

Article

Titanium-Modified MIL-101(Cr) Derived Titanium-Chromium-Oxide as Highly Efficient Oxidative Desulfurization Catalyst

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Abstract: A titanium-chromium-oxide catalyst was prepared by a facile calcination of titanium-modified MIL-101(Cr). The resulting material, possessing a surface area of $60 \text{ m}^2 \text{ g}^{-1}$ and a titania content of 50.0 wt%, can be directly used as the catalyst for oxidative desulfurization (ODS) reaction of dibenzothiophene (DBT). This novel ODS catalyst can remove 900 ppm sulfur-containing compounds in a reaction time of 30 min at $60 \text{ }^\circ\text{C}$. The experimental results showed that the specific activity increased with the titanium content. The specific activity of the catalyst with 50%Ti reached $129 \text{ } \mu\text{mol}/\text{m}^2$, which was much higher than that of reported Ti-based catalysts.

Keywords: MIL-101(Cr), anatase titania; DBT; oxidative desulfurization

1. Introduction

The sulfur-containing compounds in fuel oil combust into SO_x and result in environmental pollution [1]. To reduce pollution, many countries have established stringent regulations for the sulfur content of fuels. For example, the US has limited the sulfur level to below 15 ppm since 2006. According to Europe norms, sulfur content should be less than 10 ppm since 2005 [2]. There is a continual search for a highly efficient desulfurization method [3]. Oxidative desulfurization (ODS) has received much attention because it can be carried out under mild conditions and it is effective to remove the aromatic sulfur-containing compounds like dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) that are difficult to be desulfurized by industrial hydrodesulfurization (HDS) technique [4,5].

Transition metal (Mo, Ti, V, W, etc.) composites have been widely studied as active phases in ODS for the removal of large molecular thiophenic compounds, such as dibenzothiophene and its alkyl derivatives [6,7]. However, Mo-, V-, and W-based catalysts are most commonly used with hydrogen peroxide as an oxidant, which causes a different layer to be formed from the fuel oil and requires the use of a co-solvent, acetonitrile in most cases. In contrast, Ti active sites are more efficient in a monophasic liquid medium with oil-soluble oxidants, such as cumene hydroperoxide or tert-butyl hydroperoxide, which could favor the application of an industrial fixed-bed procedure [8,9]. What is more, titanium-based catalysts have many interesting properties, such as being cheap, abundant, and reasonably nontoxic. Several TiO_2 catalysts have been studied in oxidative desulfurization reactions [10]. Li et al. [11] found that low-temperature mediated titania as a catalyst exhibits good desulfurization reactivities. Mortazavi et al. [12] explored that a microporous titania-silica nanocomposite with 50 wt%

titania exhibits high performance for ODS of DBT; the results showed that silica improves dispersion of Ti surface active species and improves ODS performance. Puente et al. [8] carried out desulfurization with heterogeneous titanium catalysts. Luo et al. [13,14] conducted desulfurization over nano-TiO₂ and TiO₂/porous glass and found that anatase TiO₂ function as active sites in this reaction; the authors also revealed good TiO₂ dispersion could enhance reactivity.

Metal–organic frameworks (MOFs) are burgeoning materials with tunable porosity, functionality, and periodically distributed metal centers. Because of these distinctive merits, MOFs have found their applications in catalysis [15], gas adsorption [16], optoelectronics [17], and drug delivery [18]. Other than their direct use, MOFs can decompose into their corresponding metal oxides through direct heat treatment in air [19]. Calcination temperature and time influence the phase composition, distribution status, particle sizes, and surface areas of MOF-derived oxides [20,21]. The highly tunable properties of MOF-derived metal oxides along with the possibilities to combine them with highly reactive titania make them attractive candidates for highly efficient ODS catalysts [22]. Jongsik Kim and his coworkers [23] conducted works on IRMOF-3-derived Ti/NC catalysts by modifying Ti precursors on the amine groups in MOFs. The catalytic tests results showed that this MOF-templated Ti/NC material had double conversion of DBT than the pristine MOFs, illustrating the introduction of titanium species in the zinc-based MOFs could enhance the catalytic activity. Jhung et al. [24] fabricated a TiO₂-containing carbon derived from a pyrolysis of MOF composites and found it was a highly active oxidative desulfurization catalyst. The results showed smaller TiO₂ particles are much more efficient. Due to the confinement effect of pristine MOFs, TiO₂ particles formed in the pores of MOFs were much smaller. Besides, the high surface area of MOFs would improve the dispersity of TiO₂ particles. Therefore, the design of Ti-modified MOFs with well-defined structures may notably broaden the execution toolbox for the construction of enviable Ti-based ODS catalysts.

MIL-101(Cr) is well known for its extremely large surface area (BET surface area of 4100 m²/g), mesoporous cages (2.9 and 3.4 nm), and large pore volume (2.0 mL/g) [25]. The pore space is enough to accommodate large Ti precursor molecules and improve the dispersion of active titanium species. However, single MIL-101(Cr) has a lack of catalytic ODS active sites. Here, we designed a Ti-modified MIL-101(Cr) composite, in which the composition of titanium ranged from 10 to 50 wt%. Ti-modified MIL-101(Cr) was then pyrolyzed to obtain MOF-derived anatase TiO₂. The newly developed titanium-chromium-oxide showed a high specific activity in the ODS of DBT.

2. Results and Discussion

2.1. Characterization of Catalyst

The XRD patterns of 550-MIL-101, 550-TBOT, and 550-x%-MIL-101(Cr)/Ti samples exhibited well-resolved diffraction peaks (Figure 1). It is obvious that after being calcined at 550 °C, the XRD peaks of MIL-101(Cr) and TBOT were in correspondence with those of Cr₂O₃ and anatase TiO₂, illustrating the pyrolysis of MIL-101(Cr) and TBOT. Furthermore, the XRD patterns of pyrolysis of MIL-101(Cr)/Ti composites proved that the heating treatment products were composed of Cr₂O₃ and anatase TiO₂, and the intensity of TiO₂ peaks were increasing with the increasing amount of titanium-loading in the Ti modified MIL-101(Cr) precursors. Besides, based on the above XRD results, the particle sizes of various samples were calculated according to the Debye–Scherrer equation. The results are shown in Table 1. All the particle sizes of metal oxides were in the nanometer region. The small particle size would be advantageous to the following catalytic tests.

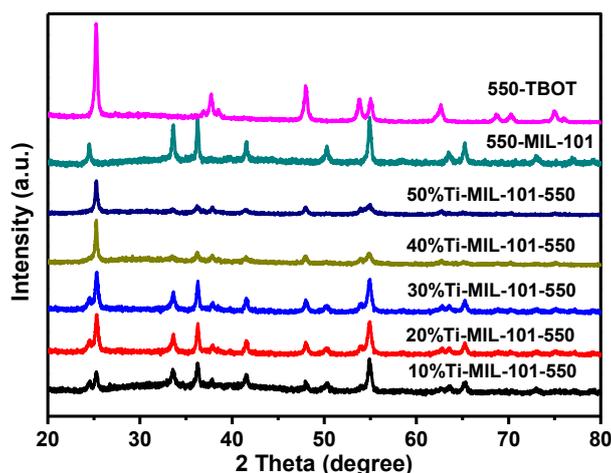


Figure 1. XRD patterns of various samples.

Table 1. Particle sizes of various materials calculated from XRD patterns.

x%Ti-MIL-101-550	10	20	30	40	50
D/nm (Cr ₂ O ₃)	24.5	20.5	18.9	11.5	15.0
D/nm (TiO ₂)	23.8	22.9	20.3	14.4	28.9

Figure 2 shows the N₂ sorption isotherms of 550-MIL-101 with different Ti loadings. As it can be seen, after heating treatment, the isotherms exhibit characteristics of type IV adsorption isotherms and there is almost no adsorption at the low pressure zone, indicating the structure of MIL-101(Cr) decomposed and the micropores diminished. Meanwhile, the hysteresis loop in the high-pressure zone illustrates the existence of mesopores. The detailed textural properties are listed in Table 2. The BET surface area of all the composites ranged from 44 to 62 m²/g. Corresponding with the sorption isotherms, no micropore volume existed after the heating treatment and mesopore volume showed downward trends while the titanium-loading was growing. Considering the particle size was small based on previous XRD results, the appearance of mesopores might be caused by nanoparticle accumulation of Cr₂O₃/TiO₂ composites. The existence of mesopores would facilitate the mass transfer of reaction substrates. The SEM-EDX elemental maps (Figure 3) reveal that the compositional distributions of the three elements (Ti, Cr, and O) in the 50%Ti-MIL-101-550 are uniform, suggesting the good dispersity of the catalyst particles, thus an improved catalytic performance.

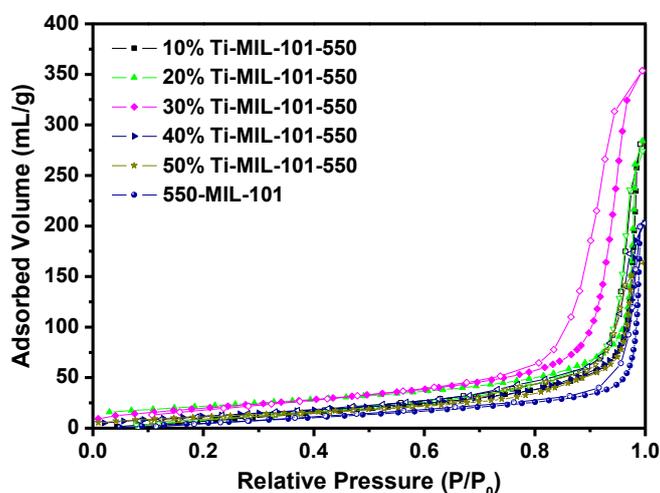
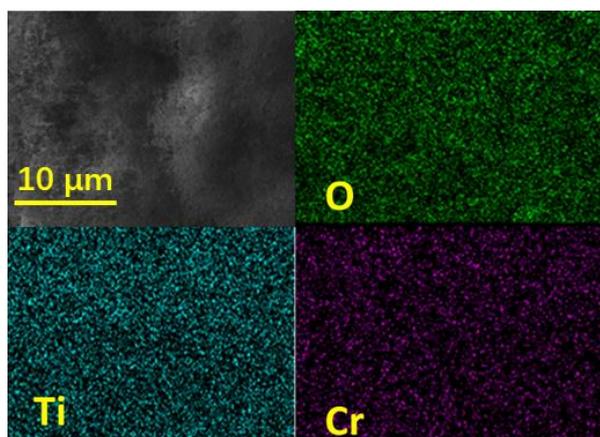


Figure 2. Nitrogen adsorption isotherms of various samples.

Table 2. Textual properties of various samples.

Material	S _{BET} (m ² /g)	Mesopore Volume (mL/g)	Pore Size (nm)
10%Ti-MIL-101-Cr-550	62	0.47	24
20%Ti-MIL-101-Cr-550	52	0.44	21
30%Ti-MIL-101-Cr-550	49	0.48	19
40%Ti-MIL-101-Cr-550	51	0.33	17
50%Ti-MIL-101-Cr-550	44	0.26	17
550-MIL-101-Cr	52	0.33	20

**Figure 3.** SEM-EDX elemental mapping image of 50%Ti-MIL-101-550.

2.2. Catalytic Activity of Catalyst

The ODS catalytic reactivities of various catalysts are shown in Figure 4. Obviously, the removal of DBT is relatively low for calcined MIL-101(Cr) and TBOT, around 7% and 46% at a reaction time of 60 min, respectively. Catalytic activity was greatly enhanced when titanium amount increased from 10% to 30%, with the removal increased from 30% to 77% at 30 min. At the same reaction time, the removal of DBT increased to 90% when Ti loading further increased to 50%. Above all, the reactivity was enhanced with the increasing Ti loading. The good ODS performance originated from the synergistic catalytic effect of the Cr₂O₃ and anatase TiO₂ nanoparticles. The small particle size and well dispersion of titanium-chromium-oxide composites derived from the MOFs precursor further facilitated the catalytic performance. As shown in Table 3, compared with the representative Ti-based catalysts, after 30 min of the reaction, 50%Ti-MIL-101-550 had the highest sulfur removal when normalized to the surface area (i.e., specific activity). The specific activities increased monotonically with the Ti loading.

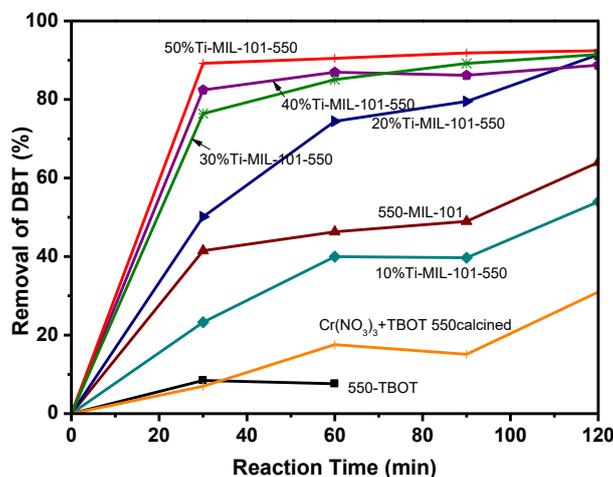
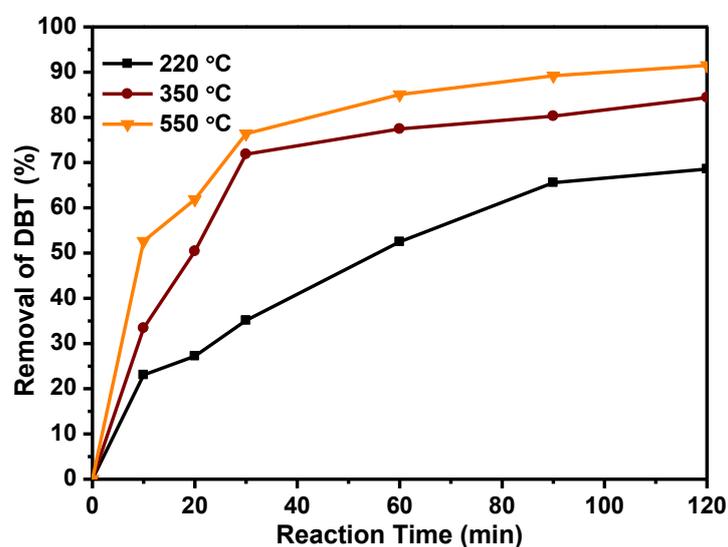
**Figure 4.** ODS catalytic reactivities of single TiO₂, single Cr₂O₃, and TiO₂/Cr₂O₃ composites.

Table 3. Catalytic performance comparison of representative Ti-based catalysts in ODS of DBT.

Catalyst	S_{BET} (m ² /g)	Initial S Content (mmol)	Reaction Temp. (°C)	Reaction Time (min)	Catalyst Amount (g)	Conversion (%)	Specific Activity (μmol S/m ²)	Ref.
MIL-125(Ti)	935	3.5	60	30	0.017	5 ^a	11.0	[26]
Meso-MIL-125(Ti)	975	0.35	80	30	0.017	47 ^a	9.92	[27]
Ti/NC	1060	3.5	100	30	0.04	22 ^a	18.2	[23]
MDC-C	374	0.22	80	30	0.02	90	26.5	[24]
TiO ₂ /porous glass	116.9	0.03	60	8	1	100	0.26	[14]
Anatase TiO ₂	24.5	0.027	70	30	0.3	80	2.94	[13]
TS-50	300	0.31	80	30	0.2	100	5.17	[12]
10%Ti-MIL-101-550	62	0.63	60	30	0.1	23	23	This work
20%Ti-MIL-101-550	52	0.63	60	30	0.1	50	61	This work
30%Ti-MIL-101-550	49	0.63	60	30	0.1	76	98	This work
40%Ti-MIL-101-550	51	0.63	60	30	0.1	82	101	This work
50%Ti-MIL-101-550	44	0.63	60	30	0.1	90	129	This work

^a Conversion calculated based on first-order reaction rate constants.

Considering the calcination temperature during catalyst preparation greatly influenced the phase composition of titania species, the calcination temperature effect on ODS performance of DBT was tested on 30%Ti-MIL-101-550 (Figure 5). The removal of DBT at the initial 10 min was 23%, 34%, and 53% when calcined at 220, 350, and 550 °C, respectively. The overall reactivity increased in the same order with the initial desulfurization rate. Therefore, it can be drawn that 550 °C was the optimum calcination temperature. A more restricted ODS experiment was carried out over 50%Ti-MIL-101-550 at a much lower temperature of 40 °C. As shown in Figure 6, the catalytic performance was greatly suppressed by low reaction temperature and the removal of DBT was maintained at 20% even after a reaction period of 120 min.

**Figure 5.** Calcination temperature effect on ODS performance of 30%Ti-MIL-101.

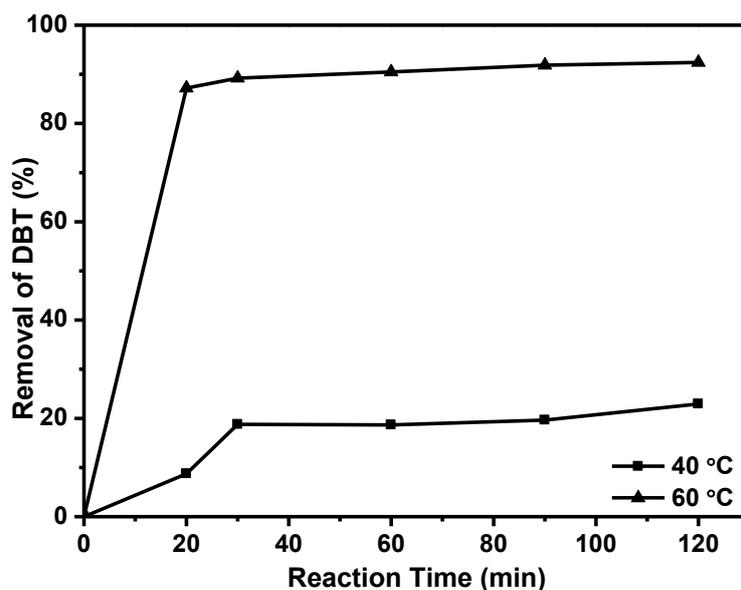


Figure 6. Reaction temperature effect on catalytic reactivity of 50%Ti-MIL-101-550.

To test the stability of the catalyst, a leaching test was conducted on 20%Ti-MIL-101-550 (Figure 7). The catalyst was filtered out at 30 min when 50% DBT was removed. Then, DBT removal remained almost unchanged until 120 min, illustrating there was no leaching of active Ti species during the reaction process, and the heterogeneity of catalyst. Since reusability is a key feature for a heterogeneous catalyst, the recyclability of 50%Ti-MIL-101-550 was investigated at 60 °C at a reaction time of 120 min. As shown in Figure 8, after the second run, removal of DBT can still reach 96%. However, after the third run, DBT removal reduced to 83%, which might be a result of the catalyst mass loss during different cycles.

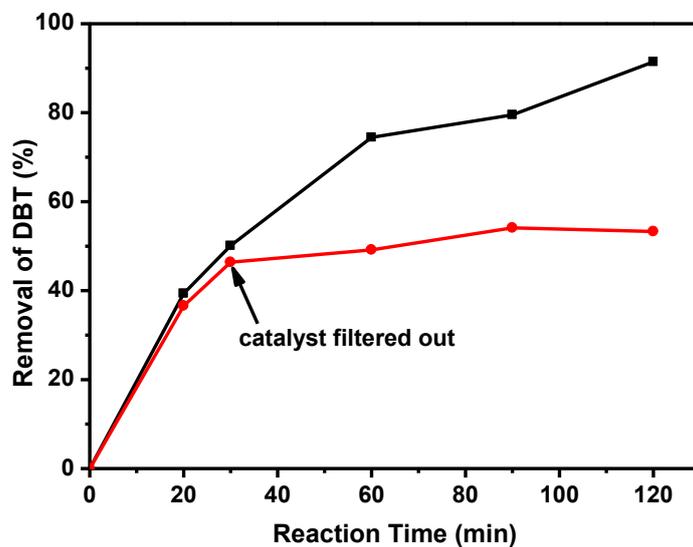


Figure 7. Leaching test of 20% Ti-MIL-101-550.

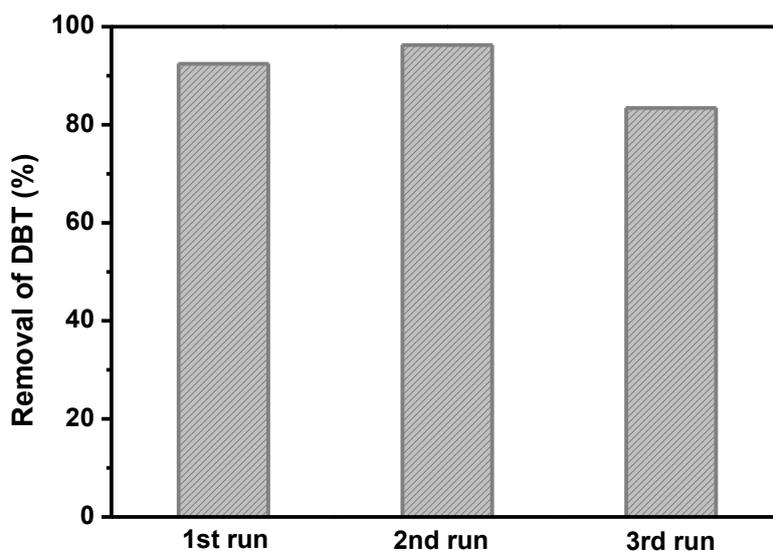


Figure 8. Recyclability of 50% Ti-MIL-101-550.

3. Experimental

3.1. Materials

Chromium(III) nitrate nonahydrate (99%), terephthalic acid ($\geq 99\%$), tetrabutyl ortho-titanate (TBOT, 98%), cumene hydroperoxide (CHP, 70%), absolute ethyl alcohol, dibenzothiophene (DBT), and *n*-octane were all purchased from Sinopharm Chemical Reagents Co (Shanghai, China) and used as received.

3.2. Preparation of Catalyst

Synthesis of MIL-101(Cr). MIL-101(Cr) was prepared according to the reported literature [28]. Specifically, 6.0 g $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2.49 g terephthalic acid were added into 60 mL deionized water, and sonicated for 20 min. The above suspension was transferred into a 100 mL stainless steel autoclave and crystallized at 218 °C for 18 h. The obtained green powder was washed twice with hot ethanol at 60 °C to remove unreacted substances, and then dried at 100 °C.

Synthesis of Ti-modified MIL-101(Cr). Ti-modified MIL-101(Cr) was prepared by the incipient wetness impregnation technique. Typically, MIL-101(Cr) was impregnated with a calculated amount of TBOT in absolute ethanol solution with a solid-to-liquid ratio of 0.3g/0.4 mL sonicated at room temperature for 20 min. Finally, the obtained product was dried at 60 °C for 12 h. Based on the calculated mass fractions of the Ti atom (10–50 wt.%), the final samples were named as 10%-MIL-101(Cr)/Ti, 20%-MIL-101(Cr)/Ti, 30%-MIL-101(Cr)/Ti, 40%-MIL-101(Cr)/Ti, and 50%-MIL-101(Cr)/Ti, respectively.

Pyrolysis of MIL-101(Cr)/Ti. MIL-101(Cr)/Ti was loaded into a Muffle furnace and calcined at the following conditions: heated at 2 °C/min to 550 °C for 5 h. Afterwards, the calcined MIL-101(Cr)/Ti was cooled to room temperature. The obtained samples were designated as x%Ti-MIL-101-550; x was the mass fraction of the Ti atom in MIL-101(Cr)/Ti. By contrast, the MIL-101(Cr) and TBOT were calcined under the same conditions, designated as 550-MIL-101 and 550-TBOT, respectively.

3.3. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (Bruker D8, Karlsruhe, Germany) equipped with a SolX detector-Cu $K\alpha$ radiation with wavelength of $\lambda = 1.5418 \text{ \AA}$. The scan speed and stepsize were 6°/min and 0.02°, respectively. Nitrogen adsorption–desorption isotherms were obtained at 77 K on a Beishide 3H-2000PS1 (Beijing, China) gas sorption and porosimetry system. Samples were normally prepared for measurement after degassing at 150 °C under vacuum until a final

pressure of 1×10^{-3} Torr was reached. The instrument error for the gas sorption and porosimetry system was $\pm 1\%$. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) elemental mapping were recorded on a Zeiss SUPRA 55 (Jena, Germany) operated with an acceleration voltage of 15 kV.

3.4. Catalytic Tests

The liquid phase oxidation removal of DBT was carried out in a three-necked round-bottom flask equipped with a reflux condenser and heated in a temperature-controlled oil bath under atmospheric pressure. In a typical run, model oil was made by dissolving 57.5 mg DBT into 10 g *n*-octane (1000 ppm). A total of 50 mg catalyst was added (which had been activated at 150 °C under vacuum before use in the reaction). The mixture was maintained at 60 °C in an oil bath. Then, 385 μ L cumene hydroperoxide solution was injected to the reaction system. The reaction was not stopped until 2 h. Liquid samples were withdrawn at regular intervals and analyzed by gas chromatography (GC) on an Agilent 7890A GC with a FID detector using a 50 m packed HP5 column. The instrument error for Agilent 7890A was $\leq 3\%$. Conversion was calculated based on the DBT reduction amount.

4. Conclusions

In summary, highly efficient Ti-based ODS catalysts were obtained by high-temperature pyrolysis of the synthesized Ti-modified MIL-101(Cr). The XRD patterns showed that the catalysts were composed of Cr_2O_3 and anatase TiO_2 . The catalytic results indicated that the chromium-titanium-oxide hybrid nanocomposites exhibited better ODS performance than single anatase TiO_2 and Cr_2O_3 . The catalyst with 50% Ti and calcined at 550 °C could remove 900 ppm sulfur in a reaction time of 30 min at 60 °C. The specific activity over 50%Ti-MIL-101-550 was much higher than those of representative Ti-based catalysts. XRD, BET, and SEM-EDX results showed such catalytic performance can be attributed to the smaller particle size and high dispersion of the catalyst.

Author Contributions: X.L.: syntheses, characterisation of catalysts, measurements and analysis of ODS catalytic activities, writing—original draft preparation. L.Z. and Y.S.: supervision, overall direction and design of project. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.

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