the pores of which were charged with template, was much lower than that of the calcined one without template. So the adsorption of pyridine over Ti−HMS mainly occurs in the pores. The same results were obtained for the adsorption of the other NCCs.

3.5. Regeneration of the Adsorbent. The adsorbent will lose much capability after being used. For instance, the removal rate of quinoline over the fresh Ti−HMS was 84 % and reduced to 17 % over the spent Ti−HMS, but the removal rate recovered to 79 % after washing the spent Ti−HMS using ethanol, as shown in Table 3. The regenerated Ti−HMS presented nearly the same FT-IR spectrum as the fresh one (Figure 10). So the Ti−HMS adsorbent can be easily regenerated by washing using ethanol and used many times with nearly the same performance.

3.6. Adsorptive Denitrogenation of Commercial Diesel. The adsorptive denitrogenation of commercial diesel was performed over Ti−HMS at ambient temperature and pressure. The removal rate of the total N compounds in diesel was over 90 %, in which the basic N-containing compounds could be removed completely and the removal rate of neutral N compounds achieved was 80 %. Ti−HMS also showed better adsorptive denitrogenation performance on real fuel.

4. Conclusion

The adsorptive removal of NCCs (pyridine, quinoline, pyrrole, and indole) from model fuel over Ti−HMS, etc. was carried out in a batch reactor at ambient pressure. NCCs in real diesel can also be removed effectively using Ti−HMS. The adsorption processes are influenced by the adsorption temperature, time, and ratio of adsorbent to oil. The thermodynamic functions are calculated, and it can be concluded that the adsorption of NCCs over Ti−HMS is an exothermic, irregularity decreased, spontaneous process. Meanwhile, the adsorptive removal of neutral NCCs was more difficult than that of basic ones. The major adsorption occurs in the pores of Ti−HMS. Ti−HMS can be regenerated by the solvent ethanol. Further investigations on the competitive adsorption of other components in real fuel are in progress.

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