PREPARATION AND SELECTIVE ADSORPTION DESULFURIZATION ACTIVITY OF Ti-Ce-Al-Ag-O ADSORBENT

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Introduction

Many efforts have begun to systematically reduce the sulfur level in transportation fuels such as gasoline, diesel and jet fuel to satisfy the upcoming environmental regulations worldwide. These requirements to produce low-sulfur fuels impose significant efforts in current desulfurization methods and in the development of new technologies. The conventional approach for deep desulfurization of fuel feedstocks in petroleum refining is based on a catalytic process, i.e. hydrodesulfurization (HDS)[1,2]. To comply with the new regulations, this approach faces an important challenge: the removal of polyaromatic sulfur-containing compounds without an unavoidable and significant capital investment, thereby drastically increasing the costs of fuels. One way to avoid the increased costs is to use different approaches. Our laboratory at the Pennsylvania State University has been exploring a new process concept called selective adsorption for removing sulfur (PSU-SARS) without the use of H_2 gas, which operates at ambient temperature and pressure. The advantages of being a low-energy demanding process, availability of regeneration of the spent adsorbent, and broad availability of adsorbents, make this approach an attractive field of research[3-4]. Extensive research in our group has been done to find adsorbent materials that are highly selective toward sulfur compounds, in the presence of the coexisting aromatic hydrocarbons and olefins in the fuels. Recently, it has been shown that Ti-Ce-Al-O adsorbent has higher sulfur capacity and sulfur selectivity, and it also can be regenerated in air[5]. In this paper, we prepared multi-metal oxide Ti-Ce-Al-Ag-O with high surface area. The sulfur adsorption capacity of real jet fuel JP-5 was increased by the addition of Ag into Ti-Ce-Al-O. Multi-metal oxide Ti-Ce-Al-Ag-O can be easily regenerated in air and there is no apparent change of sulfur capacity after regeneration.

Experimental

The metal oxides Ti-Ce-O (with molar ratio of Ti:Ce = 9:1), Ti-Ce-Al-O (with molar ratio of Ti:Ce:Al = 9:1:2.2) and Ti-Ce-Al-Ag-O (with molar ratio of Ti:Ce:Al:Ag = 9:1:2.2:2.4) were prepared by urea co-precipitation method. Commercial CoO-MoO_3/Al_2O_3 was obtained from Criterion Catalyst Company. A model fuel with a total sulfur content of 500 ppmw and a real jet fuel JP-5 with 1040 ppmw sulfur were used for adsorption desulfurization tests at room temperature under atmospheric pressure. The used adsorbent was regenerated at 500 □ for 2 hours in air. The detailed composition of the model fuel is listed in Table 1. The fuel/adsorbent ratio was 10 (wt/wt) in the batch test. The treated model fuel was separated and analyzed by GC HP 5890 with a capillary column (XTI-5, Restek) and a flame ionization detector (FID). The total sulfur concentration was determined by using an Antek 9000S total sulfur analyzer.

Table 1 The Concentration of Each Compound in Model Fuel.

Chemicals	Concentration		Molar concentration
	wt. %	ppmw S	(mmol/kg)
Tetrahydrothiophene (THT)	0.03	105	3.3
Bezothiophene (BT)	0.04	100	3.1
2-MBT	0.05	100	3.1
DBT	0.06	100	3.1
4,6-DMDBT	0.07	100	3.1
Naphthalene (Na)	0.04		3.1
1-Methylnaphthalene (1-MNa)	0.04		3.1
Phenanthrene (Phen)	0.06		3.1
1-Octene	0.04		3.1
n-Dodecane	0.05		3.1
n-Decane	49.76		
n-Hexadecane	49.76		
Total	100.00		

Results and Discussion

The sulfur adsorption capacities of the model fuel over Ti-Ce-O, Ti-Ce-Al-O, Ti-Ce-Al-Ag-O and CoO-MoO_3/Al_2O_3 are shown in Figure 1. The results showed that Ti-Ce-Al-Ag-O has higher sulfur adsorption capacity (4.1 mg-S/g-Ads.) than that of Ti-Ce-O (3.3), Ti-Ce-Al-O (3.7) and CoO-MoO_3/Al_2O_3 (2.5). After four times regeneration, Ti-Ce-Al-Ag-O still has highest sulfur capacity (3.7 mg-S/g-Ads.) among these metal oxides, the sulfur capacity of Ti-Ce-Al-Ag-O was increased 8.5% and 60.9% than Ti-Ce-Al-O and CoO-MoO_3/Al_2O_3, respectively.

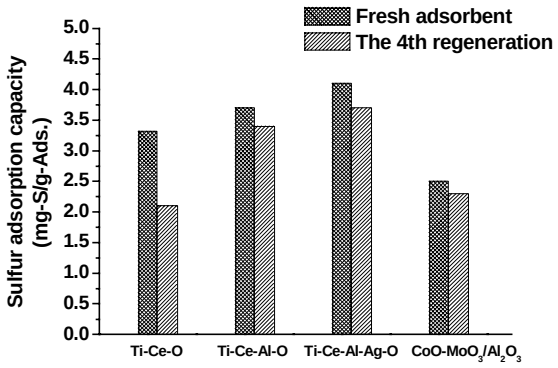

Figure 1 Sulfur adsorption capacities of model fuel over fresh and regenerated Ti-Ce-O, Ti-Ce-Al-O, Ti-Ce-Al-Ag-O and commercial CoO-MoO_3/Al_2O_3 in a batch system at ambient temperature and pressure.

The results also indicate that Ti-Ce-Al-Ag-O has better regenerable stability in air.

Figure 2 shows the relative selectivity factor of Ti-Ce-Al-Ag-O and CoO-MoO_3/Al_2O_3 for various compounds in the model fuel. The adsorption selectivity for THT is the highest in all compounds regardless of the adsorbents, which is not included in Figure 2. Multi-metal oxide Ti-Ce-Al-Ag-O show significantly higher adsorption selectivity for sulfur compounds than CoO-MoO_3/Al_2O_3. The adsorptive selectivity of Ti-Ce-Al-Ag-O is in the order of THT > DBT > 4,6-DMDBT > Phenan > BT > 2-MBT > 1-MNa > 1-Octene > Na. Ti-Ce-Al-Ag-O prefers to adsorb sulfur compounds rather than aromatics and olefins coexisting in the model fuel.

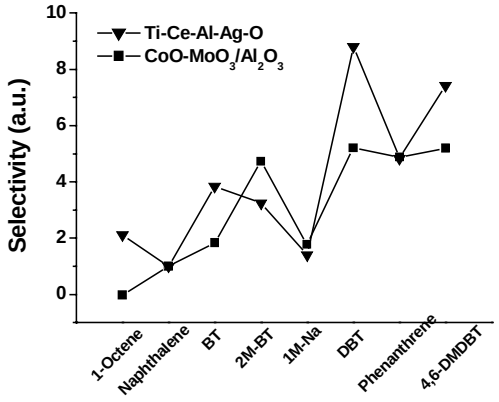

Figure 2 The relative selectivity factor (relative to naphthalene) of Ti-Ce-Al-Ag-O and CoO-MoO_3/Al_2O_3 for the various compounds in the model fuel.

The stability of the adsorptive selectivity of Ti-Ce-Al-Ag-O during the recycles was also examined. Figure 3 shows the relative selectivity factors of fresh and regenerated Ti-Ce-Al-Ag-O adsorbent. The results indicate that the adsorptive selectivity for sulfur compounds is stable within the recycles. It implies that the property of the adsorption sites of Ti-Ce-Al-Ag-O is stable during the oxidation regeneration in air.

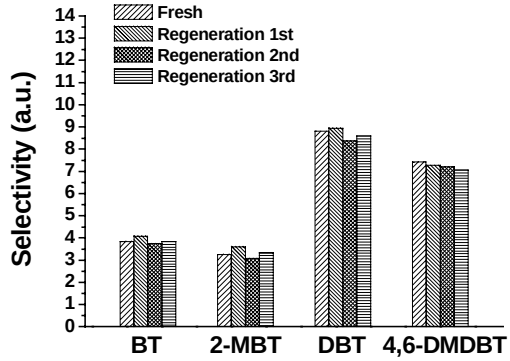

Figure 3 Relative adsorptive selectivity factors (relative to naphthalene) of the fresh and regenerated Ti-Ce-Al-Ag-O for BT, 2-MBT, DBT and 4, 6-DMDBT**.**

The adsorption desulfurization of the real JP-5 over Ti-Ce-O, Ti-Ce-Al-O, Ti-Ce-Al-Ag-O and CoO-MoO_3/Al_2O_3 was conducted and the results are shown in Figure 4. The results indicate that the sulfur adsorption capacity of Ti-Ce-Al-Ag-O can be reached to 7.5 mg-S/g-Ads., which is 2.1 and 3.3 times of Ti-Ce-Al-O and CoO-MoO_3/Al_2O_3, respectively. It implies that the addition of Ag into Ti-Ce-Al-O increases the sulfur adsorptive capacity significantly. This high sulfur capacity is due to the high surface area (279.8 m^2/g) and more adsorptive active sites on the surface of the multi-metal oxide Ti-Ce-Al-Ag-O adsorbent.

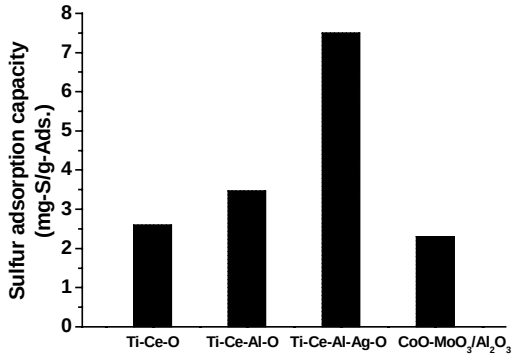

Figure 4 Sulfur adsorptive capacities of real jet fuel JP-5 over metal oxides Ti-Ce-O, Ti-Ce-Al-O, Ti-Ce-Al-Ag-O and commercial CoO-MoO_3/Al_2O_3 in a batch system at room temperature under atmospheric pressure.

Conclusions

The multi-metal oxide Ti-Ce-Al-Ag-O was prepared and investigated in adsorption desulfurization of model fuel and real jet fuel JP-5 at room temperature under atmospheric pressure. Ti-Ce-Al-Ag-O adsorbent has higher sulfur adsorption capacity than that of Ti-Ce-Al-O and commercial CoO-MoO_3/Al_2O_3. Ti-Ce-Al-O also has better oxidative regenerability and can be regenerated in air. The sulfur adsorption capacity of real jet fuel JP-5 over Ti-Ce-Al-Ag-O is 7.5 mg-S/g-Ads., which is increased 226% than that of CoO-MoO_3/Al_2O_3. The multi-metal oxide Ti-Ce-Al-Ag-O is a promising adsorbent in industrial application.

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