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Abstract: Magnetic π-complexation sorbents were studied for petroleum product desulfurization by fluorescent technique. The ability of metal cation to form π-complexation decreases in the order following: $Cu^{+} > Ni^{2+} > Co^{2+} > Al^{3+}$. The order is consistent with that of desulfurization performance of their corresponding magnetic sorbents (γ-Al_2O_3-Cu(I) > γ-Al_2O_3-Ni(II) > γ-Al_2O_3-Co(II) > γ-Al_2O_3). Both π-complexation strength and desulfurization performance of the sorbents increase with temperature. The adsorptive performances of magnetic γ-Al_2O_3-Cu(I) sorbent to different compounds have the following orders: DBT > fluorene, and pyrene > naphthalene > benzene, respectively. In this study, dibenzothiophene (DBT) was used as a model sulphur-containing compound for desulfurization.

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The maximal adsorption amount of magnetic γ-Al_2O_3-Cu(I), was 0.362 mmol DBT g^{-1}.

Keywords: Adsorption, magnetic alumina, π-complexation, dibenzothiophene (DBT), fluorescence, temperature

INTRODUCTION

Due to stricter environmental legislation, the EPA Tier II regulations require reductions of sulfur in diesel from the current average of 500 to 15 ppmw by June 2006, and that in gasoline from 350 to 30 ppmw by January 2005 (1, 2). Therefore, the desulfurization of crude oil and its distillates is becoming increasingly important. Conventional desulfurization is achieved by hydrodesulfurization (HDS). However, HDS must be operated at very high temperatures (>300°C) and pressures (20–100 atm H_2) using expensive catalyst (3). Especially, the operation conditions become more and more rigorous for desulfurization of dibenzothiophene (DBT) and its alkylated derivatives, the main objects of deep desulfurization for petroleum products (4).

Among desulfurization techniques, adsorption plays an increasingly important role (5, 6). Since the adsorption can be accomplished efficiently at ambient temperature and pressure and does not produce wastes, its success would lead to a major advance in petroleum refining. The utility of the adsorption depends entirely on the availability of separated sorbents. Conventional sorbents owe their efficiencies to van der Waals or electrostatic interactions between sorbents and sorbates. However, these interactions are usually too weak to separate efficiently target matters from their mixtures, and the result is low selectivity. A new adsorption technique using chemical complexation has been studied in the recent 10 years. Chemical complexation (7) is generally stronger than van der Waals interaction, and it is enough to be reversible. π-complexation is one of the most important chemical complexations for adsorptive separation (8–10) and has developed into many applications, such as desulfurization (8–10), olefin/paraffin, diene/olefin, and aromatics/aliphatics separations (11–13).

For desulfurization, sorbents based on π-complexation were prepared by exchanged with transition-metal cations on zeolites and alumina (14). They can remove selectively organosulfur molecules from commercial fuels like diesel and gasoline. The mechanism of π-complexation has been explained by molecular orbital calculations (15).

Gamma-Al_2O_3 is one of the most important materials used as sorbents and catalysts. In this paper, magnetic γ-Al_2O_3 microspheres were first prepared and then obtained different magnetic sorbents, which were used in desulfurization of model petroleum product. The adsorptive mechanism was studied by fluorescence spectrum. Metal cations, especially transition metal cations, can form π-complexation with aromatics or aromatic sulphur-containing compounds, such as Dibenzothiophene (DBT), Benzene, Thiophene, Pyrene, and Naphthalene.

EXPERIMENTAL SECTIONS

Chemicals

Pyrene, fluorene, and DBT with a purity of 99% were purchased from ACROS ORGANICS. N-dodecane was purchased from Tokyo Kasei Kogyo Co., Ltd (TCI, Japan). The methanol was HPLC grade, and other chemical reagents, such as naphthalene, $Cu(NO_3)_2$, $NiCl_2 \cdot 6H_2O$, and $CoCl_2 \cdot 6H_2O$, were analytical reagent grade.

Preparation of Magnetic Sorbents

Magnetic γ-Al_2O_3 microspheres were prepared by the internal gelation method (16). The size of the microspheres is about 1–10 μm. Figure 1 was an image of the magnetic γ-Al_2O_3 microspheres observed by a scan electron microscope (SEM, QUANTA 200, FEI.). Magnetic γ-Al_2O_3–Cu(I) sorbent was prepared by impregnating magnetic γ-Al_2O_3 microspheres (5.0 g) with 20 mL of $Cu(NO_3)_2 \cdot 3H_2O$ aqueous solution (0.5 M) for 48 h, and then washed with deionized water, followed by auto-reduction of Cu^{2+} to Cu^{+} at 500–600°C (22, 23). After preparation, the sorbent was quickly added into model fuel for desulfurizing. The extent of oxidization can be omitted because the exposure time in air was very short. Magnetic γ-Al_2O_3–Ni(II) and magnetic γ-Al_2O_3–Co(II) sorbents were prepared by impregnating magnetic γ-Al_2O_3 microspheres (5.0 g) with 20 mL of

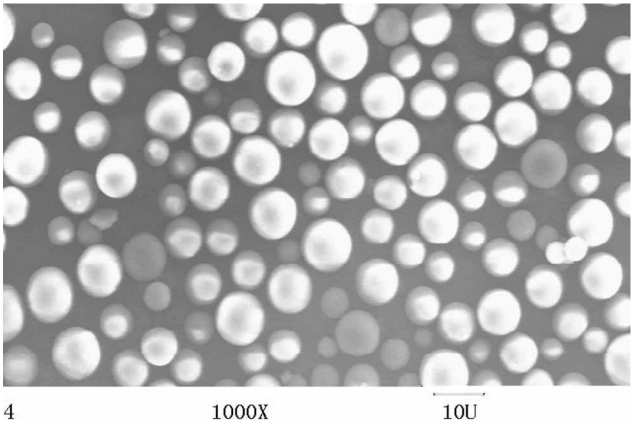

Figure 1. Scanning electron microscope image of magnetic γ-Al_2O_3 microspheres.

$NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ aqueous solutions (0.5 M), respectively, for 48 h at room temperature, and then washed with deionized water, followed by drying at 90°C for at least 24 h.

Desulfurization of Petroleum Product

Adsorptive processes were performed at normal pressure, in which 3.0 g magnetic sorbents were used per 100 mL of model petroleum, which consists of DBT and dodecane. Initial DBT concentration is 5.0 mM.

Analysis

HPLC

DBT concentration in dodecane is analyzed by HPLC (Agilient 1100 with DAD detector). The HPLC separation column was Zorbax SB-C18 (4.6 mm × 25 cm). The flow phase used contained 90% methanol and 10% water. The flow rate was $1\,mL \cdot min^{-1}$.

Fluorescence Spectrum

Steady-state fluorescence of pyrene (or DBT) in methanol was measured using a Perkin-Elmer LS-55 luminescence spectrometer, which was equipped with a Biokinetic accessory. Pyrene was excited at wavelength of 335 nm and the emission intensity from 350 to 500 nm was recorded. DBT was excited at wavelength of 280 nm and the emission intensity from 250 to 450 nm was recorded. The excitation and emission slit openings were set at 5 nm. The scan speed was set at $500\,nm\,min^{-1}$. All spectra were averaged over three scans.

A solution of 0.1 mM pyrene (or DBT) in methanol was prepared. In the experiments, 10 μL of 0.5 mM of Cu^+, Ni^{2+}, Co^{2+}, and Al^{3+}, respectively, were added in 5 mL of pyrene (or DBT) solution. The bulk of additions in the solution were so small that the shift of concentration of the solution may be neglected.

RESULTS

Adsorption Desulfurization

In the conditions of normal temperature and pressure, 3.0 g of magnetic sorbents were added into 100 mL of model petroleum. Figure 2 represents the adsorption of DBT on different magnetic sorbents. The results show that desulfurization performances of the magnetic sorbents decrease in the following order: γ-Al_2O_3–Cu(I) > γ-Al_2O_3–Ni(II) > γ-Al_2O_3–Co(II) >

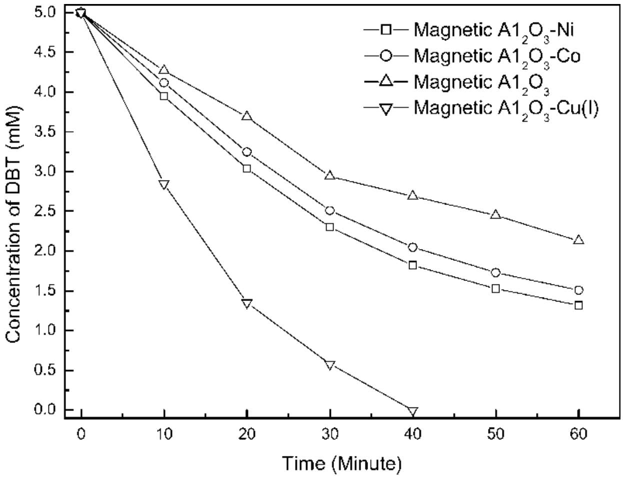

Figure 2. Adsorptive curves of DBT on different magnetic sorbents.

γ-Al_2O_3. Their adsorptive amounts are 0.167, 0.127, 0.113, 0.093 mmol(DBT) g^{-1}, respectively.

π-Complexation

Metal cations, especially transition metal cations, can form π-complexation with some compounds. In this experiment, we investigated the capability for forming π-complexation of different metal cations by monitoring fluorescent intensities of π-complexes. The equal mole of different ion was added into methanol solution of pyrene or DBT, respectively. Figures 3 and 4 show the fluorescent intensities of pyrene-π-complexes and DBT-π-complexes, respectively. The results show that the fluorescent intensity has the decreasing order as following: $Al^{3+} > Co^{2+} > Ni^{2+} > Cu^{+}$. DBT-$\pi$-complexes and pyrene-$\pi$-complexes have a similar result. The addition of Mg^{2+}, Na^{+}, and H^{+} has not changed the fluorescent intensity. It shows that Mg^{2+} and Na^{+} are not able to form π-complex. Cu^{+} has the strongest ability for forming π-complex with pyrene or DBT. According to Figs. 2, 3, and 4, the adsorptive amount of DBT on sorbent is proportional to the strength of π-complexation.

Effect of Temperature on π-Complexation and Desulfurization

Figure 5 shows the effect of temperature on the π-complexation strength of pyrene–Cu(I). The results show the fluorescent intensity of pyrene–Cu(I) π-complex decreases with temperature. Figure 6 shows the effect of temperature on the adsorptive amount of magnetic γ-Al_2O_3–Cu(I) sorbent. The results show that the adsorptive amount increases with temperature. The adsorptive

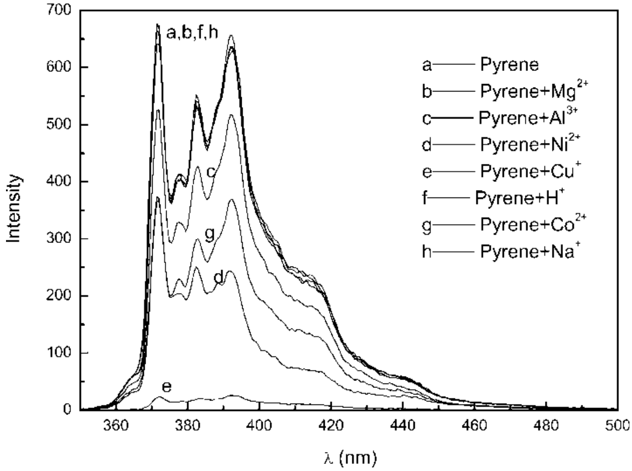

Figure 3. Fluorescent intensity of pyrene with addition of different cations.

amount increases from 0.126 to 0.142 mmol g^{-1}, when the temperature increases from 10 to 50°C. According to Figs 5 and 6, the adsorption performance of sorbent relates with the strength of π-complexation between the corresponding sorbate molecule and absorbate molecule.

Selectivity of π-Complexation

Figure 7 shows the adsorptive curves of magnetic γ-Al_2O_3–Cu(I) sorbent in a model petroleum containing DBT or fluorene. The adsorptive ability of DBT

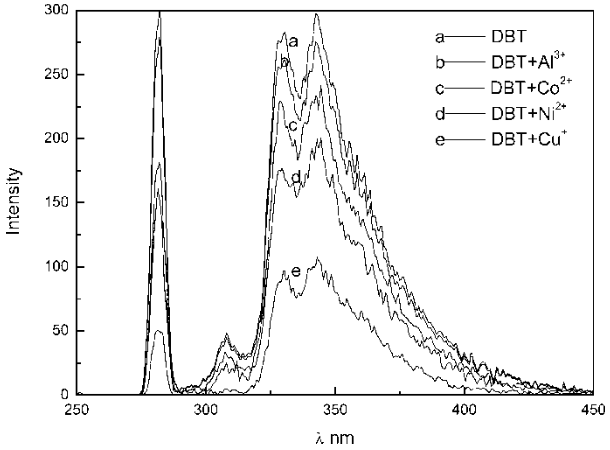

Figure 4. Fluorescent intensity of DBT with addition of different cations.

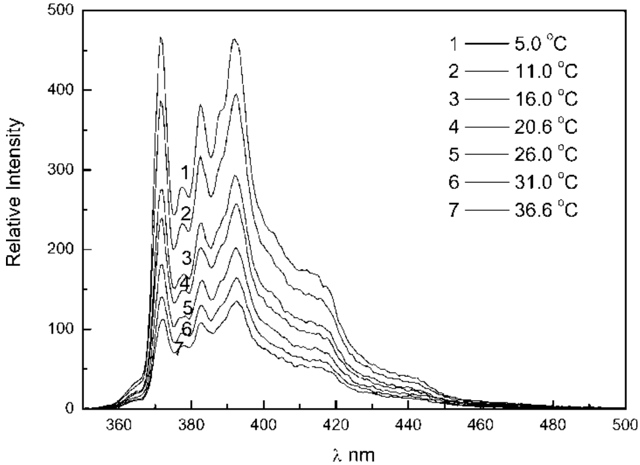

Figure 5. Change of fluorescent intensity of Cu(I)-pyrene complex with temperature.

is more than that of fluorene. Figure 8 is the adsorptive curves of magnetic γ-Al_2O_3–Cu(I) sorbent in a system containing pyrene, naphthalene, or benzene, respectively. The results show that the sorbent has a good ability for adsorbing aromatics. Adsorptive abilities of the sorbent have a decreasing order as following: pyrene > naphthalene > benzene.

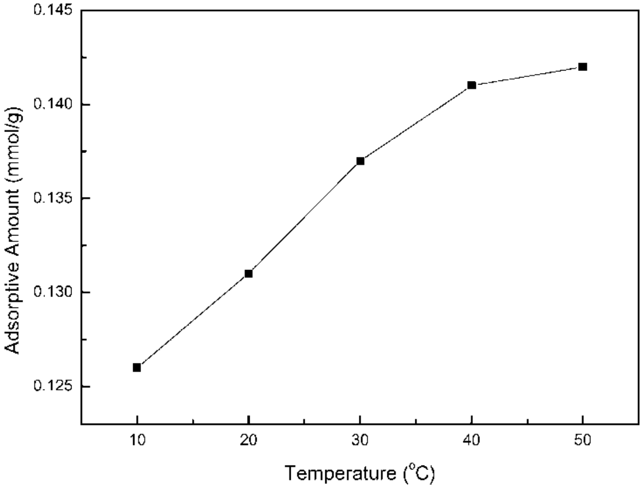

Figure 6. Change of adsorptive amount for magnetic γ-Al_2O_3–Cu(I) sorbent with temperature.

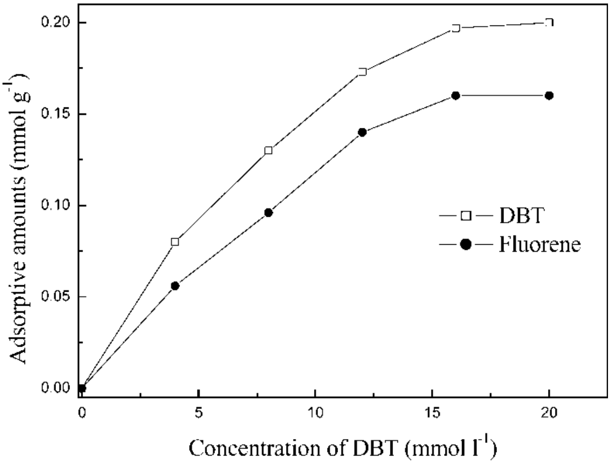

Figure 7. Adsorptive curves of magnetic γ-Al_2O_3–Cu(I) sorbent to DBT and fluorene.

Effects of DBT Concentration on Adsorptive Performance of the Magnetic Sorbent

To study the effect of DBT concentration on the desulfurization, the concentration of DBT in dodecane was changed from 1 to 20 mM. Figure 9 shows the changes of adsorptive performance of magnetic γ-Al_2O_3–Cu(I) sorbent with the concentration of DBT. Its shows the adsorptive amounts

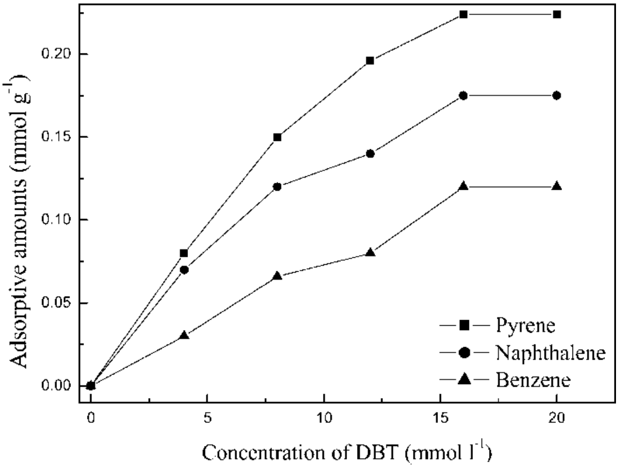

Figure 8. Adsorptive curves of magnetic γ-Al_2O_3–Cu(I) sorbent to different polycyclic aromatics.

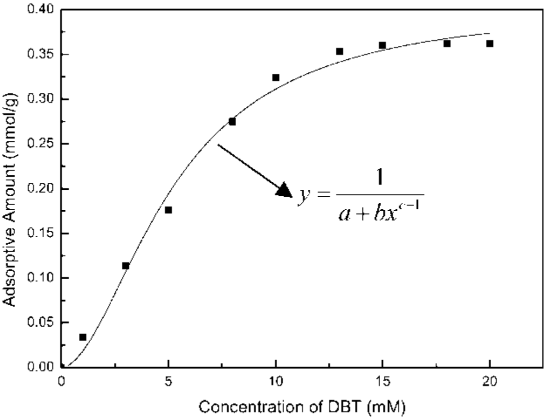

Figure 9. Change of adsorptive amount for magnetic γ-Al_2O_3–Cu(I) sorbent with DBT concentration.

increase with the concentration of DBT. The maximal adsorptive amount of magnetic sorbent is 0.362 mmol(DBT) $\cdot g^{-1}$. The relation between the adsorptive amount of DBT adsorbed on the magnetic γ-Al_2O_3–Cu(I) sorbent and DBT concentration can be represented by the Langmuir equation (Fig. 9).

$$y = \frac{1}{a + bx^{c-1}}$$

Thereinto, a was 2.4527, b was 49.99179, and c was -0.81364. The relative coefficient (R) was 0.99081 and the standard deviation (SD) was 0.00019.

DISCUSSIONS

Selective adsorption desulfurization is a promising technology for the deep desulfurization of petroleum product. The major challenge is to selectively adsorb sulfur compounds onto the solid adsorbent and that the adsorbent can be regenerated easily. Therefore, tremendous opportunity exists for developing new sorbents by weak chemical bonds such complexation. π-complexation is a subclass of chemical complexation (21), which has been studied by FT-IR technology (17) and with molecular orbital theory (15).

Molecular orbital calculations (18) have shown that the π-complexation between Cu^+ or Ag^+ and thiophene are stronger than that with benzene because sulfur atom in thiophene molecule contains a lone pair electron.

In addition, that the π-complexation bond was stronger for substituted thiophenes over nonsubstituted ones (11). Thus, π-complexation sorbents are selective for sulfur removal from petroleum product, because DBT and its derivatives can offer some π-electrons and lone pair electrons and can form π-complex with the sorbent.

However, few reports have studied the effect of sorbent on π-complexation and how to select the metal ions for preparing sorbent. In this paper, the mechanism of π-complexation was further studied by fluorescence spectrum. The effect of metal ions on the adsorptive amount and π-complexation was studied. It may act as a reference for preparing π-complexation sorbents. An electronic singlet state of certain molecules (generally polyaromatic hydrocarbons or heterocycles) is excited by optical absorption and subsequent fluorescence is emitted (19). Both pyrene and DBT can emit fluorescence. Pyrene molecule contains more conjugated π-electrons than DBT molecule. Thus, the fluorescent intensity of pyrene molecule is stronger than that of DBT molecule (Figs 3 and 4). π-complexation is formed by partially contributing of π-electrons to metal ion. The fluorescent intensity decreases with the formation of π-complexation.

Figures 3 and 4 showed that the changes of fluorescent intensities of pyrene and DBT with the addition of metal cations were similar, $Cu^{+} > Ni^{2+} > Co^{2+} > Al^{3+}$, which is because both pyrene and DBT contain many π-electrons, which relate with the intensity of fluorescence. Transition metal ions have strong abilities to accept π-electrons from the molecules and can make the fluorescent intensity weaker. The structure of valence electronic shell of these transition metal elements is $(n-1)d^{1-8}ns^{1-2}$, and all these metal ions have empty d and s orbits to accept a lone pair electrons or π-electrons (24). Thus, they can form π-complexation with pyrene molecules and make the fluorescent intensity weak. The difference of electron number in the $(n-1)d$ orbit of these transition metal ions might result in the change of the ability for accepting electrons. The electronic state of Cu^{+} is more complicated and instable than that of Cu^{2+} (20), and it is difficult to explain why Cu^{+} has the strongest ability to accept electrons. The results accord with Yang's conclusion (18) by the calculation of molecular orbital. Therefore, the adsorptive performance of sorbent is proportional to the strength of the corresponding π-complexation. This agrees well with the experimental data of adsorptive amounts.

Compared of DBT and fluorene, S atom is replaced by C atom (Fig. 10). π-complexation sorbent exhibits higher selectivity to S atom than to C atom. It is because that S atom on DBT can offer a lone electron, which can form π-complexation with transitional metal ions. Figure 8 indicates that the adsorptive abilities related with the strength of conjugated system and number of phenyl (Fig. 11). The effect of temperature on the formation of π-complexation is obvious (Fig. 5). The π-complexation becomes stronger with the increase of temperature. It is because the frequency of collision between aromatics and metal ion increases with temperature. In a word, the

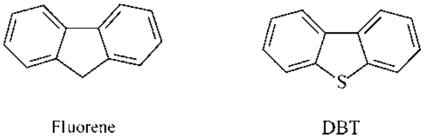

Figure 10. Fluorene and DBT molecules.

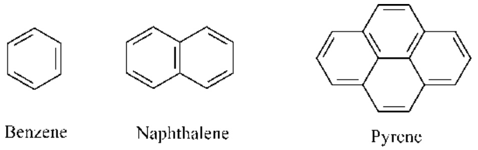

Figure 11. Benzene, naphthalene, and pyrene molecules.

adsorption process is controlled by the electron transfer of aromatics to metal ions.

CONCLUSIONS

Desulfurization of petroleum product using magnetic π-complexation sorbents was studied by a fluorescence technique. π-complexation depends on the types of metal ions, temperature, lone pair, and conjugated electrons. The capability of metal cations to form π-complexation follows the order of $Cu^+ > Ni^{2+} > Co^{2+} > Al^{3+} > Na^+$ (Mg^{2+}). The order of π-complexation strength is consistent with that of desulfurization performance of the corresponding magnetic sorbents (γ-Al_2O_3–Cu(I) > γ-Al_2O_3–Ni(II) > γ-Al_2O_3–Co(II) > γ-Al_2O_3). Thus, the adsorption performance relates with the strength of π-complexation. Among these magnetic sorbents studied in this paper, magnetic γ-Al_2O_3–Cu(I) is the best sorbent with a breakthrough adsorption capacity of $0.362\,\text{mmol(DBT)} \cdot g^{-1}$. The magnetic sorbents can be conveniently manipulated by a magnetic field because of their superparamagnetism.

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