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Preparation, characterization, and catalytic performances of cobalt catalysts supported on KIT-6 silicas in oxidative desulfurization of dibenzothiophene



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HIGHLIGHTS

• Catalysts of cobalt supported on modified KIT-6 silica were prepared and applied to oxidative desulfurization (ODS).

• A novel Co/KIT-6 catalysis system was developed and evaluated with better DBT removal.

• Response surface methodology was used to optimized the main variables for Co/KIT-6 catalytic ODS system.

• Kinetics of ODS correlated well with the pseudo-first-order equation.

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ABSTRACT

Sulfur-containing compounds in oils are harmful to the ecosystem whose cost-effective removal is still a challenge. In this study, novel heterogeneous catalysts of cobalt supported on KIT-6 mesoporous silicas were prepared and evaluated for oxidative desulfurization (ODS) under ambient conditions using cyclohexanone peroxide (CYHPO) as the oxidant. The model oil was obtained via dissolving DBT in the n-octane. The conventional wet impregnation method was applied for the preparation of the catalysts, and cobalt nitrate was used as the precursor. The catalysts were characterized by XRD, N2-physisorption, FT-IR, TGA, SEM/TEM and XPS. Then their catalytic activities in total oxidation of dibenzothiophene (DBT) were evaluated at various conditions. DBT conversion by this heterogeneous ODS system reached 98.68%. Co/KIT-6 catalysts showed high ODS activity due to Ia3d mesoporous structure resulting in better cobalt dispersion, higher activity of Co, and faster diffusion of reactant and products. The Box-Behnken design showed that the optimum values for the conversion of DBT were 93 °C (oxidation temperature), 1.6×10^{-1} g (catalyst amount) and 5.7 (O/S molar ratio), respectively. The inhibitory effect of quinoline on ODS was higher than carbazole and indole, adding quinoline into model oil under same conditions led to a decrease of the conversion of DBT from 98.68% to 65.67% when the concentration of quinoline increased from 160 ppm to 4845 ppm. Kinetics data correlated well with the pseudo-first-order equation. These data showed that this novel Co/KIT-6 catalysis system has the potential to be applied in ODS from oils.

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1. Introduction

Recently, increasingly stringent regulatory limitations on sulfur level in oils has been paid close attention. Considering

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environmental impact, sulfur level in oils must be lower than 10 ppm in many developed countries [1,2]. Some highly refractory molecules such as DBT, 4,6-DMDBT and their alkylated derivatives in oils are difficult to be removed by traditional hydrodesulfurization due to their large molecular size and substituent group's steric hindrance [3]. In order to meet the requirement on sulfur level, as well as lowering the investment cost, oxidative desulfurization (ODS) which used as a supplement to HDS shows great advantages

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in which catalyst support plays a key role and was investigated extensively [4].

Zeolites [5], carbon [6], oxides [7], mixed oxides [8], and mesoporous materials like SBA-15 [9] and MCM-41[10] were studied as supports for ODS catalysts. SBA-15 supported Ti and CoMo catalysts exhibited very high activities for sulfur removal. Kim et al. [9] reported on Ti-SBA-15 of various Si/Ti ratio for ODS of diesel fuel and suggested that Ti containing SBA-15 supported catalysts with the highest Ti contents (>2.8 mol%) and largest pore sizes (>7.3 nm) were highly active catalysts for ODS reactions. Cedeño-Caero et al. [11] reported similar results using catalysts of titanium oxide supported on SBA-15.

Li et al. [10] indicated that MCM-41 can be used as quite effective support for oxidative desulfurization catalysts. Through hydrothermal sol-gel method, Wang et al. [12] synthesized mesoporous silicas with structures of SBA-15, MCM-41 and MCM-48 aiming to obtain pure mesoporous silica materials with diverse structures and surface properties. All mesoporous silicas showed high sulfur removal ability, which increased in the order of SiS15C < SiS15E < SiM41C < SiM41E < SiM48C < SiM48E, while their surface areas increased in the same order. It is supposed that a combination of large surface areas, sufficient active sites and uniform pore-size distribution big enough to allow diffusion of large compound molecules, together with the presence of high stability and mild acidity, result in superior ODS performance.

Except for finding a suitable support, the modification of support by metal is also a important way to improve the catalytic behavior of catalysts. Cobalt based materials have gained a remarkable interest due to their quite high efficiency as catalysts in some crucial processes, such as NO_x removal, hydrodesulfurization and partial oxidation reaction. They are also regarded as a proper alternative to the expensive noble metal based catalysts for the poisonous compounds elimination. And it has been proved that the catalytic properties of such catalysts depend upon the dispersion and interaction of the Co species with the support [13]. Generally, the contents of cobalt dispersion will lead to the different number of catalytic active sites. Therefore, the preparation of cobalt species with suitable size and their stabilization under the specific reaction conditions is of great importance in the heterogeneous catalysis.

Recently, cubic mesoporous silica material with >5 nm pore diameter have attracted intensive attention for potential applications in catalysis area. F. Kleitz and coworkers [14] proposed a new synthesis method to high-quality cubic mesoporous Ia3d silica (named KIT-6), using copolymer (EO20PO70EO20) and nbutanol at low acid conditions. This mesoporous silica material, KIT-6, possesses large readily tunable pore sizes with thick pore walls, high specific surface area, high hydrothermal stability and large pore volume. Soni et al. [4] reported that modified KIT-6 supported catalysts exhibited higher activities for the removal of thiophene than γ -Al₂O₃ and SBA-15-supported catalysts. However, just like SBA-15, pure KIT-6 silica is devoid of Lewis and Brönsted acid sites. The improvement in acidity of mesoporous silicas was made through preparation of metal modified KIT-6 materials, which has important implications for the conversion of the refractory molecules, especially of 4,6-DMDBT [15]. Compared to conventional SBA-15 and MCM-41 silica, KIT-6 is expected to be vastly superior to materials with one or two-dimensional channels attribute to better dispersion of catalyst and quicker diffusion of reactants and products during catalytic reaction in the 3-D interconnected mesopores. And the metal modified KIT-6 silicas have been successfully applied in catalysis area and showed higher catalytic activity than traditional silicas. These properties make cobalt modified KIT-6 catalysts more suitable for the ODS of refractory sulfur compounds. However, until now, preparation and catalytic ODS application of Co/KIT-6 catalysts have, to our best knowledge, not been reported.

In this present research, the novel Co/KIT-6 heterogeneous catalysts were prepared and applied in ODS from oils. The model oil was obtained via dissolving DBT which is the most typical sulfur compound in the n-octane. The carrier and catalysts were characterized by various techniques. Catalytic evaluations for ODS of DBT were carried out on Co modified KIT-6 catalysts. The effects of catalyst loading, reaction temperature, molar ratio of CYHPO/DBT, the weight of catalyst and dibutyl phthalate were investigated. Comparison of ODS activity was done with the comparison of different concentration of sulfur removal with reaction time, and the comparison of absence of quinoline and existence of quinoline for the conversion of DBT respectively. The Box-Behnken design was selected to determine the optimum sulfur removal, and also to explain the connection between the conversion of DBT and three parameters: reaction temperature, catalyst amount and molar ratio of CYHPO/DBT. Finally, the kinetics of the process were proposed.

2. Experiments

2.1. Materials

All the reagents were of analytical grade and used as such without further purification. DBT ($C_{12}H_8S$, AR, 98%, Aladdin, China) was used as a model sulfur compound; Quinoline (C_9H_7N , AR, 99%, Aladdin, China) was used as a model nitrogen compound; n-octane (C_8H_{18} , AR, 96%) was obtained from Tianjin Kemiou Chemical Reagent Co. Ltd. (China); cyclohexanone peroxide (CYHPO, $C_{12}H_{22}O_5$, 50%) and N,N-dimethylformamide (DMF, C_3H_7NO , AR, 99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used as oxidant and extracting agents, respectively.

2.2. Catalyst preparation and characterization

KIT-6 material was synthesized by following the published procedure [4] using polymer surfactant micelles as structure directing agent under mild acidic conditions. The catalysts with Co loading ranging from 2 to 11 wt% were prepared via incipient wetness impregnation method using KIT-6 material as carrier and appropriate amount of cobalt nitrate. According to the weight percent requirement of Co(NO₃)₂·6H₂O, 12.5 g cobalt nitrate was dissolved in 50 mL of distilled water to prepare an aqueous solution of cobalt nitrate with a concentration of 0.25 g/ml. 5 g KIT-6 support was added to absolute ethanol and aqueous solution of cobalt nitrate, The volume ratio of absolute ethanol to aqueous solution of cobalt nitrate was 10:1. After 2–3 h stirring, The solid products were obtained by filtration, washed with deionized water and dried at 60 °C overnight. Calcination was carried out in static air at 550 °C for 6 h. The catalyst was denoted as catalyst Co/KIT-6 in this study.

The support and catalysts were characterized by X-ray diffraction (XRD, Rigaku Dmax 2500 diffractometer equipped with a monochromator and a Cu target tube) to research the crystal structure of the samples. Textural properties of the samples were attained by nitrogen-sorption analysis (Micromeritics Tristar II 3020). The surface and internal morphology of the samples were observed by using scanning electron microscope (SEM, JEOL JSM-6700) and transmission electron microscopy (TEM, JEM-3010). The Fourier Transform Infrared Spectroscopy (FTIR) of the samples, diluted with KBr and pressed into a pellet, were recorded on a FTIR spectrometer (FT-IR, nIcoLET 6700). The cobalt contents of the catalyst were measured by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, USA), and the thermogravimetric analysis were performed using STA449 c TGA.

2.3. Catalytic performance studies

The DBT was dissolved into n-octane to make a stock solution with the sulfur content of 400 ppm. Oxidation of DBT with CYHPO was carried out in the Erlenmeyer flask (250 mL) at an atmospheric pressure. Firstly, a certain amount of CYHPO (molar ratio of CYHPO/DBT of 4) were added into the Erlenmeyer flask, Then about 0.1 g of the catalyst and 20.0 ml of model oil were also added into the middle of the reactor respectively. The reactor was heated to different constant temperature (60 °C-130 °C) with the help of oil bath and simultaneously stirred magnetically. The resulting mixture obtained after 40 min of reaction were cooled down and separated. Subsequently, the clear mixtures were extracted with 10 ml DMF and repeated two times in order to make sure that sulfur was completely removed. Following the end of each reaction, the separated catalysts could be reused again after being washed with ethanol and dried in vacuum oven at 60 °C for 12 h [16]. All experiments were repeated in three times to ensure the reproducibility of results.

2.4. Analysis

DBT or quinoline concentration in samples after catalytic oxidation reaction were analyzed by a gas chromatograph (GC) (Agilent 6890 N, USA) using a HP-5 capillary column (30 m × 0.32 mm × 0.25 μ m film thickness) equipped with a flame ionization detector (FID, HP6890), using highly purified nitrogen(mass concentration \geq 99.9999%) as the carrier gas at a flow rate of 1 ml/min.

The conversion of DBT was calculated to evaluate the performance of the catalyst Co/KIT-6. The reaction equations for oxidative desulfurization was based on the following equation:

$$\eta = [(C_0 - C)/C_0] \times 100\% \tag{1}$$

In which η represents the DBT conversion rate, C_0 and C correspond to the initial and final concentration of DBT in model oil, respectively (Untis: ppm).

The yield rate of model oil was evaluated according the following equation:

$$\varepsilon = \left[(m_0 - m)/m_0 \right] \times 100\% \tag{2}$$

where ε is the yield rate of model oil, m_0 and m represent the initial and final weight of the model oil, respectively (Untis: g).

2.5. Box-Behnken design

In order to study the effect of main operating variables on catalytic ability of Co/KIT-6, Box-Behnken design (BBD) with three effective variables: reaction temperature, X₁ (60 °C–130 °C), catalyst amount, X₂ (2.0×10^{-2} – 2.5×10^{-1} g) and molar ratio of CYHPO/DBT, X₃ (1.0–8.0) was used to obtain the optimum reaction conditions for maximum conversion of DBT. With statistical analysis of the related experimental data, an empirical model in the form of quadratic equation was used for the optimization procedure.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$$
(3)

where Y is the response variable; β_0 , β_i , β_{ii} and β_{ij} are intercept coefficient, linear coefficient, quadratic coefficient and interaction coefficient, respectively; X_i and X_j are independent variables that determine the value of Y. The statistical significance of the coefficient and the second-order model were analyzed by F-test and P-value, respectively. Besides, the interactions of the independent variables were studied by constructing the response surface and the contour plot [17].

3. Results and discussion

3.1. Structural characterization

The intensity of the characteristic peaks due to (211) and (220) planes were clearly observed in these materials, as shown in Fig. 1A. The XRD pattern clearly showed that the material was well ordered mesoporous structure and belonged to mesoporous bicontinuous cubic space group Ia3d [18]. The unit cell constant (a₀) and d-spacing values for these materials were displayed in Table 1. Nitrogen adsorption-desorption isotherms for the cobalt-containing and the parent KIT-6 materials were exhibited in Fig. 1B, and other derived data were presented in Table 1. The average mesopore diameter decreased with the increase of Co loading (Table 1). No changes were observed in the general shape of the hysteresis loop or in the category of isotherm indicating that the carrier pore structure was retained after Co deposition. Significant decrease in BET surface area and pore volume could attributed to high extent of cobalt promoter location inside the support pores.

The IR spectra of KIT-6 and Co/KIT-6 with varying Co loading were depicted in Fig. 1C. Both spectrum of parent and Co modified KIT-6 exhibit intensive absorption bands at ~1085, 799 and 1660 cm⁻¹, which arise from the silica host matrix [18]. The bands at around 960 cm⁻¹ appear to be due to Si-OH and Si-O-stretching vibrations [19]. But a simultaneous slight shifting of the peaks at around 1085 and 960 cm⁻¹ was observed after cobalt modification. The reason might be due to the existence of strong interaction between the loaded cobalt oxide species and the silica support [18]. The thermostability analysis of KIT-6 and Co/KIT-6 were shown in Fig. 1D. The template began to break down at around 300 °C and was decomposed completely when the temperature beyond 550 °C. The better stability of 5% Co catalyst may be attributed to the stronger combination actions between the 5 wt% Co promoter and the support when compared to other catalysts.

The surface and internal morphologies of KIT-6 and Co/KIT-6 were shown in Fig. 2. SEM pictures showed that the KIT-6 motes have a spherical matrix with smooth surface and motes size of 1-5 µm. The Co modified material exhibited aggregates of rocklike morphology. There was no definite shape given for any particles but the edges seemed to be sharp. TEM graphs further verified that Co/KIT-6 catalyst possessed Ia3d cubic structure as does parent KIT-6 [19]. The places with darker contrast might be assigned to the existence of cobalt oxide motes with different dispersion, and no significant agglomerations were observed on support surface indicating that Co was well dispersed on the silica surface and in the mesopores. These observations agreed with the XRD and N₂ adsorption results. The loading amounts of Co on support surface were obtained from XPS analysis. It can be seen from Table 1 that the impregnation amounts were a little lower than theoretical value, which might be attributed to the processes of migration and the agglomeration of cobalt oxide species in mesopores, thus decreasing the loading amounts on support surface.

3.2. Catalytic studies

3.2.1. Effect of cobalt loading (%)

In order to establish the optimum loading amount of Co on KIT-6 support, catalysts were studied with variation of cobalt concentration from 0 to 11 wt%. The results were presented in Fig. 3A. It can be seen that the conversion of DBT was only 82.5% in the absence of CYHPO, which was similar to pioneering studies [17]. It also suggested that the high catalytic activities could be exhibited only when KIT-6 carrier was modified with metal Co. Pure KIT-6 support cannot show catalytic activity, it was possibly due to the fact that Co promoter could contribute to increase in anion



Fig. 1. Characterization: **(A)** Wide-angle XRD pattern of supported Co catalysts:(a) 0% Co, (b) 2% Co, (c) 5% Co, (d) 8% Co, (e) 11% Co. **(B)** Nitrogen adsorption-desorption isotherms of supported Co catalyst: (a) 0% Co, (b) 2% Co, (c) 5% Co, (d) 8% Co, (e) 11% Co. **(C)** FT-IR spectra of supported Co catalysts: (a) 0% Co; (b) 5% Co; (c) 8% Co; (d) 11% Co. **(D)** TGA analysis of supported Co catalysts.

Table 1

Structural and textural parameters of mesoporous Co/KIT-6 at various Co contents.

Co (wt%)	BET (m ² /g)	$V_{p} (cm^{3} g^{-1})$	$V_{mic} (cm^3 g^{-1})$	D _{pores} (nm)	a ₀ (nm)	δ (nm)
0 (0) ^x	928	0.67	0.08	8.1	20.4	12.3
2	762	0.54	0.07	5.7	20.4	14.7
5 (4.36) ^x	670	0.32	0.05	5.3	20.4	15.1
8	667	0.21	0.03	5.2	20.4	15.2
11	654	0.15	0.02	5.2	20.4	15.2

x = the Co wt% by XPS.

BET-specific surface area, V_p-pore volume, V_{mic}-microporous pore volume, D_{pores}-average mesopore diameter, a₀-unit cell parameter calculated from the formula $a_0 = d_{211} \times 6^{1/2}$, δ -pore wall thickness calculated from the formula $\delta = a_0$ -D_p.

vacancies [4], which are the active sites for ODS. However, The conversion of DBT was lowered with further increasing of Co loading. This was probably because increasing Co loading produced more polymerization of Co, leading to decrease of the catalytic activity especially in catalytic reaction as discussed by Gnanamani et al. [20]. Additionally, the decrease in the activity of catalyst at highest loading of Co may be attributed to the aggregation of Co oxides particles on KIT-6 support. Consequently, 5 wt% Co promoter concentration loading gave the best result for the conversion of DBT.

3.2.2. Effect of reaction temperature

The experiment under various temperatures were carried out at given conditions. As can be seen in Fig. 4A, The removal of substrate enhanced dramatically from 84.16% to 97.48% in 40 min with the increasing reaction temperatures from 40 °C to 100 °C. Higher temperature not only speeded up the movement of molecular, but also promoted the desorption of sulfone (DBTO₂) from active sites of the catalyst [21]. DBTO₂ would be strongly adsorbed on the surface of catalyst at lower temperature, preventing further



Fig. 2. SEM and TEM images of : (A and C) KIT-6, (B and D) Co/KIT-6 catalyst.

adsorption of substrate to be oxidized and leading to low conversion of DBT [12].

However, the conversion of DBT decreased sharply from 97.48% to 81.29% when reaction temperature was over 100 °C. This was probably due to the low thermostability of CYHPO at higher temperature. Qiu et al. [17] also found that the decomposition rate of CYHPO was enhanced significantly at higher temperature.

Too high temperature would also cause model oil lost. Fig. 4A demonstrated that the yield rate of model oil decreased with increasing of reaction temperature. Obviously, it attributed to the volatilization and gasification of model oil at higher temperature. Hence, the reaction temperature of 100 °C was recommended.

3.2.3. Effect of oxidant/sulfur molar ratio

The effect of the amount of CYHPO on the catalytic oxidative desulfurization of model oil under various CYHPO /sulfur (O/S) molar ratios at 100 °C catalyzed by Co/KIT-6 was shown in Fig. 4B. 1 mol DBT usually need 2 mol CYHPO when the substrate all convert to corresponding sulfone in theory, but the actual results showed that the removal of sulfur can only reach 85.25%, because the oxidant decomposed inevitably in the actual oxidation reaction [22]. The removal of sulfur could reach 98.68% when the equivalent of cyclohexanone was 4. It can be seen from the data of the experiments that when the CYHPO/DBT molar ratio was increased from 1:1 to 8:1, the removal of DBT increased from 81.16% at O/S = 1 to 98.83% at O/S = 4 in 40 min, when increasing the amount of CYHPO slightly. Further increasing the O/S molar ratio to 6 and 8, the conversion of DBT didn't change too much since the dynamic phase equilibrium was reached already. Besides, the effect of DBP on oxidizing ability of CYHPO was also investigated when O/S ratio remain unchanged, it can be seen that the DBP has little promotion effects on DBT conversion and the yield rate.

3.2.4. Effect of amount of catalyst and dibutyl phthalate

The effect of catalyst amount on oxidation of DBT was studied varying the catalyst content from 2.0×10^{-2} to 2.5×10^{-1} g and

the conversion-catalyst amount (g) plots were shown in Fig. 4C. Conversion was improved from 83.06% to 97.48% as the catalyst weight increased from 2.0×10^{-2} g to 1.0×10^{-2} g. Because more active sites were provided and more DBT would be adsorbed on catalyst active center, which would make sulfur more easily to be oxidized and then removed. The reaction rate could not be further improved obviously when the catalyst amount was increased from 1.5×10^{-2} g to 2.5×10^{-2} g, likely because excess Co/KIT-6 would supply excess active center sites that the system is required and reactants are limiting at higher catalyst amount, thereby the conversion of DBT did not change appreciably. Similar results were also observed by other researches [16,22]. Moreover, catalyst amount had little impacts on the yield rate of model oil. Based on these results, 1.0×10^{-2} g was suitable in further experiments.

Pure CYHPO is not very stable and it is generally store in dibutyl phthalate to ensure the use safety. The effect of DBP on oxidizing ability of CYHPO was also studied at different concentration of CYHPO using DBP as diluent (see Fig. 4D). The product yield was increased with increasing in DBP contents whereas the DBT conversion decreased and became 81.01% when the mass concentration of CYHPO was only 10%. This phenomenon was due to the dilution of CYHPO by excess dibutyl phthalate.

3.3. Statistical analysis and optimization by Box-Behnken design

In the Box-Behnken design, 17-experimental runs were carried out at random orders for the optimization of DBT removal in the catalytic oxidation process. Table 2 showed the data resulting from the related experiments, in which three variables were selected: reaction temperature (X₁), catalyst amount (X₂) and molar ratio of CYHPO/DBT (X₃). The experimental results were analyzed by RSM to obtain an empirical quadratic model for the best response. In this process, the reaction time remained unchanged at 40 min. The estimated response seemed to have a functional relationship only near the central points or in a local region of the model [23]. The final second-order equation was attained to explain the



Fig. 3. Influences of cobalt loading and quinoline content on the conversion of DBT: **(A)**: Effect of cobalt loading. (a) DBT was extracted without oxidation; (b) DBT was oxidized by CYHPO without catalyst; (c) DBT was catalyzed by pure KIT-6 support; (d) DBT was catalyzed by 2 wt%Co/KIT-6; (e) DBT was catalyzed by 5 wt%Co/KIT-6; (f) DBT was catalyzed by 8 wt%Co/KIT-6; (g) DBT was catalyzed by 11 wt%Co/KIT-6. **(B)**: Effect of quinoline content. Conditions: $M_{catalyst} = 0.1$ g, $V_{model gasoline} = 20$ mL, CYHPO/DBT = 4(mol/mol) and T = 100 °C.

mathematical relationship between three independent variables and the dependent responses (Y) and is represented by:

$$\begin{split} Y &= 98.60 - 1.24X_1 + 1.50X_2 + 3.37X_3 - 0.67X_1X_2 \\ &- 0.33X_1X_3 - 0.067X_2X_3 - 11.86X_1^2 - 3.90X_2^2 - 4.95X_3^2 \end{split} \tag{4}$$

The consequences of analysis of variance (ANOVA) showed in Table 3 indicated the successful fitting of the laboratorial data to the quadratic model. The degree of freedom value (F-test) was 385.30 and the corresponding p-value was <0.0001 for this model, which indicated the model was significant. The large value of F indicated that majority of the variation in the response could be explained by the assumed second order polynomial (Eq. (3)). A low p-value (p < 0.05) implied that the obtained model was statistically significant for DBT conversion. Therefore, the model ensured an accurate representation of the laboratorial data. The value of adjusted R² and R² were 0.9954 and 0.9980, respectively, which meant that experimental and predicted sulfur removal efficiencies were accordance to a very great extent. The comparison between experimental and predicted results of DBT conversion (%) was showed graphically with a 45 °C-line in Fig. 5A.

The importance of each of the three independent parameters (reaction temperature, catalyst amount and O/S molar ratio) on sulfur removal was decided by illustrating the response surfaces contours and three-dimensional (3D) plots. The resulting of both contours and 3D surface response plots as a function of two variables, (a) reaction temperature and catalyst amount (O/S = 4.5), (b) reaction temperature and O/S molar ratio (cat. amount = 1.4×10^{-1} g) and (c) catalyst amount and O/S molar ratio (T = 95 °C) are exhibited in Fig. 6A, B and C, respectively.

Response optimization technique helped to identify a combination of input variable settings that jointly optimized a single response or a set of responses. Joint optimization need to satisfy the requirements for all responses in the set, which was measured by the composite desirability [24]. The particular desirability of both the seal strength and the variance was 1.0, which implied that the composite or combined desirability of the two variables was also 1.0. To obtain this desirability smoothly, the factor levels were fixed at the values given under maximize the DBT conversion. The factor setting could be adjusted to get the initial optimization. The optimum values of three independent variables were attained considering the starting values of oxidation temperature, catalyst amount and O/S molar ratio of 100 °C, 1.0×10^{-1} g and 4, respectively. The maximum sulfur removal of 99.36% could be obtained by choosing the optimum oxidation temperature of 93 °C, catalyst amount of 1.6×10^{-1} g with molar ratio of CYHPO/DBT of 5.7. Thus, RSM was successfully applied in the optimization of catalytic oxidative desulfurization experiment to maximize the conversion of DBT after comprehensive consideration of the related affecting factors

3.4. Comparative experiments

Comparative experiments including the comparison of different concentration of sulfur removal with reaction time, and the comparison of absence of quinoline and existence of quinoline for the conversion of DBT respectively were investigated. As plotted in Fig. 5B, the sulfur removal increased fast at first and then increased slowly to the maximum at a certain time. But low sulfur model oil was oxidized faster than high sulfur model oil, the model oil containing 50 ppm sulfur was oxidized completely at 15 min while the removal of 150 ppm sulfur and 400 ppm sulfur were only 88.62% and 78.38% at 15 min, respectively. A reason for the results might be that more sulfone were adsorbed on active centers of catalyst in high sulfur oil reaction system, which would inhibit the adsorption and oxidation of DBT on active centers, and consequently reducing the removal rate of sulfur. Comparatively, the yield rate of model oil containing different concentration of sulfur changed less significantly.

According to Caero et al. [25], the inhibitory effect of quinoline on oxidative desulfurization activity was higher when compared with carbazole and indole. The effects of quinoline on sulfur removal was shown in Fig. 3B. Sulfur removal was 98.68% when nitrogen was actually absent in the evaluated feedstock (the data not shown in Fig. 3B). And it decreased from 98.68% to 65.67% when the concentration of quinoline increased from 160 ppm to 4845 ppm. Nitrogen removal was close to 100% as contents of quinoline were gradually increased. The reason might be that nitrogen compounds were more prone to be removed from model oil than sulfur compounds, considering the very same oxidative desulfurization conditions.

3.5. Kinetics of ODS reaction

Experiments to attain kinetic parameters of the oxidation of DBT were performed using Co/KIT-6 as catalyst. Reaction kinetics were great significant parameters in oxidative desulfurization.



Fig. 4. Influence of reaction conditions. **(A)** Effect of reaction temperature on the conversion of DBT. Conditions: $M_{catalyst} = 0.1$ g, CYHPO/DBT = 4.0(mol/mol), $V_{model \ gasoline} = 20$ mL, t = 40 min. **(B)** Effect of the molar ratio of CYHPO/DBT on the conversion of DBT. Conditions: $M_{catalyst} = 0.1$ g, $V_{model \ gasoline} = 20$ mL, t = 40 min, T = 100 °C. **(C)** Effect of the catalyst Co/KIT-6 amount on the conversion of DBT. Conditions: CYHPO/DBT = 4.0(mol/mol), $V_{model \ gasoline} = 20$ mL, t = 40 min, T = 100 °C. **(D)** Effect of the conversion of DBT. Conditions: CYHPO/DBT = 4.0(mol/mol), $V_{model \ gasoline} = 20$ mL, t = 40 min, T = 100 °C. **(D)** Effect of concentration of CYHPO on the conversion of DBT. Conditions: $M_{catalyst} = 0.1$ g, CYHPO/DBT = 4.0(mol/mol), $V_{model \ gasoline} = 20$ mL, t = 40 min, T = 100 °C.

Table 2								
Experimental d	esigns and	actual and	predicted	response	values f	or the	Box-Behnken	ı design.

Observation	Coded values			Actual value	Actual values			Sulfur removal (%)		
	X1	X2	X3	X1	X2	X3	Actual	Predicted	Residual	
1	0	0	0	95.00	0.14	4.50	98.58	98.60	-0.016	
2	0	-1	1	95.00	0.02	1.00	84.95	84.81	0.14	
3	-1	1	0	60.00	0.25	4.50	86.88	86.24	0.64	
4	0	-1	1	95.00	0.02	8.00	91.94	91.69	0.25	
5	0	0	0	95.00	0.14	4.50	98.60	98.60	0.00	
6	0	1	1	95.00	0.25	8.00	94.41	94.55	-0.14	
7	1	0	-1	130.00	0.14	1.00	78.01	77.51	0.50	
8	0	1	-1	95.00	0.25	1.00	87.69	87.94	-0.25	
9	0	0	0	95.00	0.14	4.50	98.61	98.60	0.014	
10	0	0	0	95.00	0.14	4.50	98.60	98.60	0.00	
11	-1	-1	0	60.00	0.02	4.50	82.16	81.91	0.25	
12	1	1	0	130.00	0.25	4.50	82.19	82.44	-0.25	
13	-1	0	-1	60.00	0.14	1.00	78.94	79.33	-0.39	
14	0	0	0	95.00	0.14	4.50	98.60	98.60	0.00	
15	1	0	1	130.00	0.14	8.00	83.99	83.60	0.39	
16	-1	0	1	60.00	0.14	8.00	86.23	86.73	-0.50	
17	1	-1	0	130.00	0.02	4.50	80.13	80.77	-0.64	

Table 3

	(
Results of variance	(ANOVA) for the	conversion of DBT.

Source	SS ^b	DF ^b	MS ^b	$\mathbf{F}^{\mathbf{b}}$	P ^b	CE ^b
Model ^a	945.26	9	105.03	385.30	< 0.0001	
Temperature, X ₁	12.23	1	12.23	44.85	0.0003	-1.24
Catalyst amount, X ₂	17.97	1	17.97	65.92	< 0.0001	1.50
Molar ratio, X ₃	90.99	1	90.99	333.80	< 0.0001	3.37
X ₁ X ₂	1.77	1	1.77	6.49	0.0382	-0.67
X ₁ X ₃	0.43	1	0.43	1.57	0.2499	-0.33
X ₂ X ₃	0.018	1	0.018	0.067	0.8034	-0.067
X ₁ ²	591.80	1	591.80	2171.01	< 0.0001	-11.86
X ₂ ²	64.06	1	64.06	235.00	< 0.0001	-3.90
X ₃ ²	103.09	1	103.09	378.17	< 0.0001	-4.95
Residual	1.91	7	0.27			-1.24
Lack of fit	1.91	3	0.64	4891.35	< 0.0001	
Pure error	5.200E-004	4	1.300E-004			
Cor total	947.17	16	105.03			

^a R-Sq = 99.80%; R-Sq (adj) = 99.54%; R-Sq (pred) = 96.78%.

^b SS: sum of square; DF: degree of freedom of different source; MS: mean of square; F: degree of freedom; P: probability; CE: coefficient estimate.





Fig. 5. (**A**): The relationship of predicted and actual values. (**B**): Data of comparison experiments. Conditions: $M_{catalyst} = 0.1$ g, CYHPO/DBT = 4(mol/mol), $V_{model gasoline} = 20$ mL, T = 100 °C. (**C**): Pseudo-first-order kinetics for oxidation of DBT at different concentrations.



Fig. 6. Contours and 3D surface plots of the conversion of DBT as a function of: (A) reaction temperature and catalyst amount, (B) reaction temperature and O/S molar ratio and (C) catalyst amount and O/S molar ratio.

The kinetic profiles of the oxidation of model oil containing different contents of sulfur were shown in Fig. 5C, which exhibited that this catalyst presented very high activity in the conversion of various amounts of DBT. The reaction rate constants for the apparent consumption of various contents of DBT were obtained from the pseudo-first-order equation.

$$-\frac{\mathrm{d}\mathbf{c}_{\mathrm{t}}}{\mathrm{d}\mathbf{t}} = \mathbf{k}\mathbf{c}_{\mathrm{t}} \tag{4}$$

$$\ln \frac{c_0}{c_t} = kt \tag{5}$$

where C_0 and C_t are the concentration of sulfur at time zero and time t (min), respectively. k is the first-order rate constant (min⁻¹).

The plot of $\ln(C_0/C_t)$ against t, three straight lines with different slope k were obtained (Fig. 5C). Half-live periods were calculated by $t_{1/2} = \ln 2/k$, which was derived from Eq. (5) through replacing C_t with C₀/2:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.1959} = 3.54 \tag{6}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.1407} = 4.93 \tag{7}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.1096} = 6.32 \tag{8}$$

$$E_{a} = RT^{2} \frac{d \ln k}{dT}$$
(9)

The apparent rate constants of 50 ppm sulfur, 150 ppm sulfur 400 ppm sulfur were 0.1959 min^{-1} , 0.1407 min^{-1} , and 0.1096 min^{-1} and the half-lives were 3.54 min, 4.93 min and 6.32 min, respectively. Using the rate constants at different temperatures and the Arrhenius equation (Eq. (8)), The activation energy (E_a) of DBT is 25.26 kJ/mol. The apparent rate constants were decreased with the decreasing of sulfur concentration. The reason mainly be that the molecules would be adsorbed on the catalyst surface more easily and reacted with oxidant much faster in low sulfur oils, which would promote the catalytic reaction to its equilibrium more quickly [25]. Besides, The impacts of diffusion and adsorption on the kinetic were not taken into account in this article, considering the mass ratio of model oil to catalyst was 100/1. Other researches [25-27] ignored these effects as well, and obtained the similar results. The reaction kinetic of oxidative DBT follows the pseudo-first-reaction-order.

5. Conclusions

Cobalt has been successfully introduced into mesoporous KIT-6 under certain conditions utilizing a soft template. SEM/TEM and wide-angle XRD analyses revealed that the cubic Ia3d mesostructure is reserved after Co incorporation. The IR spectral analysis gave clear evidence for the existence of cobalt species after Co deposition.

Co/KIT-6 catalyst showed excellent desulfurization performance for sulfur removal. The conversion of DBT reached 98.68% in 40 min at a catalyst dosage of 1.0×10^{-1} g, temperature of 100 °C, O/S of 4.0 and the volume of model oil of 20 ml.

The Box-Behnken design was used to assess the effects of the main three operating parameters,. The degree of importance was: O/S molar ratio > catalyst amount > reaction temperature. The maximum sulfur removal was 99.36% and 98.68% for the predicted and experimental results, respectively under the optimum conditions of oxidation temperature of 93 °C, catalyst amount of 1.6×10^{-1} g and O/S of 5.7.

The conversion of DBT dropped from 98.68% to 65.67% when the concentration of quinoline increased from 160 ppm to 4845 ppm. The related data indicated that the kinetics followed the pseudo-first order first-order equation.

The Co/KIT-6-CYHPO reaction system showed the potential to make up the drawbacks of existing technologies such as high pressures and high temperatures. This higher activity is due to 3-D mesopore connectivity resulting in better active component dispersion and faster diffusion of reactants and resultants in case of KIT-6 supported catalysts.

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