



Oxidative desulfurization using ordered mesoporous silicas as catalysts



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ABSTRACT

Ordered mesoporous silicas with structures of MCM-41, MCM-48 and SBA-15 were synthesized. Oxidative desulfurization activities of dibenzothiophene and 4,6-dimethyl dibenzothiophene on the mesoporous silicas were investigated using *tert*-butyl hydroperoxide as an oxidant. Textures and surface properties of the synthesized mesoporous silicas were studied by X-ray diffraction, N₂-sorption, FT-IR and NH₃-temperature programmed desorption. The results show that oxidative desulfurization catalytic activities increase with surface area and surface acidity of the mesoporous silicas. Oxidative desulfurization mechanism on MCM-41 was investigated by the addition of surface silanol inhibitor such as acetic acid, water and triethylamine or silylation of surface silanol groups using trimethylchlorosilane. A hypothetical mechanism based on surface silanol-mediated oxidation desulfurization is proposed. Oxidative desulfurization activities for Mo catalysts supported on MCM-41 were also investigated to identify the difference in oxidative desulfurization mechanism between MoO₃ catalysts and pure mesoporous silicas.

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1. Introduction

Sulfur in transportation fuels is a major source of air pollution. Ultra-deep desulfurization of fuels attracted many attentions not only because of increasing environmental concern and legal requirements on a sulfur content, but also because of the application of ultra-low-sulfur fuels for fuel cell [1–3]. For example, the very stringent environmental regulations have limited the level of sulfur in diesel to less than 15 ppm since 2006 in the United States, less than 10 ppm since 2005 in Europe, and less than 50 ppm since 2008 in China. In addition, liquid hydrocarbons are considered a potential fuel for automotive and portable fuel cells due to their higher energy density and readily existing infrastructure for production, delivery and storage [2]. However, trace amounts of organic sulfur presented in liquid fuels, particularly gasoline and diesel, are sufficient to considerably poison the noble metal catalysts used in reforming and transforming process of fuels and the electrode catalysts used in fuel cell stacks, then reduce the activity and lifetime of the catalysts [4].

Hydrodesulfurization (HDS) is highly efficient for removal of thiols, sulfides, and disulfides. However, it is difficult to reduce refractory sulfur compounds such as dibenzothiophene (DBT) and its alky-substituted derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) to an ultra low level using only conventional HDS [5,6] due to their alky chain steric hindrance. Severe operating conditions with high temperatures, high pressures, and high hydrogen consumption are required for HDS to achieve ultra-deep desulfurization of diesel with S concentration <10 ppm. High capital and operating costs are inevitable. Therefore, it is necessary to develop alternative ultra-deep desulfurization processes of adsorption [7], extraction [8], oxidation [9] and bioprocesses [10]. Among these, oxidative desulfurization (ODS) combined with extraction or adsorption is considered to be one of the most promising processes. Much interest has been shown over the last decade for the application of ODS to liquid fuels [11–15].

During oxidative desulfurization, sulfur-containing organic compounds can be oxidized by the electrophilic addition of oxygen atoms with the sulfur atoms to form sulfoxides and sulfones. The chemical and physical properties of sulfoxides and sulfones are significantly different from those of hydrocarbons in fuel oil, and consequently they can be removed by distillation, solvent extraction, or adsorption. The refractory-substituted DBTs are easily

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oxidized under mild reaction conditions (atmospheric pressure and relatively low temperature) without use of expensive hydrogen, therefore, the capital requirement for an ODS unit is significantly less than that for a deep HDS unit.

Otsuki et al. [16] investigated the relationship between electron densities of the sulfur atoms and oxidative reactivities of the sulfur-containing compounds using hydrogen peroxide and formic acid as oxidants for ODS. The results indicate ODS activities for DBTs increase with an increase in the electron densities of the sulfur atoms in sulfur compounds. It is suggested that in ODS reaction 4,6-DMDBT can be more easily oxidized than DBT due to its higher electron density. ODS is confirmed to be a potential route for desulfurization of sterically hindered sulfides such as 4,6-DMDBT.

In our previous study [17], using *tert*-butyl hydroperoxide (TBHP) as an oil-soluble oxidant, the oxidative reaction mechanism and the reactivities of the sulfur compounds (DBTs) in the presence of various catalysts were investigated with a flow reactor. It is found that $\text{MoO}_3/\text{Al}_2\text{O}_3$ exhibits the highest ODS activity for DBT among the catalysts examined. The ODS mechanism on $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst is inferred that the coordination of hydroperoxide to Mo–O is prompted by the polarization of $\text{Mo}^{\delta+}-\text{O}^{\delta-}$ bond when MoO_3 is dispersed on Al_2O_3 . Via the formation of a five-member ring, the electrophilicity of peroxy oxygen is prompted, and therefore high oxidative activity can be obtained. Further, the oxidation reactor was combined with an adsorption reactor disposed in line and a continuous oxidation/adsorption process was developed [18]. The oxidation of undesirable sulfur compounds presented in a desulfurized light gas oil (LGO; sulfur content: 39 ppm) was performed with TBHP as the oxidant on 16 wt.% $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst. The total sulfur content can be decreased to the value less than 5 ppm, which is under the most drastic future restrictions imposed by environmental laws.

Chica et al. [19] synthesized well-designed titanium containing MCM-41 mesoporous materials, which successfully reduced sulfur content in a simulated diesel from 200 ppm to 0 ppm by ODS using TBHP as the oxidant. Stranger and Angelici [20] reported that using silica gel as an ODS catalyst, sulfur concentrations in simulated petroleum solutions containing 374 ppm sulfur of DBT or 4,6-DMDBT could be reduced to 1 ppm within 40 min at 90 °C using TBHP. In addition, Kropp et al. [21] have studied the mechanisms of surface-mediated reaction on silica gel and alumina in the oxidation of various sulfur containing organic compounds using TBHP.

Above all these reports, there is no research focused on the ODS reactivity and the mechanisms catalyzed over pure mesoporous silicas with various structures which presented ordered structures and large surface areas compared with silica gel. In this paper, we synthesized mesoporous silicas with structures of MCM-41, MCM-48 and SBA-15 aiming to acquire pure mesoporous silica materials with different structures and surface properties. The de-template procedures were carried out with calcination or extraction. The ODS activities were investigated in both batch reactor and fix-bed reactor using TBHP as an oxidant. The ODS active sites on pure mesoporous silicas were studied by introducing protic solvent in the ODS reaction or silylation of the surface silanol groups before reaction. According to the results, the ODS mechanisms on pure mesoporous silicas are discussed.

2. Experimental

2.1. Materials

MCM-41 and MCM-48 samples were synthesized as reported elsewhere [22–24]. Typically tetraethyl orthosilicate (TEOS) was slowly added to a stirred solution of NaOH and cetyltrimethylammonium bromide (CTABr) at 303 K. The

molar compositions of gel for MCM-41 and MCM-48 are $\text{TEOS}/\text{NH}_3\cdot\text{H}_2\text{O}/\text{CTABr}/\text{H}_2\text{O}=1/8/0.13/60$ and $\text{TEOS}/\text{Na}_2\text{O}/\text{CTABr}/\text{H}_2\text{O}=1/0.25/0.65/62$, respectively. After being stirred for 3 h, the gel was crystallized at 393 K for 48 h in stainless reactors with Teflon liners. In case of molybdenum containing sample, a certain amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was added in the solution.

SBA-15 samples were synthesized according to the method of reference [25]. Typically 8.5 g TEOS was added to a stirred solution of 120 g 2 M HCl and 4.0 g P123 at 308 K. After stirring for 24 h, the gel was crystallized at 363 K for 12 h in a stainless reactor with Teflon liner.

All the synthesized samples were washed with deionized water and ethanol, and then dried at 313 K under vacuum condition. The MCM-41 containing molybdenum was calcined in air under 823 K for 5 h (MoM41C) [26]. Each one of pure silica samples was divided into two parts for calcination (marked with suffix C) and extraction (marked with suffix E). The first part was calcined at 623 K in air for 5 h (SiM41C, SiM48C and SiS15C). The second part of MCM-41 and MCM-48 (2.0 g) was extracted in a mixed solution of ethanol/concentrated hydrochloric acid (75 ml, v/v: 8/1) using a round-bottom flask equipped with a condenser pipe at 363 K for 8 h, then filtered, washed with ethanol/acetone and vacuum dried at 333 K for 4 h (SiM41E and SiM48E) [27,28]. In case of SBA-15 sample, 2.0 g powder was soaked in 20 g 15% H_2O_2 solution in a stainless reactor with Teflon liner, hydrolyzed at 398 K for 24 h, then washed with deionized water and ethanol, dried at 333 K for 4 h under vacuum condition (SiS15E).

6% Mo/M41C and 16% Mo/ Al_2O_3 catalysts were synthesized as follows: 0.08 g or 0.21 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved in 10 g deionized water, then 1.0 g SiM41C or Al_2O_3 supports were impregnated in this aqueous solution with stirring, dried at 393 K for 4 h, then calcined in air flow at 823 K for 4 h.

2.2. Desulfurization of DBT as model sulfur compound

Oxidative desulfurization of DBT was carried out in both glass batch reactor and fixed-bed reactor. The simulated diesel oils used in this work are MD500 (500 ppm DBT), MD800 (500 ppm DBT and 300 ppm 4,6-DMDBT) and MD5000 (5000 ppm DBT). Typically, the simulated diesel MD 500 was prepared as follows: 0.5 g DBT was dissolved in 99.5 g decalin to obtain 5000 ppm DBT solution. 0.752 g 65% TBHP was dissolved in 99.3 g decalin to obtain about 5000 ppm TBHP solution. Due to the molar mass of DBT is about 2 times of TBHP, so equal amount of DBT solution and TBHP solution was weighed just before ODS reaction, then 10 times diluted with decalin to obtain MD 500 with TBHP/DBT (O/S) molar ratio of 2.

A typical ODS process in a batch reactor is as follows: in a 50 ml round bottom flask, simulated diesel (MD500 or MD800) was heated to a desired temperature with stirring, then 0.1 g catalyst was added, the oxidation reaction last for about 3 h.

Oxidative desulfurization was also carried out in a stainless steel fix-bed reactor (i.d. 3 mm). 0.10 g catalyst was loaded in the reactor and heated at 353 K. Then the feed (MD5000) was introduced by a peristaltic pump at atmospheric pressure with WHSV of 40 h^{-1} . The outflow was analyzed per half hour by GC-FID.

2.3. Analysis

Powder X-ray diffraction (XRD) patterns were obtained on Rigaku D MAX using $\text{CuK}\alpha$ radiation (40kv, 100 mA), from 0.6 to 20° (2 θ) with a scanning rate of 1°/min. Small angle X-ray scattering of SBA-15 sample was measured on Bruker AXS Nano-Star with scanning range of 0–3°. N_2 adsorption–desorption analysis was carried out at 77 K on a Micromeritics TriStar 3000 apparatus. FT-IR spectra were recorded on KBr pellets by a BRUKER VECTOR 22 spectrometer

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