

Selective Removal of Nitrogen-Containing Heterocyclic Compounds from Transportation Diesel Fuels with Reactive Adsorbent^{*}

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Abstract This paper presents a new selective adsorbent to remove nitrogen-containing heterocyclic compounds from model and commercial transportation diesel fuels based on characteristic reaction designed to occur in the pores of substrate. This reactive adsorbent is composed of formaldehyde, phosphotungstic acid and Santa Barbara USA (SBA)-15. The experiment was based on assumed hydroxymethylation reaction of nitrogen-containing heterocyclic compounds with formaldehyde using phosphotungstic acid as catalyst in batch and fixed-bed systems. The nitrogen concentration in the model fuel was $237.33 \text{ ng} \cdot \mu\text{l}^{-1}$, carbazole and toluene were used as model nitrogen-containing heterocyclic compound and solvent, respectively. The effectiveness of reactive adsorbent for removal of nitrogen-containing heterocyclic compounds from commercial 0[#] diesel fuel containing $224.86 \text{ ng} \cdot \mu\text{l}^{-1}$ nitrogen was examined in a fixed-bed reactor at 70 °C. The results showed that nitrogen in the model fuel was very low and the nitrogen concentration in the commercial diesel reduced to $2.44 \text{ ng} \cdot \mu\text{l}^{-1}$. The demand for transportation fuel with ultra-low nitrogen is satisfied.

Keywords denitrogenation, fuel, carbazole, adsorption, SBA-15

1 INTRODUCTION

Atmospheric pollution and acid rain have drawn growing concern in recent years. Exhaust gases, especially SO_x and NO_x pollutants, contribute to these phenomena. Thus transportation fuels with ultra-low sulfur and nitrogen will be needed in the years to come. However, the reactivity of nitrogen-containing compounds in hydrodenitrogenation is significantly lower than that of sulfur-containing compounds in hydrodesulphurization (HDS). It is difficult to remove nitrogen-containing compounds by hydrogenation reaction. Different content of nitrogen-containing compounds has corresponding adverse effect on HDS performance [1–12], so the removal of nitrogen-containing heterocyclic compounds from transportation fuels is crucial to obtain fuels with ultra-low sulfur and nitrogen [13–20]. There are two kinds of nitrogen-containing compounds in fuel oils: (1) basic nitrogen-containing compounds, *i.e.*, aniline, pyridine, quinoline and their derivatives; (2) non-basic compounds, *i.e.*, pyrrole, indole, carbazole and their derivatives. Most refractory nitrogen-containing compounds in transportation fuels belong to the family of carbazoles [21]. Carbazole compounds can adsorb on the catalyst sites prior to refractory sulfur compounds, and higher pressure and temperature and more hydrogen are needed because of their lower reactivity. Thus, carbazole compounds should be removed for the deep desulfurization of transportation fuels. Non-hydrogenation denitrogenation technologies can be applied at mild temperature and atmospheric pressure. Much work has been devoted to the removal

of nitrogen-containing compounds from transportation fuels by intensified selective methods, such as biotechnology, oxidative-extraction, adsorption and oxidative adsorption methods. Selective adsorbent has drawn growing concerns in the last few years, which can selectively remove the nitrogen-containing compounds from transportation fuels at ambient temperature [22–29]. In this sense, selective adsorbents are promising to obtain ultra-low sulfur and nitrogen fuels, while its selectivity and adsorption capacity for nitrogen-containing compounds need improvement.

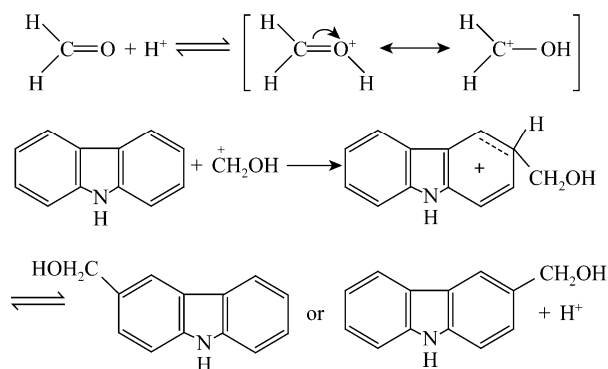
The previous work presented one selective, reliable and efficient adsorbent for the removal of thiophenic compounds from model and commercial transportation fuels based on characteristic condensation reaction between thiophenic compounds and formaldehyde catalyzed by heteropoly acid under moderate conditions [30–32]. We recently found that the selective adsorbent can remove carbazole compounds having similar structure with dibenzothiophenes in transportation fuels, but the mechanism for the adsorptive removal of nitrogen-containing compounds from transportation fuels may be different. The assumed characteristic hydroxymethylation reaction between formaldehyde and carbazole catalyzed by heteropoly acid in the pores of adsorbent is shown in Scheme 1: electrophilic substitution reaction between protonized formaldehyde and carbazole to form hydroxymethyl carbazole.

Heteropoly acid and formaldehyde have no adverse effects on the fuel quality because they are preloaded in the pores of the substrate and the products derived from the nitrogen-containing compounds are

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Scheme 1 Assumed mechanism for the removal of carbazole compounds from transportation diesel fuels occurred in pores of SBA-15

also adsorbed in the pores. Thus it is feasible and promising to meet the requirement of ultra-low nitrogen fuel with the aid of the selective adsorbent. The reliability of this approach is examined for commercial diesel fuel in the batch and fixed-bed adsorption experiments.

2 EXPERIMENTAL

2.1 Preparation of reactive adsorbent

The reactive adsorbent was composed of 7.6% (by mass) SBA-15, 33.3% (by mass) phosphotungstic acid (PTA) and 19.1% (by mass) formaldehyde. SBA-15 (0.154–0.180 mm) used as substrate was impregnated with 8% (by mass) water solution of PTA. The mixture was stirred for 1 h, dried at 100 °C for 12 h before placed into a vacuum oven at 120 °C for 5 h. PTA/SBA-15 was obtained. Carried by nitrogen gas, formaldehyde vapor passed through a fixed bed filled with PTA/SBA-15 at room temperature. The adsorbent was obtained when the loading of formaldehyde reached 19.1% (by mass). SBA-15 and PTA/SBA-15 were characterized by using N₂ adsorption-desorption analyzer at −196 °C.

2.2 Reagents

Carbazole of analytical grade was purchased from J&K Chemical Ltd. (Beijing, China). Toluene of chromatography grade was purchased from Kemiou Chemicals Center (Tianjin, China). PTA of analytical grade was purchased from Kewei Company (Tianjin, China). Formalin of analytical grade was purchased from Sanhe Chemicals (Yantai, China).

2.3 Preparation of fuels

Two kinds of transportation fuels were used in the adsorption experiments: model fuel containing 237.33 ng·μl^{−1} nitrogen, with carbazole and toluene as model nitrogen-containing heterocyclic compound and

solvent, respectively. Commercial 0[#] diesel fuel containing 224.86 ng·μl^{−1} nitrogen was purchased from Sinopec Tianjin Co., (China). The total nitrogen concentration in the fuels was analyzed by TDN-2000 analyzer (Kedi Instrument Plant, Jiangsu, China). The samples of the fuels were injected into the cracking furnace tube where the temperature was set to 1000 °C. Based on chemiluminescence principle, the total nitrogen concentration in the fuel was determined according to external standard method.

2.4 Batch tests and fixed bed breakthrough experiments

Batch adsorption experiments for removal of nitrogen-containing heterocyclic compounds from transportation fuels were performed in a flask equipped with a thermostat, which provided circulating water to keep the temperature constant. The mixture of 2.1 g adsorbent and 30 g fuel in a 250 ml flask was stirred by a magnetic mixer. The nitrogen concentration in the fuel was detected every 10 min by taking samples from the fuel. Experimental verification of denitrogenation effect *via* commercial diesel fuel was conducted in the same batch adsorption experiment.

The breakthrough experiments were carried out in a vertical glass column (length 250 mm, diameter 10 mm) filled with reactive adsorbent at 70 °C. The fuel was pumped up through the column at the velocity of 0.5 ml·min^{−1}. In terms of the breakthrough data, the transient total nitrogen concentration was plotted against cumulative fuel and normalized with the total nitrogen concentration of the feed, while the cumulative fuel with the total substrate weight. The equations employed to calculate the normalized breakthrough capacity and the normalized saturation capacity were the same as that in reference [31].

2.5 Regeneration and recycle of reactive adsorbent

After the reactive adsorbent was regenerated at 400 °C in the air for 3 h and adsorbed formaldehyde at

room temperature, it was reused in the denitrogenation of model and commercial diesel fuels.

3 RESULTS AND DISCUSSION

3.1 Characterization of SBA-15 and PTA/SBA-15

As shown in Fig. 1, type IV isotherms of SBA-15 and PTA/SBA-15 confirm the existence of mesoporous structure. The values of pore structure parameters of SBA-15 after loading PTA are smaller than those of SBA-15 (see Table 1). Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of the adsorbent on the basis of N_2 adsorption isotherm [33]. Pore size distribution of SBA-15 and PTA/SBA-15 was calculated according to Barrett-Joyner-Helena (BJH) method [34]. The results show that the highly ordered pore structure of PTA/SBA-15 is unchanged and the N_2 adsorption-desorption isotherms indicate the full dispersion of PTA in SBA-15.

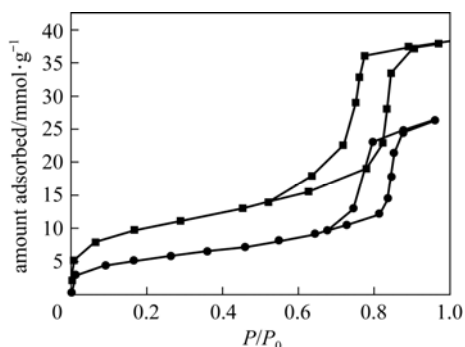


Figure 1 N_2 adsorption-desorption isotherms of SBA-15 before and after loading PTA at $-196\text{ }^{\circ}\text{C}$

■ SBA-15; ● 70% PTA/SBA-15

Table 1 Pore structure parameters of SBA-15 before and after loading PTA

Sample	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	d_{por}/nm	$V/\text{cm}^3\cdot\text{g}^{-1}$
SBA-15	798	7.7	1.31
70%PTA/SBA-15 (by mass)	374	6.2	0.79

3.2 Denitrogenation of model and commercial diesel fuels

Figure 2 shows remarkable improvement for the denitrogenation reaction rate with formaldehyde present in the reactive adsorbent. The total removal of carbazole from model fuel occurs at 20 min with formaldehyde, while it is only 40.34% after 40 min without formaldehyde, in which the adsorption reaches equilibrium with the acid-base interaction between heteropoly acid and carbazole compounds.

The effectiveness of denitrogenation using the reactive adsorbent was investigated in commercial 0# diesel fuel and the result is shown in Fig. 2. The nitrogen concentration is reduced from $224.86\text{ ng}\cdot\mu\text{l}^{-1}$ to

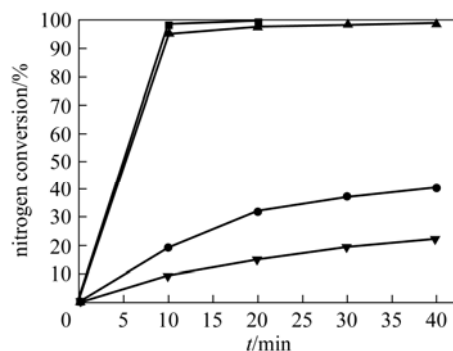


Figure 2 Effect of formaldehyde on the removal of nitrogen-containing compounds from model and commercial fuels in batch tests at $70\text{ }^{\circ}\text{C}$ (reactive adsorbent: 2.1 g ; fuel: 30 g)
■ model fuel; ● model fuel in the absence of formaldehyde; ▲ commercial fuel; ▼ commercial fuel in the absence of formaldehyde

$2.44\text{ ng}\cdot\mu\text{l}^{-1}$, while the removal of nitrogen-containing compounds is only 22.24% without formaldehyde. In general, most of the nitrogen-containing compounds in diesel are carbazole compounds and their content in nitrogen-containing compounds is even higher than 90% in China diesels. The results show that most carbazole compounds in the commercial diesel are removed and the reactive adsorbent is effective for the removal of carbazole compounds from transportation diesel fuel.

Breakthrough curves of reactive adsorbent for model and commercial diesel are shown in Figs. 3 and 4. Breakthrough capacity of unit mass fresh SBA-15 for model fuel and commercial diesel is $10.68\text{ mg}\cdot\text{g}^{-1}$ and $1.67\text{ mg}\cdot\text{g}^{-1}$, respectively. The adsorbent was regenerated and recycled in the breakthrough experiment. The regenerated adsorbent was recycled 5 times in the denitrogenation of model fuels and the nitrogen breakthrough capacities of the regenerated adsorbent accounted for 98.9%, 98.0%, 85.6%, 84.5%, and 83.3% of the original value, while the nitrogen saturation capacity recovered 92.8%, 90.7%, 88.9%, 87.9%, and 86.7%. The regenerated adsorbent maintains relatively high capacity and the efficiency decline of the

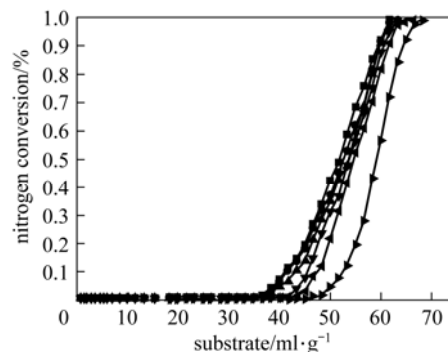


Figure 3 Breakthrough curves of reactive adsorbent for model fuel at $70\text{ }^{\circ}\text{C}$

■ regenerated 5th; ● regenerated 4th; ▲ regenerated 3rd; ▼ regenerated 2nd; ◀ regenerated 1st; ▶ original one

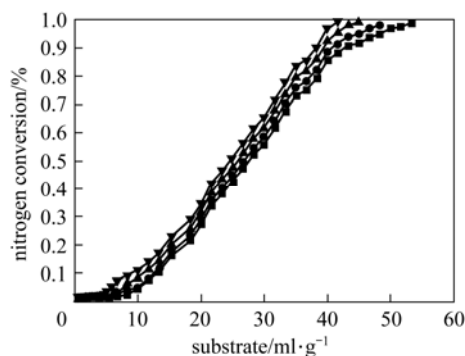


Figure 4 Breakthrough curves of reactive adsorbent for commercial fuels at 70 °C

■ original one; ● regenerated 1st; ▲ regenerated 2nd; ▼ regenerated 3rd

capacity may attribute to the loss of catalyst during recycle process or the poisonous effect of carbazole on the active sites of catalyst.

The breakthrough curves of regenerated adsorbent in the denitrogenation of commercial diesel agreed well with the one with fresh adsorbent. The nitrogen saturation capacity of recycled adsorbent for the diesel fuel accounts for 96.0%, 91.2% and 86.4% of the original value. The results indicate that the regenerated adsorbent maintains relatively high efficiency in denitrogenation of commercial fuels at mild temperature. The breakthrough results show that the reactive adsorbent is promising to obtain ultra-low nitrogen fuels at mild temperature and atmospheric pressure. Figs. 5 and 6 show scanning electron microscope (SEM) and transmission electron microscopy (TEM) morphologies of the reactive adsorbent with multi-cycle experiment in the denitrogenation of model fuels after regeneration. The highly ordered pore structure of reactive adsorbent is unchanged and the structure of substrate still appears to be of two-dimensional hexagonal column after recycled five times.

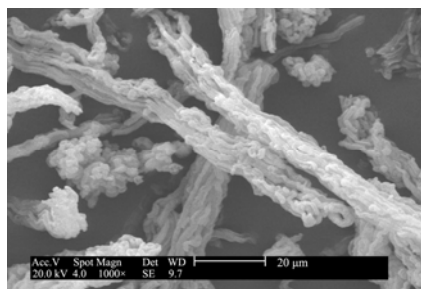
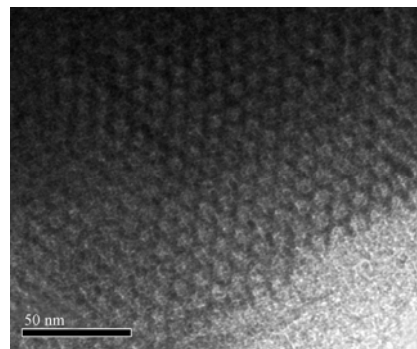


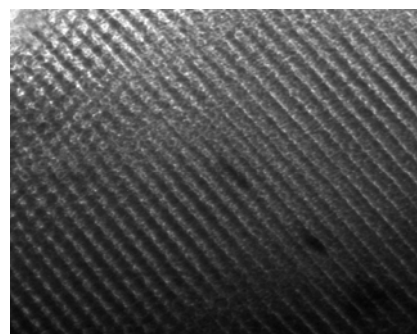
Figure 5 SEM morphology of reactive adsorbent after recycled five times

3.3 The roles of heteropoly acid, formaldehyde and SBA-15 in denitrogenation process

Formaldehyde plays a key role in denitrogenation. Both the denitrogenation reaction rate and breakthrough capacity of substrate are benefited from it.



(a) Electron beam parallel to the direction of main channels



(b) Electron beam perpendicular to the direction of main channels

Figure 6 TEM morphologies of reactive adsorbent after recycled five times

Similar to the desulfurization of transportation fuels, their denitrogenation also accords with the first order reaction kinetics [31]. At the initial stage, the characteristic reaction occurs in the pores of the substrate where the concentration of formaldehyde is excessive compared with that of heterocyclic compounds. The reaction continues with the diffusion of heterocyclic molecules into the pores. The products formed from heterocyclic compounds increases, so the concentration of formaldehyde and the reaction rate decrease. The denitrogenation reaction rate in the adsorbent without formaldehyde is much less than that with it. The adsorbent is saturated soon after the protonation of heterocyclic compounds reaches equilibrium, which is based on the interaction between heteropoly acid and heterocyclic molecule.

Heteropoly acids also produce a dramatic effect on the denitrogenation reaction rate. The rapid reaction needs more heteropoly acid, reducing the specific surface area, pore diameter and pore volume, so that less formaldehyde is adsorbed and denitrogenation reaction rate is lower. Therefore, the load of heteropoly acids should be appropriate. Both the denitrogenation reaction rate and breakthrough capacity of reactive adsorbent are benefited from larger specific surface area and pore diameter of SBA-15.

Table 2 shows the nitrogen breakthrough and saturation capacities of regenerated adsorbent, indicating that the adsorbent still has relatively high efficiency

Table 2 Breakthrough capacities of SBA-15 for model and commercial diesel fuels after recycled

Fuel	Recycled times	Original nitrogen concentration $C_i/\text{ng}\cdot\mu\text{l}^{-1}$	$Q_b/\text{mg}\cdot\text{g}^{-1}$	$Q_s/\text{mg}\cdot\text{g}^{-1}$
model fuel	fresh	237.33	10.68	13.94
	recycled 1st	237.33	10.56	12.94
	recycled 2nd	237.33	10.47	12.64
	recycled 3rd	237.33	9.14	12.39
	recycled 4th	237.33	9.02	12.25
	recycled 5th	237.33	8.90	12.08
commercial diesel fuel	fresh	224.86	1.67	6.26
	recycled 1st	224.86	1.61	6.01
	recycled 2nd	224.86	1.57	5.71
	recycled 3rd	224.86	0.97	5.41

after regenerated and the efficiency decline of the capacity may arise from the poisonous effect of nitrogen-containing compounds on the active sites of catalyst or the loss of catalyst in recycle processes.

4 CONCLUSIONS

It is demonstrated that the reactive adsorbent can effectively remove carbazole compounds from model fuel and remove nitrogen-containing heterocyclic compounds from commercial diesel fuel at mild temperatures. The transportation fuels with ultra-low nitrogen can be obtained. The regenerated reactive adsorbent is almost totally recovered and maintains relatively high efficiency after recycled a few times. The reaction rate for the removal of carbazole from fuels is much faster than that of dibenzothiophene under the same conditions. The reactive adsorbent can efficiently remove nitrogen-containing heterocyclic compounds, which have adverse effect on the catalytic reaction in the HDS process. Thus it is feasible and promising to satisfy the ultra-clean fuel demands after the treatment of hydrogenation followed by the selective adsorption of reactive adsorbent.

NOMENCLATURE

C_i	initial total nitrogen concentration in fuel, $\text{ng}\cdot\mu\text{l}^{-1}$
d_{nor}	normalized diameter, nm
P/P_0	pressure ratio
Q_b	normalized nitrogen breakthrough capacity, $\text{mg}\cdot\text{g}^{-1}$
Q_s	normalized nitrogen saturation capacity, $\text{mg}\cdot\text{g}^{-1}$
S_{BET}	BET specific surface area
t	time
V	volume

Subscripts

BET	Brunauer-Emmett-Teller
nor	normalized

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