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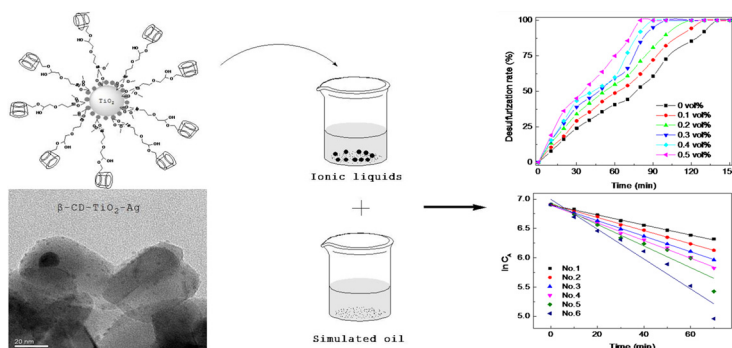
Deep desulfurization of gasoline by synergistic effect of functionalized β -CD- TiO_2 -Ag nanoparticles with ionic liquid

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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the Ag elementary substance and β -cyclodextrin were connected with the surface of TiO_2 nanoparticles by coupling agent to synthesize functionalized β -CD- TiO_2 -Ag nanoparticles. A variety of characterization methods were used to show the characteristic of β -CD- TiO_2 -Ag nanoparticles. After that, the desulfurization of simulation the gasoline was tested by adding β -CD- TiO_2 -Ag nanoparticles in ionic liquids (ILs) with synergistic reaction. The desulfurization efficiency followed the order: pure ILs < TiO_2 /ILs < β -CD- TiO_2 -Ag/ILs. Especially, when the sulfur content of the simulated oil in sample of 0.5 vol% β -CD- TiO_2 -Ag nanoparticles was nearly 0 ppm, the sulfide content of the sample of 0.5 vol% TiO_2 nanoparticles was 425.62 ppm at room temperature. Meanwhile, the volume fractions of nanoparticles, experimental temperature and the desulfurization time have a corresponding impact on the desulfurization rate. Kinetics of desulfurization process was studied and the desulfurizing agent (ionic liquids with β -CD- TiO_2 -Ag nanoparticles) could be recycled and re-used for five times with an unnoticeable decrease. Hence, our research is promising in gasoline desulfurization.

1. Introduction

In recent years, global warming and haze phenomenon are more and more serious. One of the important reasons for the formation of fog and haze are a large number of emissions of harmful gas from automobile exhaust in recent years. Especially a large number of

combustion products from sulfide of oil emissions, it brings a threat to the ecological environment and people's health. In order to improve the environment and governance haze pollution, the quality requirements of vehicle fuel oil is strict for adapting the increasingly stringent emission standards [1–3]. Therefore, it is one of the contents of the world's sustainable development strategy to strictly limit the sulfur

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content in gasoline and reduce the emission of harmful substances. How to produce low sulfur gasoline at an ideal operating cost has become a top priority to oil refining industry.

Gasoline desulfurization can be achieved through a variety of methods, non hydro-desulfurization technology is particularly widely used and it is simple, convenient, fast and economical. Non hydro-desulfurization technology includes catalytic cracking desulfurization, catalytic hydro-desulfurization, biological desulfurization, solvent extraction desulfurization, photocatalytic oxidation desulfurization, adsorptive desulfurization and oxidative desulfurization [4–9]. With the urgent need to improve the desulfurization industry, this kind of method has been paid more and more attention in recent years. Tawfik A. Saleh [10] held a view of an-bimetallic Ce/Fe nanoparticles on the desulfurization of thiophenes using activated carbon. Hongying Lü and his partners [11] did a lot research about oxidative desulfurization of model diesel via dual activation by a pore ionic liquid. Rong Wang et al. [4] did an experiment about an improvement of MCM-41 supported phosphoric acid catalyst for alkylation desulfurization of fluid catalytic cracking gasoline. Takuro Kobayashi [5] studied the performance and characterization of a newly developed self-agitated anaerobic reactor with biological desulfurization. Wei Jiang et al. [7] did a report on biodegradable choline-like deep eutectic solvents for extractive desulfurization of fuel. There are advantages and disadvantages of each method. The method of ionic liquids extraction desulfurization can be carried out at room temperature without changing the chemical composition and it dose low energy consumption. At the same time, ionic liquids also can be recycled. Hence, this approach is widely used in desulfurization [12–14].

In recent years, TiO_2 is the most widely used in the degradation of environmental pollutants. In order to solve the increasingly serious environmental pollution problems, photocatalytic oxidation technology of nano- TiO_2 has great research and practical value. TiO_2 nanoparticle is cheap, non-toxic, stable, excellent optical properties, catalytic properties and photoelectric conversion properties which lead to be favored [15]. At the same time, metal oxides have been widely used as adsorbents in desulfurization [16–19]. The adsorption desulfurization principle of metal oxide is mainly that the surface of metal oxide is Lewis acid center which can be used to adsorb sulfur compounds in gasoline, because most of the sulfur compounds are Lewis base. The Ti in TiO_2 is a transition metal, which lead TiO_2 to have good adsorption properties to sulfide. However, the particle size of TiO_2 nanoparticles is small, the specific surface area of them is large, the surface of them is high, and they are in the non thermodynamic stable state, which lead them to easily agglomerate. Therefore, the surface modification of TiO_2 nanoparticles is needed [20–22]. The surface modified TiO_2 nanoparticles can reduce the effect of the surface hydroxyl groups and the hydrophilicity of the surface groups, so as to prevent particles agglomeration. In this study, TiO_2 nanoparticles were modified with Ag elementary substance and β -cyclodextrin (β -CD). Ag has a strong antibacterial properties, the combination of the two materials will greatly enhance the antibacterial properties of TiO_2 nanoparticles to achieve synergistic antibacterial effect. The Ag elementary substance and TiO_2 nanoparticles are connected by coupling agent 3- (trimethyl silyl) propyl -2- methyl -2- acrylate (MPS), which reduces the active hydroxyl groups on the surface of TiO_2 nanoparticles, thus reducing the agglomeration of particles. Since 1970s, the researchers found β -cyclodextrin inclusion compound and has carried on the analysis. With the study of β -cyclodextrin inclusion compound deeply, people found that the β -cyclodextrin inclusion compounds have the ability to bind different types of organic sulfides [23]. Hence, it can improve the absorption ability of the particles by bridging β -CD. From this research, the novel functionalized β -CD- TiO_2 -Ag nanoparticles were added into the ionic liquids and their effects on the gasoline desulfurization were studied.

Moreover, the research on gasoline desulfurization in which adding novel β -CD- TiO_2 -Ag nanoparticles into ionic liquid to extraction-

adsorption desulfurization didn't exist. Desulfurization time, temperature and volume fraction of β -CD- TiO_2 -Ag nanopaticles was researched. Desulfurization kinetics was also investigated. The novel β -CD- TiO_2 -Ag nanoparticles were characterized by TEM, EDS, FTIR and XRD, and the results were correlated with ionic liquid in the experiment. Meanwhile, we chose ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{C}_8\text{H}_{15}\text{N}_2\text{PF}_6$) in this research in which $\text{C}_8\text{H}_{15}\text{N}_2\text{PF}_6$ belongs to imidazolium ionic liquid with great desulfurization capacity.

2. Experimental

2.1. Materials and chemicals

TiO_2 nanoparticles were purchased from Beijing island gold Deco Technology Co. Ltd. Ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{C}_8\text{H}_{15}\text{N}_2\text{PF}_6$ CAS Number: 174501-64-5) was purchased from Lanzhou Institute of Chemical Physics Chinese Academy of Sciences. Benzothiophene (BT, $\text{C}_8\text{H}_6\text{S}$ CAS Number: 95-15-8), (3- mercaptopropyl) triethoxysilane (MPS CAS Number: 14814-09-6) and sodium borohydride (NaBH_4 CAS Number: 16940-66-2) were got from Shanghai Macklin Biochemical Co. Ltd. Octane (C_8H_{18} CAS Number: 111-65-9), Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$ CAS Number: 64-17-5), silver nitrate (AgNO_3 CAS Number: 7761-88-8), N, N-dimethyl formamide ($\text{C}_3\text{H}_7\text{NO}$ DMF CAS Number: 68-12-2), another coupling agent Gamma (2,3-) - Epoxy Acrylate (KH-560 CAS Number:2530-83-8), sodium hydroxide (NaOH CAS Number:1310-73-2), β - cyclodextrin (β -CD CAS Number: 7585-39-9), carbon tetrachloride (CCl_4 CAS Number: 56-23-5) and ammonia solution (25%) ($\text{NH}_3\cdot\text{H}_2\text{O}$ CAS Number: 1336-21-6) were part was mainly that modifying TiO_2 nanoparticles with Ag elementary substance provided by Chengdu Kelong Chemical Reagent Factory. The average crystallite size of TiO_2 nanoparticles is 15 nm and the specific surface area of it is $160\text{ m}^2/\text{g}$ which is offered by manufacturers.

2.2. Preparation for β -CD- TiO_2 -Ag nanoparticles

β -CD- TiO_2 -Ag nanoparticles were synthesized by modifying TiO_2 nanoparticles with β -CD and Ag elementary substance. The synthesis of this type of particles was mainly divided into three parts. First bridging Ag elementary substance on the surface of TiO_2 by bridging capability of coupling agent MPS. Grafting another coupling agent KH-560 onto the surface of the β -CD was second parts. Last part of production process was connecting β -CD with TiO_2 -Ag nanoparticles by coupling agent KH-560.

First, a certain amount of TiO_2 nanoparticles was dispersed in the 40 mL ethanol solution and adding 0.3 μL MPS solution into ethanol solution. Then researches mixed the mixture at room temperature (25°C) for 48 h. During this process, the coupling agent MPS took off the hydroxyl group, and the hydroxyl group on the surface of the TiO_2 nanoparticles took off a hydrogen atom to produce condensation reaction to generate water molecules and form a stable structure of “Si-O-Si”(seeing from Supporting information Fig. 1(a)). The TiO_2 nanoparticles which were modified by MPS were centrifugal washing with deionized water and alcohol. After that, the washed TiO_2 -MPS nanoparticles were dispersed in the alcohol solution and stirred for 10 min at room temperature (25°C). Afterward, adding 40 μL AgNO_3 solution into suspension to mix 30 min. The 60 μL NaBH_4 solution was rapidly added to the suspension. As the solution changing from white to yellow, Ag elementary substance was successfully grafted onto the surface of the TiO_2 nanoparticles. The resulting suspension was centrifuged with deionized water to obtain TiO_2 -Ag nanoparticles. The principle of the main application of this process was that metal chelating effect of MPS link Ag^+ to the surface of TiO_2 nanoparticles and then using reducing agent to reduce Ag^+ to Ag elementary substance (seeing from Supporting information Fig. 1(a)).

The second part of process was mainly based on coupling agent KH-560 modifying β -CD (seeing from Supporting information Fig. 1(b)). A

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