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Oxidation of dibenzothiophene with cumene hydroperoxide on MoO_3/SiO_2 modified with alkaline earth metals

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ABSTRACT

Catalytic oxidation of dibenzothiophene (DBT) in decalin was performed using an oil-soluble oxidant, cumene hydroperoxide (CHP), over molybdenum oxide (MoO_3) supported on silica. The effects of MoO_3 loading, reaction time and the molar ratio of CHP/DBT were investigated. At a MoO_3 loading of 15 wt%, the conversion of DBT reached 82% at 70 °C, WHSV 30 h^{-1}, and O/S molar ratio 3. Alkaline earth metals, such as Ca, Ba, Sr and Mg were introduced on the surface of silica, prior to the impregnation of MoO_3. The results showed that the activity in the oxidation of DBT with CHP decreased in the order: MoO_3/Ca-SiO_2 > MoO_3/Ba-SiO_2 > MoO_3/SiO_2 > MoO_3/Sr-SiO_2 > MoO_3/Mg-SiO_2. The MoO_3/Ca-SiO_2 catalysts were characterized by XRD. The DBT conversions on MoO_3/Ca-SiO_2 catalysts with various Ca/Mo ratios were studied. When the Ca/Mo ratio was 0.05, the DBT conversion was the highest (95%) at 60 °C, WHSV 30 h^{-1}, and O/S molar ratio 3.0.

1. Introduction

In recent years, much attention has been paid to deep desulfurization of diesel fuel because the exhaust gases containing SO*x* are the major origin of air pollution and acid rain. In a refinery, the removal of sulfur from petroleum distillates is mainly through the so-called hydrotreating process, in which hydrodesulfurization (HDS) is involved. However, it is considerably difficult to achieve ultra low sulfur levels by HDS, due to the significantly low reactivity of sulfur containing polyaromatic compounds, such as dibenzothiophene (DBT) and its derivatives [1]. Another disadvantage of HDS is the high consumption of hydrogen, which is costly and sometimes not readily available.

An alternative or polishing process is therefore desirable. Several non-HDS approaches to desulfurization have been extensively investigated recently [2–6]. Among them, oxidative desulfurization (ODS) is considered to be one of the promising new methods for ultra-deep desulfurization of engine fuels. ODS generally takes place under mild conditions (<100 °C and atmospheric pressure). In an oxidation process, DBT, which is one of the most refractory sulfur compounds in HDS, is readily oxidized to yield the corresponding sulfone [7]. The chemical and physical properties of the resulting sulfone are significantly different from those of hydrocarbons in fuel. Therefore, they can be easily removed by distillation, solvent extraction, and adsorption [1].

Quite a few types of oxidants have been reported, such as hydrogen peroxide [8–15], nitrogen dioxide or nitric acid [16], air [17,18], O_2/aldehyde [19,20], tert-butyl hydroperoxide [21], cyclohexanone peroxide [22], and cumene peroxide [23]. Hydrogen peroxide is the most commonly used oxidant among these oxidants. Nevertheless, the ODS by H_2O_2 usually takes place in a batch reactor, because at least two phases are involved in the reaction. It is apparent a flow-type reaction system is preferable in a modern refinery with a high throughput. Wang et al. [21] used tert-butyl hydroperoxide (t-BuOOH) as oxidant in DBT ODS in a flow-type fixed-bed reactor. They found that Al_2O_3-supported MoO_3 showed higher catalytic activity than those supported on TiO_2 and SiO_2–Al_2O_3. Nevertheless, our preliminary study showed that Al_2O_3-supported MoO_3 was not stable in the oxidation.

In the present study, cumene hydroperoxide (CHP), an intermediate in the simultaneous production of phenol and acetone, was used as an oil-soluble oxidant. Alkaline earth metal modified Mo/SiO_2 was used as the catalyst in DBT ODS in a fixed-bed reactor.

2. Experimental

2.1. Catalysts preparation

Aerosil silica (surface area 250 m^2/g) was used as the support. Ammonium heptamolybdate, calcium nitrate, magnesium nitrate,

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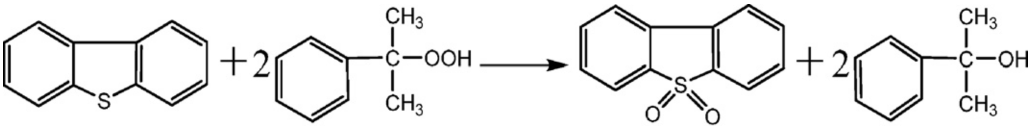

Scheme 1. Oxidation of DBT by CHP.

strontium nitrate and barium nitrate were all of CR grade. SiO_2-supported MoO_3 catalysts with various Mo contents were prepared by an incipient wetness impregnation method. An amount of 1 g silica was impregnated with 3 ml aqueous solution of ammonium heptamolybdate with required concentration, and then kept for 8 h at room temperature. The obtained slurry was dried overnight at 100 °C, and the resulting solid was calcined in air at 550 °C for 5 h. MoO_3 loading level was varied from 5 to 35 wt%.

The preparation of Ca promoted MoO_3/SiO_2 (MoO_3/Ca-SiO_2) is illustrated as an example. An amount of 1 g silica was impregnated in 3 ml aqueous solution of calcium nitrate solution (4–8 g/l) for 8 h at room temperature, followed by drying overnight at 100 °C and calcination at 550 °C for 5 h. The resulting materials was impregnated with 3 ml aqueous solution of ammonium heptamolybdate with required concentration, and then kept for 8 h at room temperature. The obtained material was dried overnight at 100 °C, followed by calcination at 550 °C for 5 h. In all alkaline earth metal promoted catalysts, the MoO_3 loading was 15 wt%, and the Ca/Mo molar ratio was varied from 0.05 to 0.2. The preparation of other alkaline earth metal modified catalysts was prepared in a similar procedure, and molar ratio of alkaline earth metal to Mo was 0.1.

2.2. DBT oxidation

Both decalin and cumene hydroperoxide (CR grade) were used without purification.

The oxidation of DBT was performed in a fixed-bed glass reactor (8 mm i.d.). Typically, the reactor was loaded with 0.2 g catalyst particles (the catalyst bed height was about 2 cm). The feed (1000 ppm DBT in decalin) was fed into the reactor at the reaction temperature by a syringe pump. The oxidation conditions were as follows: atmospheric pressure; WHSV, 30 h^{-1}; O/S molar ratio, 3; reaction temperature, 40–80 °C. The liquid products were collected every 60 min. The reaction was carried out for 4 h. In our study, only DBT sulfone was detected, and no DBT sulfoxide was found. Both feed and product were analyzed on an Agilent-6890+ gas chromatograph equipped with an FID using an HP-5 capillary column (5% phenyl methyl polysiloxane, 30.0 m × 320 μm × 0.25 μm).

2.3. Characterization

X-ray powder diffraction (XRD) patterns of catalysts were collected on a D/max-2400 diffractometer using Cu-Kα radiation.

3. Results and discussion

The oxidation of DBT by CHP is represented in Scheme 1. The product from the oxidation of DBT was DBT sulfone, whereas CHP was transformed to 2-phenyl-2-propanol after donating the oxygen atom. These compounds were confirmed by GC–MS. It was found that no oxidation of DBT was observed in the absence of the catalyst.

3.1. MoO_3/SiO_2

Fig. 1 shows DBT conversion in the oxidation over Mo/SiO_2 catalysts at various MoO_3 loadings at 70 °C, WHSV 30 h^{-1} and O/S molar ratio 3.0. With increasing MoO_3 loading level, the conversion of DBT increased initially and then decreased. A maximum conversion of DBT (82%) was observed at a MoO_3 loading of 15 wt%. The highest activity may be attributed to the monolayer dispersion of MoO_3 on SiO_2 at 15 wt%. The decrease in the activity of the catalyst at higher MoO_3 loading may be attributed to the aggregation of MoO_3 particles on SiO_2 [24]. Poor dispersion reduces the coordination of Mo–O bond to SiO_2, leading to a lowered polarity of Mo–O bond and the decreased ODS activity.

Fig. 2 shows DBT conversion as a function of temperature over MoO_3/SiO_2 catalysts with various MoO_3 loadings. Maximum DBT conversions were observed at 70 °C for all loading levels. The increase of DBT conversion with increasing reaction temperature is

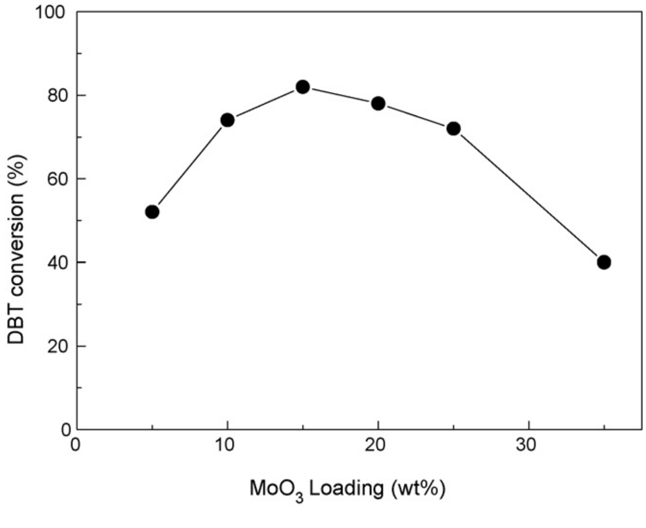

Fig. 1. Variation of DBT conversion with MoO_3 loading in the oxidation over MoO_3/SiO_2 catalysts.

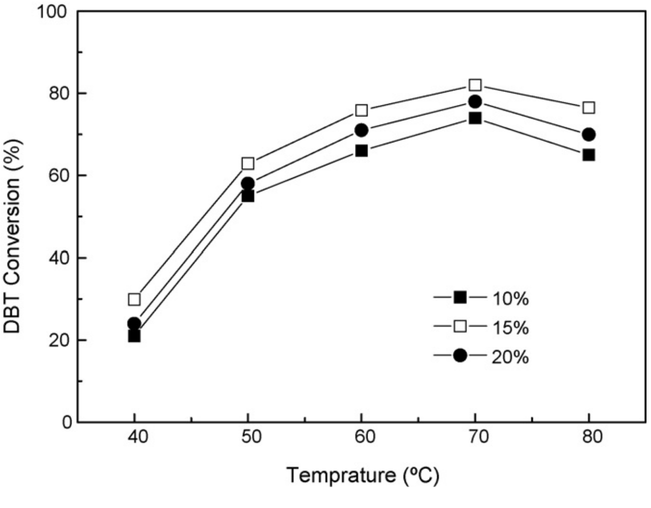

Fig. 2. Oxidation activities of DBT as a function of temperature over MoO_3/SiO_2 catalysts at various MoO_3 loading.

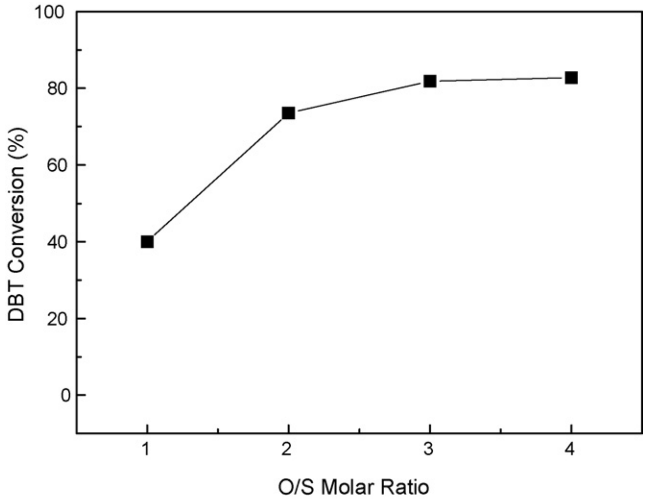

Fig. 3. Oxidation activities of DBT over MoO_3/SiO_2 catalyst at various O/S ratios.

due to the enhanced reaction kinetics. Because all three catalysts showed decreased ODS activity at temperatures over 70 °C, the decrease in DBT conversion might be related with the increased decomposition of CHP at high temperatures.

The effect of O/S molar ratio on DBT conversion was investigated at 70 °C and WHSV 30 h^{-1}. Stoichiometrically, 2 mol of CHP is required for converting 1 mol of DBT to its sulfone. As shown in Fig. 3, DBT conversion increased with the increase of O/S molar ratio until 3.0. This ratio is higher than the stoichiometric O/S molar ratio. The difference may be attributed to the thermal decomposition of CHP. When the O/S molar ratio was over 3.0, DBT conversion was leveled off, probably due to the limitation of residence time in the fixed-bed.

3.2. MoO_3/SiO_2 modified by alkaline earth metals

Malka and Tatibouët [25] reported that Ca was a promoter of MoO_3/SiO_2 catalyst in the oxidation reaction of methanol. In the present study, several alkaline earth metals were used to modify MoO_3/SiO_2 catalysts in DBT oxidation. Fig. 4 shows that the activity of catalysts for oxidation of DBT with CHP decreased in the order: $MoO_3/Ca\text{-}SiO_2 > MoO_3/Ba\text{-}SiO_2 > MoO_3/SiO_2 > MoO_3/Sr\text{-}SiO_2 > MoO_3/Mg\text{-}SiO_2$. Moreover, the highest DBT conversion was obtained at 60 °C for $MoO_3/Ca\text{-}SiO_2$ and $MoO_3/Ba\text{-}SiO_2$, whereas at 70 °C for MoO_3/SiO_2, $MoO_3/Sr\text{-}SiO_2$, and $MoO_3/Mg\text{-}SiO_2$. Both Ca and Ba significantly improved the performance of MoO_3/SiO_2 catalyst in the oxidation.

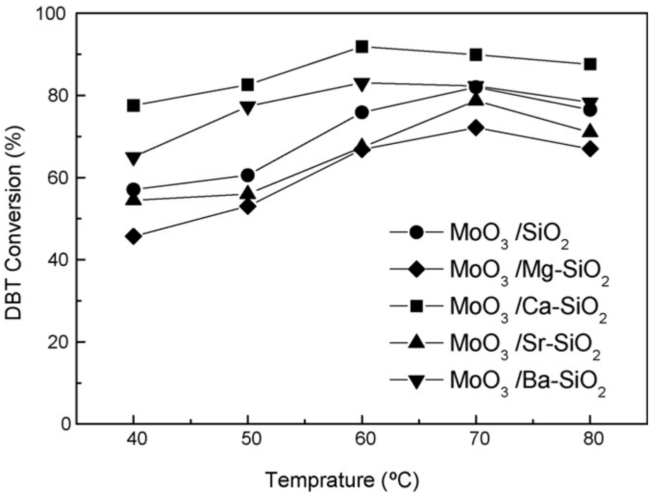

Fig. 4. Catalytic performance of MoO_3/SiO_2 modified by various alkaline earth metals in DBT oxidation as a function of temperatures.

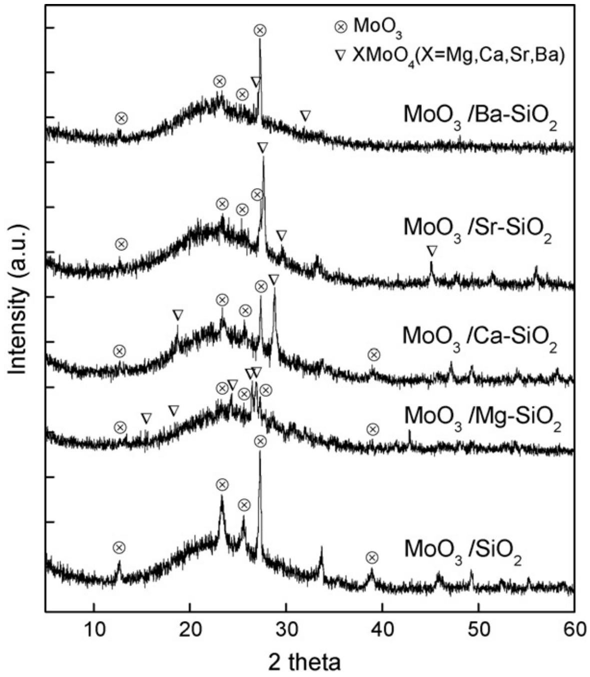

Fig. 5. XRD patterns of MoO_3/SiO_2 modified by various alkaline earth metals.

According to Wachs and coworkers [26], molybdenum oxide supported on silica was a typical example of poorly dispersed catalyst, because molybdenum oxide, such as MoO_3, and silica are considered to have an acidic character, thus weak interaction between molybdenum oxide and silica is expected. Since alkaline earth metals possess strong basic characters, it is therefore possible to improve the dispersion of MoO_3 on silica by the introduction of alkaline earth metals. On the other hand, the presence of alkaline earth metals may lead to the formation of molybdates, which are not active phases in DBT oxidation. The XRD patterns of the modified MoO_3/SiO_2 (Fig. 5) indicate the appearance of various molybdates. It is reported that Ca can act as germination sites towards molybdenum oxide [25], which might be responsible for the improved dispersion of Mo oxides and enhanced oxidation performance of $MoO_3/Ca\text{-}SiO_2$. BaO react readily with CHP to form complex [27], suppressing CHP decomposition and leading to an improved performance of $MoO_3/Ba\text{-}SiO_2$. Among the alkaline earth metals, Ca modification most significantly improved the performance of MoO_3/SiO_2. Therefore, the modification of Ca was investigated in more detail.

Fig. 6 shows the oxidation activity of DBT in presence of $MoO_3/Ca\text{-}SiO_2$ catalysts at various Ca/Mo ratios. The highest DBT conversion (95%) was observed at Ca/Mo ratio of 0.05. At higher Ca/Mo ratio, such as 0.1, DBT conversion was decreased slightly. Crystalline molybdenum oxide (MoO_3) is the dominant species at higher loadings and stable against dehydration [28]. The polarity of Mo–O bond is the main factor that affects the activity in oxidation. Increasing the polarity of Mo–O bond leads to an increased electrophilicity of peroxy oxygen. Ca cations at low Ca/Mo ratio may increase the polarity of Mo–O bond and thus the activity of CHP on $MoO_3/Ca\text{-}SiO_2$ catalyst. At high Ca/Mo molar ratio, however, calcium molybdate ($CaMoO_4$) may

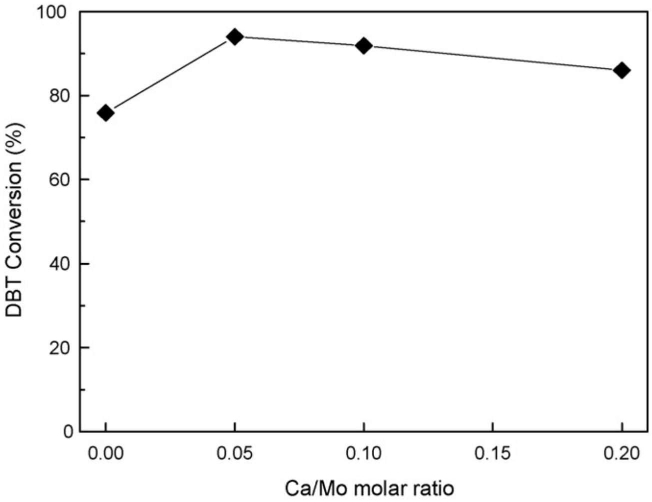

Fig. 6. DBT conversion over MoO_3/Ca-SiO_2 with Ca/Mo atomic ratio.

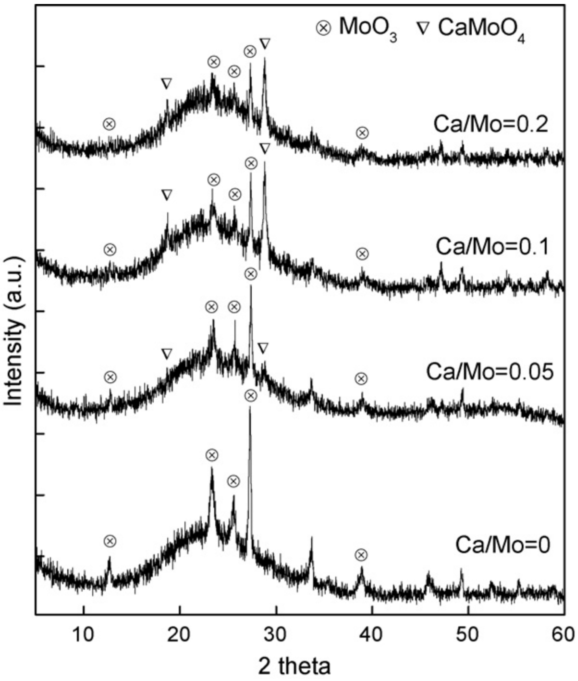

Fig. 7. The XRD patterns of MoO_3/Ca-SiO_2 catalysts with different Ca/Mo ratios.

generate on the support [25]. Fig. 7 indicates that only the diffraction peaks of crystalline MoO_3 were present in MoO_3/SiO_2. With the introduction of Ca, $CaMoO_4$ appeared, and the peak intensity of $CaMoO_4$ was increased with increasing Ca/Mo ratio. The decreased ODS activity at high Ca loading may be attributed to the formation of $CaMoO_4$, which is not active in DBT oxidation (Fig. 6).

For comparison, 4,6-DMDBT was oxidized under the same conditions for DBT oxidation over MoO_3/Ca-SiO_2 (MoO_3 15%, Ca/Mo ratio 0.05). The results show that the conversion of 4,6-DMDBT was lower than that of DBT in the temperature range of 40–80 °C (Fig. 8). This was consistent with the results reported by Wang et al. [21]. This may be due to steric hindrance of the methyl groups in the molecule of 4,6-DMDBT, which adsorbs on the surface of the catalyst prior to oxidation.

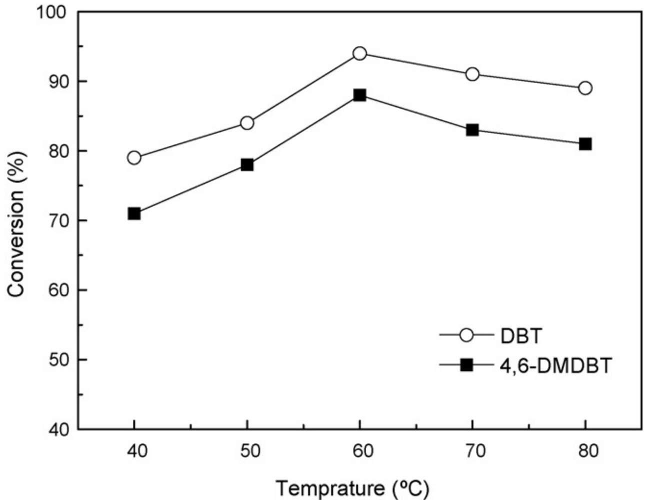

Fig. 8. Comparison in oxidation reactivity of DBT and 4,6-DMDBT over MoO_3/Ca-SiO_2 at various temperatures.

4. Conclusions

CHP is a suitable oil-soluble oxidant, which can be used to oxidize DBT over silica supported MoO_3-based catalysts in a fixed-bed reactor. When MoO_3 loading was 15 wt%, DBT conversion reached 82% at 70 °C, WHSV of 30 h^{-1} and O/S molar ratio of 3. Modification of MoO_3/SiO_2 by alkaline earth metals could have positive or negative effects on the performance in DBT oxidation. The activities in DBT oxidation decreased in the order: MoO_3/Ca-SiO_2 > MoO_3/Ba-SiO_2 > MoO_3/SiO_2 > MoO_3/Sr-SiO_2 > MoO_3/Mg-SiO_2. The introduction of Ca cation not only increased the conversion of DBT, but also decreased the optimal reaction temperature. When the Ca/Mo ratio was 0.05, the DBT conversion could reach 95%. 4,6-DMDBT showed lower oxidation activity than DBT, probably due to the steric hindrance of methyl groups in the molecule of 4,6-DMDBT.

Acknowledgements

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