

Article

Complete Hydrodesulfurization of Dibenzothiophene via Direct Desulfurization Pathway over Mesoporous TiO₂-Supported NiMo Catalyst Incorporated with Potassium

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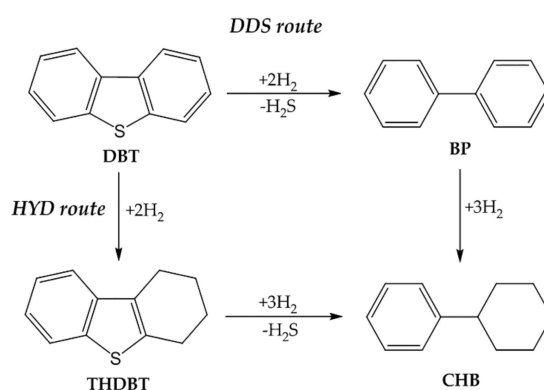


Abstract: Mesoporous TiO₂ containing different potassium content was prepared from potassium titanate by mediating the pH value of the ion exchange, which was used as catalytic support to load NiMo for hydrodesulfurization of dibenzothiophene. The as-prepared samples were characterized by X-ray diffraction, N₂ physical adsorption/desorption, temperature-programmed reduction, scanning electron microscope/energy dispersive X-ray mapping analysis, high resolution transmission electron microscopy, and pyridine-adsorbed Fourier transform infrared spectroscopy. The characterization results showed that NiO and MoO₃ were well dispersed on mesoporous TiO₂ with varying potassium content. A crystal NiMoO₄ phase was formed on the TiO₂ with relatively high potassium content, which could decrease the reduction temperature of oxidized active species. The evaluation results from the hydrodesulfurization displayed that as the potassium content of the catalyst increased, the dibenzothiophene conversion firstly increased and then slightly decreased when potassium content exceeded 6.41 wt %. By contrast, the direct desulfurization selectivity could continuously increase along with the potassium content of catalyst. Furthermore, the change in direct desulfurization selectivity of a TiO₂-supported NiMo catalyst was independent of the reaction condition. The mesoporous TiO₂-supported NiMo catalyst incorporated with potassium could have near both 100% of dibenzothiophene and 100% of direct desulfurization selectivity. According to the structure–performance relationship discussion, the incorporation of potassium species could benefit the formation of more sulfided active species on mesoporous TiO₂. Moreover, excessive free potassium species may poison the active sites of the hydrogenation pathway. Both factors determined the characteristics of complete hydrodesulfurization of dibenzothiophene via a direct desulfurization pathway for potassium-incorporated mesoporous TiO₂ supported NiMo catalysts.

Keywords: TiO₂; potassium; hydrodesulfurization; dibenzothiophene; direct desulfurization; selectivity

1. Introduction

Driven by increasingly strict environmental requirements, the production of high-quality low sulfur fuels has become an urgent task [1–3]. To date, hydrodesulfurization (*HDS*) has been a general industrial technology for fuel oil desulfurization. The sulfur-containing compounds, e.g., dibenzothiophene (*DBT*), are usually catalytically removed through two main reaction pathways (as seen in Scheme 1: (i) direct C-S bond cleavage (the so-called direct desulfurization pathway, *DDS*), yielding the corresponding biphenyl (*BP*) product; (ii) initial hydrogenation followed by C-S bond rupture (the hydrogenation pathway, *HYD*), yielding first tetrahydrodibenzothiophene (*THDBT*) and then the corresponding cyclohexylbenzene product (*CHB*) [4,5]. The *DDS* pathway has an advantage in having less hydrogen consumption for desulfurization. Simultaneously, the *DDS* pathway is beneficial for achieving relatively high unsaturated hydrocarbon content of oil for improving their antiknock performance [6]. Therefore, it is of industrial importance to accomplish both superior hydrodesulfurization efficiency and high *DDS* selectivity.



Scheme 1. Reaction network of dibenzothiophene (*DBT*) hydrodesulfurization process.

In the past decades, significantly more efforts have been devoted to improving the hydrodesulfurization efficiency of catalysts than their *DDS* selectivity. In most literatures, the studies on *HDS* selectivity of catalysts were usually affiliated to that of dibenzothiophene conversion, which was used to provide the morphological information of active species [7–12]. It is generally acknowledged that the direct desulfurization takes place on the edge planes of metal sulfide, while hydrogenation occurs at rim sites of metal sulfide [10]. Based on this, researchers found that larger stacking numbers or longer slab lengths of metal sulfides had higher selectivity due to having a higher proportion of edges [13]. The adjustment in active sites, e.g., dispersion or promoter incorporation, could change their edge proportions to some degrees [6,14]. Moreover, the reaction condition of hydrodesulfurization was required to be optimized [15–19]. Many literatures reported that high H_2S partial pressure severely inhibited the *DDS* pathway [18,19]. The in-depth researches showed that the decrease in *DDS* selectivity was attributed to the strong adsorption of H_2S on the edges of metal sulfide, i.e., the active site of direct desulfurization.

By contrast, the regulation of acid-base property of support is a more effective approach to influence the *DDS* selectivity. In early stages, researchers found the highest *DDS* selectivity for Mo/MgO compared with that on Al_2O_3 , TiO_2 , and SiO_2 in the *HDS* of *DBT* [20,21]. Further, elements of the same family, e.g., Ca and Ba, also showed a similar achievement that could promote the *DDS* selectivity [22,23]. This confirmed the contribution of support basicity on the *DDS* selectivity of corresponding catalyst. Accordingly, the incorporation of first group elements, e.g., Li, Na, and K, into hydrodesulfurization catalyst could increase their *DDS* selectivity [24–32]. To date, most related researches were performed on some typical support materials, e.g., $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and so on [25,27,28]. The active support TiO_2 was rarely used as a hydrodesulfurization catalyst support to study *DDS* selectivity improvement. Only one research study showed that incorporation of sodium could increase the *DDS* selectivity of titania nanotube-supported hydrodesulfurization catalysts but decrease its *DBT*

conversion [30]. However, different alkali elements or different supports could lead to completely different *HDS* reaction result of catalysts [32]. In some literatures [25,26,33], the catalysts could have both increased *DDS* selectivity and *HDS* conversion. Solís-Casados, D. et al. found that potassium species enhanced the *DDS* pathway of *DBT HDS* [26]. Therefore, it is worth expecting to explore the effect of other unreported alkali elements on TiO_2 for improving both its *HDS* performance and *DDS* selectivity.

The present work reports a mesoporous TiO_2 incorporated potassium prepared from potassium titanate by regulating pH value of ion exchange. This kind of material used as a catalytic support could exhibit both enhanced *HDS* performance and improved *DDS* selectivity, which could carry out almost 100% of *DBT* conversion and 100% of *DDS* selectivity. The support and its corresponding catalyst were systemically studied by various characterizations. Simultaneously, the structure–performance relationship was also discussed in the following context.

2. Results

2.1. Structural Properties

Figure 1 shows XRD patterns of various TiO_2 supports and their corresponding NiMo/ TiO_2 catalysts. All samples almost show the same obvious peaks at 25.3° , 37.8° , 48.1° , 53.9° , and 55.1° , which are ascribed to (101), (103), (004), (112), and (200) planes of anatase crystal phase, respectively [34]. This indicates that the pH value of the ion exchange and loading process of Ni and Mo could not influence the main crystal phase of TiO_2 support. In comparison, the intensities of diffraction peaks ascribed to the anatase phase are relatively weakened by the increasing pH value of supports and catalysts. The crystal phase size of anatase TiO_2 of various samples is calculated according to the Scherrer equation and their corresponding results are summarized in Table 1. The titania with a higher pH value has a relatively smaller crystal particle size. Moreover, there are two weak peaks at 23.9° and 29.8° observed in NiMo/ TiO_2 -8 and TiO_2 -8, which correspond to the diffraction pattern of potassium hexatitanate [35,36]. This demonstrates the formation of potassium hexatitanate in NiMo/ TiO_2 -8 and TiO_2 -8 under a high pH value of ion exchange. As also shown in Table 1, the potassium content of TiO_2 is increased as the pH value increases. Among them, TiO_2 -6 and TiO_2 -8 are obviously higher potassium content than those of other TiO_2 .

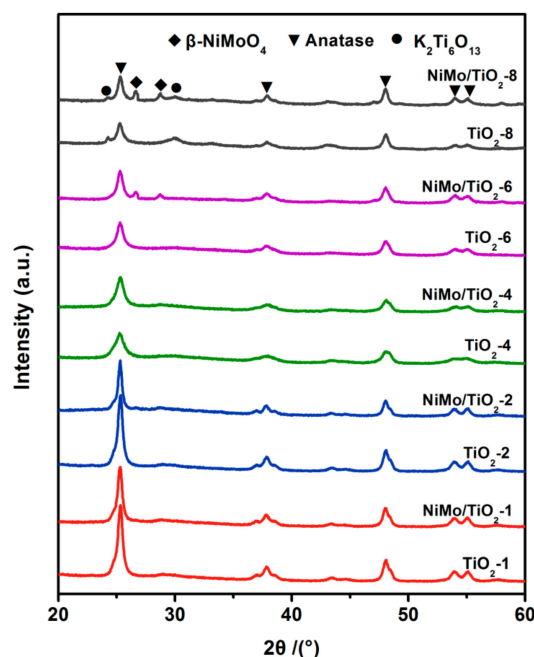


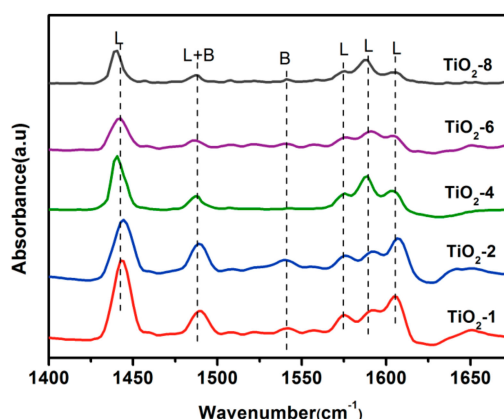
Figure 1. XRD patterns of various catalysts and their corresponding supports.

Table 1. Chemical composition and textural characteristics ^a of various supports and their corresponding catalysts.

Sample	Potassium Content (wt %)	Crystal Particle Size ^b (nm)	S _{BET} (m ² ·g ^{−1})	d _p (nm)	V _p (cm ³ ·g ^{−1})
TiO ₂ -1	0.15	17.2	49.9	19.9	0.25
TiO ₂ -2	1.84	16.2	74.5	12.4	0.22
TiO ₂ -4	2.97	12.0	84.5	9.9	0.21
TiO ₂ -6	6.41	13.3	48.2	16.5	0.20
TiO ₂ -8	8.31	13.4	47.4	13.9	0.16
NiMo/TiO ₂ -1	-	16.1	45.7	20.8	0.21
NiMo/TiO ₂ -2	-	16.5	48.7	11.7	0.20
NiMo/TiO ₂ -4	-	13.7	55.8	10.2	0.20
NiMo/TiO ₂ -6	-	13.0	45.8	14.7	0.18
NiMo/TiO ₂ -8	-	14.4	39.7	14.7	0.14

^a: S_{BET}, specific surface area calculated by BET method; V_p, total pore volume; d_p, average pore diameter determined from adsorption isotherm by the BJH method. ^b: calculated from (101) plane of anatase TiO₂.

Furthermore, there is no observation of diffraction peaks ascribed to Ni and Mo species in the catalysts with low potassium content. This means there is a good dispersion of Ni and Mo species on these TiO₂ supports, including TiO₂-1, TiO₂-2, and TiO₂-4 [37,38]. By contrast, both NiMo/TiO₂-6 and NiMo/TiO₂-8 appear to have new diffraction peaks at 26.7° and 28.8°, which are ascribed to crystal NiMoO₄ phase [39]. Generally, Mo and Ni species are individually dispersed on TiO₂ in the forms of MoO₃ and NiO, respectively [40]. NiMoO₄ are more easily formed on the alkaline surface of the support [41]. Herein, the surficial basicity of TiO₂ with different potassium content was studied by Py-FTIR. As shown in Figure 2, four strong bands assigned to the chemisorption of pyridine onto Lewis site are observed at around 1448, 1575, 1585, and 1606 cm^{−1}, respectively [42,43]. Additionally, a small band located at 1542 cm^{−1} is assigned to the vibrational mode of pyridine adsorbed onto Brønsted sites, while a band at 1490 cm^{−1} is assigned to pyridine associated with both Lewis and Brønsted sites [42]. Obviously, all the TiO₂ have Lewis acid characteristics. In comparison, there were a small amount of Brønsted sites which only existed in TiO₂-1 and TiO₂-2. Note that the signal intensity ascribed to the Lewis acid is gradually decreased and that to the Brønsted acid disappears with the increasing potassium content of TiO₂. This demonstrates the enhancement in basicity of TiO₂ with a high potassium content, especially for TiO₂-6 and TiO₂-8. This could be responsible for the formation of crystal NiMoO₄ phase in NiMo/TiO₂-6 and NiMo/TiO₂-8.

**Figure 2.** Py-FTIR spectra of TiO₂ prepared by different pH values.

Nitrogen adsorption–desorption isotherms and pore size distributions of samples are shown in Figure 3. All the supports and catalysts show typical type IV adsorption isotherms with a noticeable hysteresis loop. This indicates the presence of mesoporous structures in all samples, as is also

demonstrated by their pore-size distribution patterns [44,45]. Further, it can be observed from Figure 3a that TiO_2 with different pH values have remarkably different shapes of hysteresis loops. TiO_2 -2 and TiO_2 -4 have a combination of H1 and H3 types of hysteresis loop. Type H1 is the characteristic of mesoporous materials having uniform nearly cylindrical channels, whereas H3 hysteresis is frequently associated with particle aggregations or slit-shaped pores with non-uniform size [44]. By contrast, the TiO_2 - n ($n = 1, 6, 8$) supports nearly exhibit typical H3-type hysteresis loops at relatively high pressure ($0.8 < P/P_0 < 0.99$), which indicates that three TiO_2 have slit-shaped mesoporous structures [44]. After adding Ni and Mo, nitrogen adsorption–desorption isotherm of the catalysts still have similar shapes to those of their corresponding supports. This indicates that the incorporation of Ni and Mo species could not remarkably influence the porous structure of TiO_2 , which could also reflect the good dispersion of Ni and Mo species.

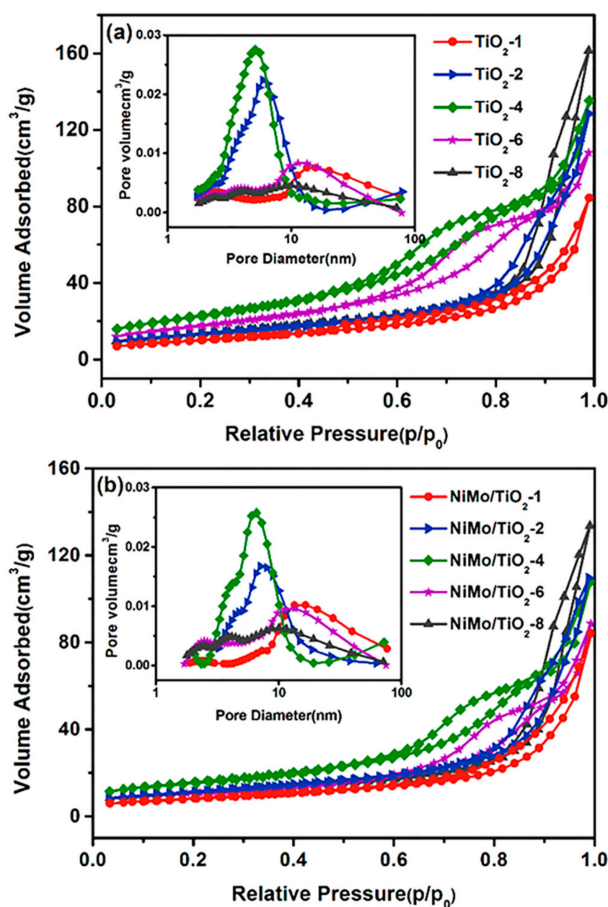


Figure 3. Nitrogen adsorption–desorption isotherms and pore size distributions of (a) supports and (b) catalysts.

Table 1 exhibits the structural data of various TiO_2 and their corresponding catalysts. The surface area of TiO_2 is increased initially and decreased afterwards with the increasing potassium content. An excessively low pH value of ion exchange may partially dissolve the titanate framework, which is adverse to the achievement of a porous structure of TiO_2 [46]. Our previous work has demonstrated the optimal pH value of ion exchange is 2–4 for constructing mesoporous TiO_2 [47,48]. Under this condition, the titanate layers could be phase-transferred into columnar pores. This accordingly is responsible for achieving the relatively high surface area of TiO_2 -2 and TiO_2 -4. Furthermore, a high pH value for ion exchange gives rise to excessive residual potassium, so that a certain amount of titanate exists in TiO_2 -8. Consequently, the TiO_2 with high pH values and their corresponding catalysts have relatively low surface areas.

The morphological transformation of TiO_2 and catalysts as a function of potassium content is studied by SEM characterization. As shown in Figure 4a–c, all the TiO_2 , regardless of high or low their pH values, could show abundant gaps between crystal particles, which are ascribed to pores. Moreover, some slices could be observed in SEM image of TiO_2 -1 and TiO_2 -6. This demonstrates the presence of slit shaped pores, which is consistent with BET analysis results. After adding Ni and Mo, TiO_2 crystal particles in all catalysts seem to be covered by some species and their pore sizes slightly decrease.

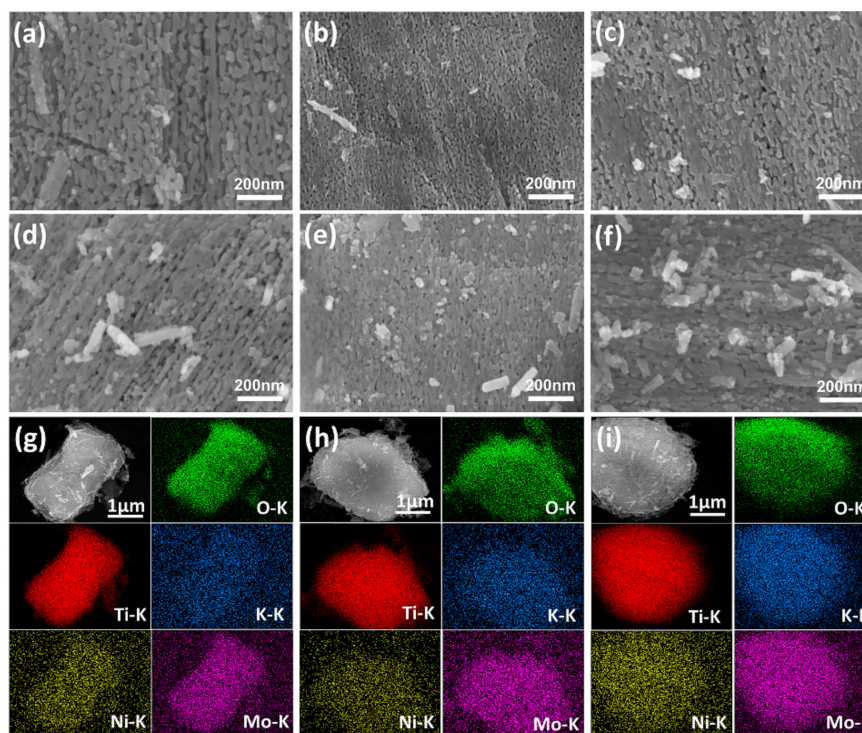


Figure 4. FESEM images of representative catalysts with different potassium content and their corresponding supports: (a) TiO_2 -1, (b) TiO_2 -2, (c) TiO_2 -6, (d) NiMo/TiO_2 -1, (e) NiMo/TiO_2 -2, and (f) NiMo/TiO_2 -6. EDS mapping images of catalysts: (g) NiMo/TiO_2 -1, (h) NiMo/TiO_2 -2 and (i) NiMo/TiO_2 -6.

Furthermore, FESEM-EDS mapping images (Figure 4g–i) display the dispersion state of various elements in catalysts. The comparison among various elements could confirm that potassium species (blue) are well dispersed on their corresponding supports due to similar distribution of potassium elements to that of titanium elements (red). This illustrates the ion exchange process is beneficial to achievement of well potassium-dispersion titania. As pH value of ion exchange increases, the image profile of potassium becomes gradually clear. That means increasing potassium content, which is in accordance with XRF analysis result (Table 1). Moreover, molybdenum (purple) and nickel (yellow) elemental images are also identical to the shape of various catalysts. This proves the well dispersion of Mo and Ni elements on supports, as also supported by XRD analysis results. Note that XRD result has showed the presence of crystal NiMoO_4 phase in NiMo/TiO_2 -6, no observation of Ni and Mo aggregations is appeared in Ni-K and Mo-K images of Figure 4i. This indicates the formation of crystal NiMoO_4 phase could not apparently influence the global dispersion state of Ni and Mo in NiMo/TiO_2 -6.

Oxidized molybdenum and nickel species need to be reduced into the sulfided ones under a presulfidation process, which are the main active species in an *HDS* reaction [49]. Hence, the reducibility of the active phase is an important factor for influencing *HDS* performance of catalysts. H_2 -TPR patterns as shown in Figure 5, different catalysts show significantly varying reduction processes. Generally, the reduction of oxidized molybdenum and nickel species on TiO_2 experience three main stages. The first stage below 450 °C is ascribed to the reduction of Mo^{6+} to Mo^{4+} of octahedral Mo species. Subsequently, the second one contains the reduction of oxidized nickel species

and superficial Ti^{4+} , which usually occurs at 500–600 °C. Finally, the reduction of Mo^{4+} to Mo^0 of octahedral Mo species and Mo^{6+} to Mo^{4+} of tetrahedral Mo species are carried out in the last stage at above 700 °C [50–52]. Apparently, TPR patterns of NiMo/TiO_2 -1, NiMo/TiO_2 -2, and NiMo/TiO_2 -4 show three above-mentioned reduction processes, which demonstrates the presence of corresponding forms of Mo and Ni-oxygen species. In comparison, the reduction process of NiMo/TiO_2 -6 and NiMo/TiO_2 -8 are relatively more complex compared with that of NiMo/TiO_2 catalysts with low potassium content. Both NiMo/TiO_2 -6 and NiMo/TiO_2 -8 have a new reduction peak at above 800 °C, which is related to the reduction of TiO_2 -6 and TiO_2 -8 rather than that of Ni and Mo species. Additionally, the first and second reduction stage of NiMo/TiO_2 -6 and NiMo/TiO_2 -8 are obviously different from those of catalysts with low pH values. Jose, A., Rodriguez, et al., found that NiMoO_4 phase was easier to be reduced than pure MoO_3 [53]. Thus, decrease in reduction temperature of NiMo/TiO_2 -6 and NiMo/TiO_2 -8 could be attributed to the existence of NiMoO_4 phase.

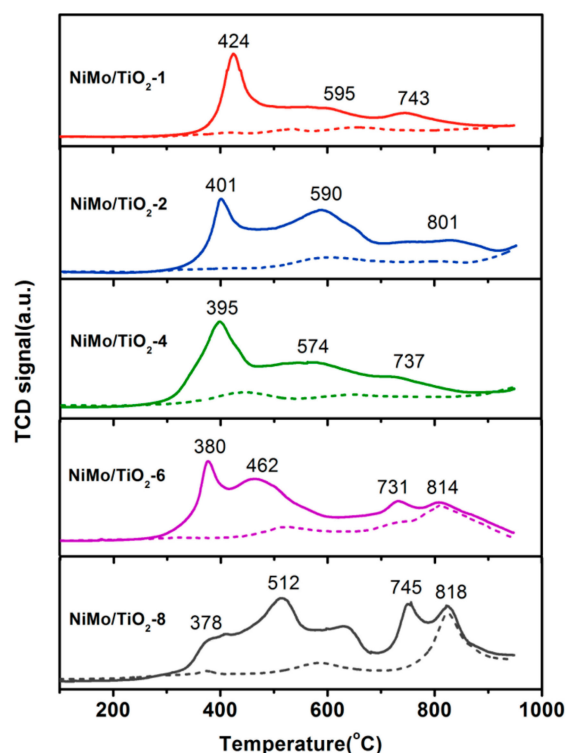


Figure 5. H_2 -TPR profiles of various catalysts (solid lines) and their corresponding supports (dashed lines).

Representative HRTEM micrographs of sulfided NiMo/TiO_2 catalysts were shown in Figure 6. It can be seen that there are numerous slabs randomly dispersed in all catalysts, which are ascribed to the molybdenum sulfide [11]. Nickel sulfides are not observed due to their small sizes. They usually stay between MoS_2 slabs to form Ni-Mo-S active phase [54,55]. Generally, Ni-Mo-S type I phase presents the monolayer structure, the formation of which could be attributed to high dispersion or strong interaction between active species and support [11,56]. In comparison, the multilayered Ni-Mo-S type II phase has more excellent deep hydrodesulfurization performance than type I one [49,54]. Accordingly, the slab length and stacking number of the MoS_2 crystallites in various catalysts are measured and the corresponding results are summarized in Table 2. For NiMo/TiO_2 -1, the average slab length and average stacking number are 2.4 nm and 1.3, respectively. The appearance of an average slab length suggests that active species of such catalysts consist of Ni-Mo-S type I phase. Both the average slab length and average stacking number of MoS_2 crystallites are increased with an increasing potassium content of mesoporous TiO_2 . NiMo/TiO_2 -8 has an average slab length of 4.5 nm and an average

stacking number of 3.3. An average stacking number of above 2.0 of for NiMo/TiO₂-6 and NiMo/TiO₂-8 indicates the dominant amount of Ni-Mo-S type II phase in MoS₂ crystallites.

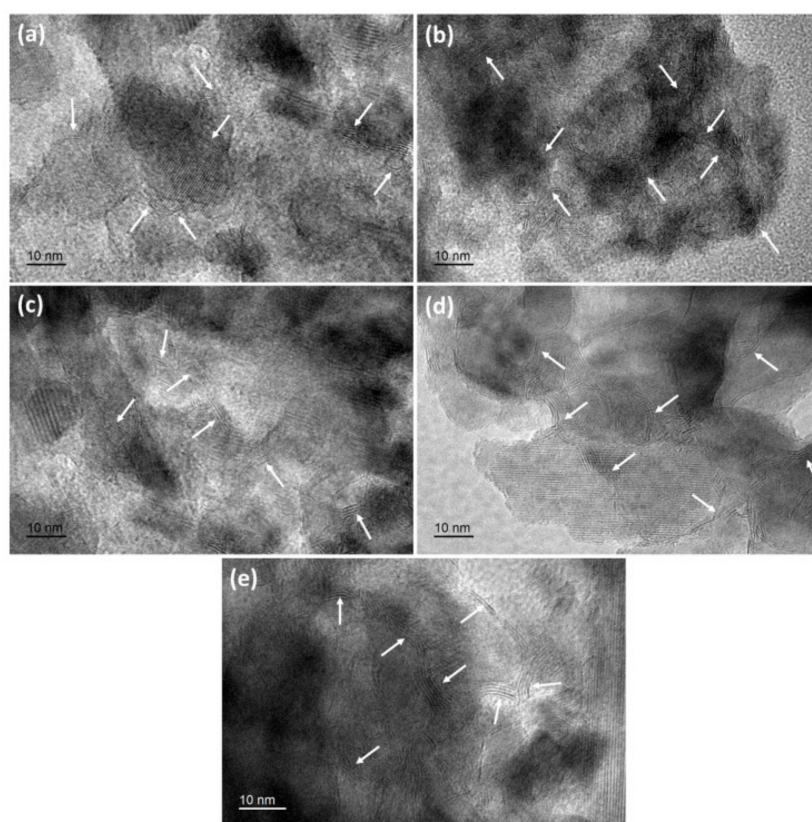


Figure 6. HRTEM images of various sulfided catalysts: (a) NiMo/TiO₂-1, (b) NiMo/TiO₂-2, (c) NiMo/TiO₂-4, (d) NiMo/TiO₂-6, (e) NiMo/TiO₂-8.

Table 2. Statistical HRTEM results of various catalysts.

Catalyst	Average Slab Length (nm)	Average Stacking Number	f_e/f_c	f_{Mo}
NiMo/TiO ₂ -1	2.4	1.3	2.25	0.46
NiMo/TiO ₂ -2	2.5	1.5	2.41	0.42
NiMo/TiO ₂ -4	3.0	1.9	3.19	0.36
NiMo/TiO ₂ -6	3.5	2.3	3.97	0.32
NiMo/TiO ₂ -8	4.5	3.3	4.91	0.25

Generally, the structural transformation of MoS₂ crystallite would cause one of the morphological parameters (average slab length or average stacking number) to increase and the other to decrease [30]. In some cases, formation of more sulfided active species could lead to an increase in both average slab length and average stacking number of MoS₂ crystallites, for example higher metal loading or their easy reduction [8,30,50]. As shown in TPR results, the catalyst with a high potassium content could have a decreased reduction temperature of Mo species. Additionally, all the present catalysts have an identical metal loading that are 1.56 wt % of NiO and 6 wt % of MoO₃. Thus, these results adequately demonstrate that incorporation of potassium species into mesoporous TiO₂ could accelerate the formation of sulfided active species.

2.2. Catalytic Performance

Figure 7a shows DBT conversion and DDS selectivity of different catalysts as a function of potassium content. For NiMo/TiO₂-1 catalyst, the DBT conversion is about 25% and the DDS selectivity

is about 80%. The *DBT* conversion of catalysts firstly rises with increasing potassium content and then declines. NiMo/TiO₂-6 catalyst could show better *HDS* performance than other catalysts, which has 40% of *DBT* conversion. In contrast, the *DDS* selectivity of catalysts is continuously increasing along with an increasing potassium content. Both NiMo/TiO₂-6 and NiMo/TiO₂-8 catalysts possess near 100% of *DDS* selectivity. This means completely switching off *HYD* catalytic activity of NiMo/TiO₂-6 and NiMo/TiO₂-8 catalysts.

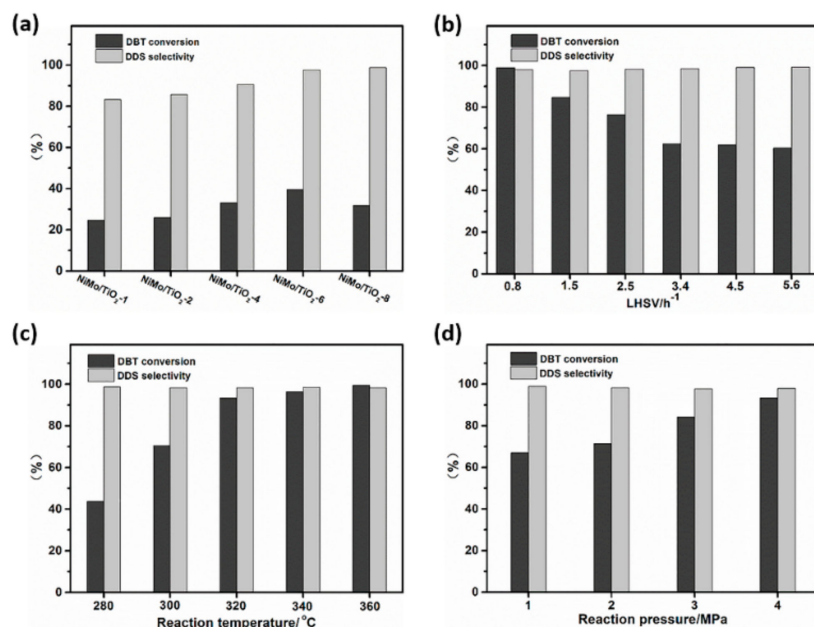


Figure 7. *DBT* conversion and direct desulfurization pathway (*DDS*) selectivity of (a) different NiMo/TiO₂ catalysts (0.33 g catalyst, 300 °C, 2 MPa, LHSV of 5.6 h⁻¹, H₂/oil ratio of 606), (b) NiMo/TiO₂-6 catalyst at various LHSV values (0.75 g catalyst, 300 °C, 2 MPa, LHSV of 0.8–5.6 h⁻¹, H₂/oil ratio of 606), (c) NiMo/TiO₂-6 catalyst at various reaction temperatures (0.75 g catalyst, 280–360 °C, 2 MPa, LHSV of 5.6 h⁻¹, H₂/oil ratio of 606), (d) NiMo/TiO₂-6 catalyst at various reaction pressures (0.75 g catalyst, 300 °C, 1–4 MPa, LHSV of 5.6 h⁻¹, H₂/oil ratio of 606).

Furthermore, NiMo/TiO₂-6 catalyst is chosen to be the key sample for studying the influence of reaction condition. Figure 7b displays the variation in *DBT* conversion and *DDS* selectivity of NiMo/TiO₂-6 catalyst as a function of liquid hourly space velocity (LHSV). It can be seen that the *DBT* conversion could reach up to 100% at 0.8 h⁻¹ of LHSV. Note that the *DDS* selectivity of NiMo/TiO₂-6 catalyst is kept constant and maintains ~99% of different LHSVs. Figure 7c shows the influence of reaction temperature on *DBT* conversion and *DDS* selectivity of NiMo/TiO₂-6 catalyst. With increase in reaction temperature, the *DBT* conversion of NiMo/TiO₂-6 catalyst could gradually promote as expected. When reaction temperature reaches at 360 °C, the *DBT* conversion of NiMo/TiO₂-6 is 100%, and simultaneously, its corresponding *DDS* selectivity always remains above 98%. Analogously, the last key reaction parameter, pressure, could significantly influence the *DBT* conversion of NiMo/TiO₂-6 catalyst but does not change its *DDS* selectivity. Thus, it can be confirmed that the *DDS* selectivity of NiMo/TiO₂-6 catalyst is independent of reaction condition. What is more, nearly 100% of *DDS* selectivity and 100% of *DBT* conversion demonstrates the complete hydrodesulfurization of *DBT* via *DDS* pathway over NiMo/TiO₂-6 catalyst. As shown in Table 3, the present catalysts could also exhibit certain advantage in *DBT* conversion and *DDS* selectivity under similar reaction condition compared with other catalysts reported in literatures.

Table 3. Comparison of catalyst performance with literature reports in *DBT* hydrodesulfurization.

Catalyst	Active Component Composition	Additive Composition and Content	Model Compounds	Reaction Temperature (°C)	Reaction Pressure (Mpa)	H ₂ /Oil Ratio (mL/mL)	LHSV (h ⁻¹)	Hydrodesulfurization (HDS) Activity (%)	DDS Selectivity (%)	Reference
NiMo/TiO ₂ -6	Ni, Mo	6.41 wt % K	<i>DBT</i>	300	2.0	606	0.84	99.0	98.0	This work
NiMo/TiO ₂ -6	Ni, Mo	6.41 wt % K	<i>DBT</i>	340	2.0	606	5.6	96.2	98.5	This work
NiMo/TiO ₂ -6	Ni, Mo	6.41 wt % K	<i>DBT</i>	300	4.0	606	5.6	93.3	97.9	This work
CoMo/Al ₂ O ₃ -MgO-Li	Co, Mo	5.0 wt % Li ₂ O	<i>DBT</i>	320	5.59	-	-	73.0	96.2	[24]
CoMo/Al ₂ O ₃ -MgO-K	Co, Mo	5.0 wt % K ₂ O	<i>DBT</i>	320	5.59	-	-	89.0	94.4	[26]
NiMo/MCM-41-Nb	Ni, Mo	5.0 wt % Nb	<i>DBT</i>	300	7.3	-	-	80.0	30.4	[57]
K-Ni-PW/Al ₂ O ₃	Ni, W	7.5 wt % K	Thiophene	250	1.5	100	5	5.9	28.6	[58]
K-PW/Al ₂ O ₃	W	7.5 wt % K	Thiophene	250	1.5	100	5	2.0	90.1	[58]
K _{7.5} -CoMo/Al ₂ O ₃	Co, Mo	7.5 wt % K	Thiophene	250	1.5	100	5	16.3	68.3	[31]
CMANa	Co, Mo	3.0 wt % Na	2-methylthiophene	250	1.7	500	6	80.8	75.0	[59]
NiMo/MCM-41-Na	Ni, Mo	1.4 wt % Na	<i>DBT</i>	300	5.0	1200	12	60.0	95.2	[60]
NiMo/MCM-41-Na	Ni, Mo	1.4 wt % Na	<i>DBT</i>	340	5.0	1200	12	90.0	99.1	[60]
5-K _{1.5} CoMoP/Al ₂ O ₃	Co, Mo	3.0 wt % K	FCC gasoline	280	1.5	100	7.5	84.0	93.0	[61]

2.3. Discussion

The following section discusses the influence of potassium content of mesoporous TiO_2 on their *HDS* performances. From the above characterization results, it can be seen that as the potassium content changes, many structural factors of support and active species are altered. These are directly or indirectly related to *DBT* conversion or *DDS* selectivity. Thus, it is necessary for clarifying their relationship to definite the mechanism of the potassium content of mesoporous TiO_2 on the *DBT* hydrodesulfurization reaction behavior of a NiMo catalyst.

Preliminarily, XRD analysis results show that anatase is the only crystal phase of various TiO_2 apart from a small amount of potassium hexatitanate in TiO_2 -8. The crystal particle size of titania decreases firstly and then slightly increases, which further influences their pore structures as demonstrated by BET results. The difference in pore structure of the catalyst may change the dispersion of Ni and Mo species or mass transfer of reactants. As shown in Table 1, the average pore size of all supports and their corresponding catalysts are 9.9–20.8 nm, which are obviously larger than the kinetic diameter of *DBT* molecule (0.8 nm) [62]. This means the mesoporous structure of various TiO_2 and their catalysts is beneficial to the diffusion of *HDS* reactants, which could ignore the mass transfer resistance of hydrodesulfurization.

As for the dispersion state of Ni and Mo species, it requires to preliminarily analyze the surface area of TiO_2 . Table 1 shows that the surface area of TiO_2 is firstly increased with pH value below 4 and then decreased. M. Breyse and his coworkers found that the 7 Mo/nm² was a suitable Mo loading amount for achieving a good Mo dispersion on mesoporous TiO_2 and an excellent *HDS* performance [63]. TiO_2 -1 has a similar porous structure to those of TiO_2 -6 and TiO_2 -8. Three corresponding catalysts also do not show distinct difference in surface area (47.4–49.9 m²/g). According to Breyse's results, the ideal MoO_3 loading of TiO_2 -1, TiO_2 -6, and TiO_2 -8 is about 7.9 wt %, which is higher than the real amount in three present catalysts (6.0 wt %). Theoretically, all NiMo/ TiO_2 catalysts in the present work have a good dispersion of Ni and Mo species. Nevertheless, XRD results show that MoO_3 and NiO are well dispersed on TiO_2 -1, whereas crystal NiMoO_4 phase is formed on TiO_2 -6 and TiO_2 -8. Hence, the dispersion of Ni and Mo species is mainly uninfluenced by the geometric construction of TiO_2 .

Obviously, surface properties of supports should be the key factor for different dispersion of oxidized active species of corresponding catalysts. Py-FTIR has demonstrated the relatively strong basicity of TiO_2 with high potassium content. As described previously, the formation of crystal NiMoO_4 phase occurs easily on the alkaline support [41]. Hence, this could explain the formation of crystal NiMoO_4 phases under dispersion threshold. Even in the presence of crystal NiMoO_4 phase, SEM analysis results have demonstrated the good dispersion of Ni and Mo elements on TiO_2 -6 and TiO_2 -8. Furthermore, TPR patterns have demonstrated that crystal NiMoO_4 phase could accelerate the reduction of oxidized active species on TiO_2 with a high potassium content. This benefits the formation of more sulfided active species.

According to the classical corner-edge model, *DBT* hydrodesulfurization is performed at the corner and edge of sulfided active species [10]. Therefore, the morphological transformation of active species could directly influence the *HDS* performance of catalyst. The active species with larger stocking number have a relatively higher proportion of edge and more active sites. As demonstrated by HRTEM analysis results, the multilayered Ni-Mo-S type II phase is dominated in the catalyst with high potassium content, which accordingly shows a relatively higher *DBT* conversion. The current consensus is that the Ni-Mo-S type II phase of active species could have more excellent deep hydrodesulfurization performance than that of Ni-Mo-S type I one [49,54,56]. Furthermore, a parameter f_{Mo} was calculated by dividing the total number of Mo atoms at the edges by the total number of Mo atoms to evaluate the fraction of Mo atoms located on the edge surface of MoS_2 crystallites [11]. As seen in Table 2, the f_{Mo} of the catalyst is gradually decreased with the increasing pH value, which suggests a decreased number of active sites. The increase in slab length of MoS_2 crystallites is the main reason for the decrease in f_{Mo} . Accordingly, the morphological transformation of active species does not account for high *DBT* conversion of the catalyst with a high pH value. Combined with TPR and HETEM analysis results,

oxidized active species of the catalysts with high pH value are obviously easily reduced into sulfided ones due to the presence of the NiMoO_4 phase. Thus, even with smaller f_{Mo} , the catalyst prepared by a high pH value of ion exchange could have a higher absolute number of active sites compared with that with low pH value.

As for the difference in *DDS* selectivity of catalysts, it is generally accepted that the edge sites of sulfided active species can catalyze the *DDS* reaction while the corner ones only catalyze more *HYD* reaction [12]. As also listed in Table 2, a parameter $f_{\text{el}}/f_{\text{c}}$ represents the fraction of edge to corner. The catalyst with a high potassium content has the higher $f_{\text{el}}/f_{\text{c}}$ value, which means a high proportion of edge of sulfided active species [12]. This could be responsible for the high *DDS* selectivity of catalysts with high pH value. Moreover, it is noteworthy that NiMo/TiO_2 -6 and NiMo/TiO_2 -8 have almost 100% of *DDS* selectivity, which indicates no active site of *HYD* reaction. However, HRTEM images have showed the real existence of the corner structure of MoS_2 crystallites in all catalysts. Therefore, the morphology of active sites according to a corner–edge model is inadequately interpreting the switching off *HYD* reaction pathway of NiMo/TiO_2 -6 and NiMo/TiO_2 -8. Based on above-mentioned discussion, it could be deduced that influence of potassium species on *HYD* selectivity may be similar to the inhibition of H_2S molecules on *DDS* reaction pathway. H_2S molecules were strongly adsorbed on the active sites of *DDS* reaction pathway, which severely inhibited the *DDS* route of *DBT*. The structure of active species was maintained to be constant in the H_2S -inhibited reaction process [19,64]. Accordingly, it is likely that the disappearance of *HYD* catalytic performance of the present catalyst is attributed to the adsorption of free potassium species onto *HYD*-related active sites. Consequently, NiMo/TiO_2 with relatively high potassium content could have near both 100% of *DBT* conversion and 100% of *DDS* selectivity.

3. Experimental

3.1. Synthesis

A series TiO_2 with different potassium contents were controllably synthesized from potassium titanate by mediating the pH value of ion exchange. As introduced in our previous work, the precursor potassium titanate was prepared by high-temperature calcination using potassium carbonate (K_2CO_3 , CAS: 584-08-7, 99%, Macklin, Shanghai, China) and hydrated titanium oxide as raw materials [47,65,66]. Subsequently, the ion exchange process of potassium titanate was carried out using hydrochloride (HCl , CAS: 7647-01-0, 36–38%, Yonghua Chemical Technology Co., Ltd., China) aqueous solution and the specific pH value was on-line monitored. The aqueous solution of ion exchange needed to be renewed every 8 h. After 6–8 times of solution renewal, white precipitation were collected, dried and calcined at 500 °C to obtain the mesoporous TiO_2 with specific potassium content. pH values 1, 2, 4, 6 and 8 of ion exchange were performed in the present work. The corresponding support was denoted as TiO_2 - n , where n represented pH value of ion exchange.

The loading of molybdenum and nickel species was carried out by incipient wetness impregnation using nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CAS: 13478-00-7, 98%, Aladdin, Shanghai, China) and ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, CAS: 12027-67-7, 99.9%, Macklin, Shanghai, China) as precursors. NiO and MoO_3 loading amounts of catalyst were 1.6 wt % and 6.0 wt %, respectively. After being mixed well, the impregnate was placed at room temperature for 4 h and then dried at 100 °C for 12 h. Followed by calcination at 500 °C for 2 h, the final catalyst was achieved, which was denoted as NiMo/TiO_2 - n .

3.2. Characterization

XRD analysis of the samples was carried out on a D/max 2200 X-ray diffractometer (Rigaku, Tokyo, Japan) equipped with $\text{Cu K}\alpha$ radiation. A diffraction pattern having a 2θ value ranging from 20°–60° was recorded at a rate of 0.2 s/step. N_2 adsorption/desorption isotherms were measured by a Micromeritics TriStarII 3020 M system (Micromeritics, Norcross, GA, USA) at −196 °C. The tested sample was degassed

under vacuum at 150 °C for 4 h. Surface area of sample was calculated by BET method. Pore size distribution of the samples was calculated by the Barrett–Joyner–Halenda (BJH) method. Pore volume of the samples was determined by N₂ adsorption at a relative pressure of 0.99. The morphology of catalyst and support was characterized by FESEM (Hitachi, Tokyo, Japan) at 5 kV in a high-vacuum mode, and the elemental distribution analysis of the samples was carried out by EDS mapping at 20 kV, 20 mA. H₂-TPR experiments were performed on TP-5000 equipment (Tianjin Xianquan Co., Ltd., China). Specifically, 100 mg of the sample (20–40 mesh) was filled in a quartz reactor, and first pretreated at 300 °C for 2 h under air flow. The reduction step was performed under a stream of 10 vol% H₂/N₂ mixture with a heating rate of 10 °C/min up to 950 °C. Py-FTIR measurements were performed on a Nicolet-6700 spectrometer (Thermo Fisher Scientific, MA, USA) apparatus equipped with a diffuse reflectance attachment. First, the sample was treated at 300 °C for 1 h in a N₂ flow, and then cooled to room temperature. Scanning spectrum of sample was used as the background. The adsorption process of pyridine was performed at room temperature until the sample was saturated with adsorption spectra. After being warmed at 200 °C and purged with pure He for 20 min, the infrared spectrum of 1700–1400 cm^{−1} region was recorded at room temperature. HRTEM studies were performed using a JEM-2100 Plus electron microscope (Jeol, Tokyo, Japan). The catalyst after reaction was collected, washed by anhydrous alcohol, and dried for HRTEM analysis. Average slab length ($\bar{L}$) and stacking number ($\bar{N}$) of MoS₂ particles in each sample were established from the measurement of at least 200 crystallites detected on several HRTEM pictures. MoS₂ dispersion (f_{Mo}) was statistically evaluated by using the slab sizes determined from the TEM micrographs.

3.3. Catalytic Performance Evaluation

DBT hydrodesulfurization performance evaluation of various catalysts was performed in a continuous fix-bed reactor. The studied catalyst was in-situ presulfided at 300 °C for 6 h under 2 MPa. Carbon disulfide (CS₂, CAS: 75-15-0, 99%, Macklin, Shanghai, China) was used as presulfurization agent. Then, the HDS performance of catalyst was evaluated under various reaction conditions. The liquid reactant was DBT/decalin (C₁₀H₁₈, CAS: 91-17-8, 98%, Macklin, Shanghai, China) solution with sulfur content of 1773 ppm. After 6 h of reaction, the product of each reaction was periodically sampled and analyzed by Lunan 6890 gas chromatography equipped with an FID detector and OV-101 capillary column (Shandong Lunan Ruihong Co., Ltd., China). The DBT conversion was calculated according to following Equation (1).

Moreover, HDS of DBT proceeded through two main reaction pathways, which could be seen in following Scheme 1 [50,67]: the DDS route to produce biphenyl (BP) and the hydrogenation (HYD) route to produce cyclohexylbenzene (CHB), respectively. The selectivity for DDS pathway could be defined as shown in Equation (2). The final data of catalyst were confirmed when difference in DBT conversion and DDS selectivity among at least three consecutive samples were less than 1%.

$$\text{Conversion of DBT} = \frac{DBT_{in} - DBT_{out}}{DBT_{in}} \times 100\% \quad (1)$$

$$\text{DDS selectivity} = \frac{BP}{DBT_{in} - DBT_{out}} \times 100\% \quad (2)$$

4. Conclusions

The present work reported a series of mesoporous TiO₂ containing different potassium contents for loading NiO and MoO₃ to prepare the hydrodesulfurization catalyst. The potassium species could influence the porous structure of TiO₂ and simultaneously increase their basicity. All the catalysts had a good dispersion state of Ni and Mo species. A crystal NiMoO₄ phase was formed on the TiO₂ with a high potassium content. What is more, the incorporation of moderate potassium could accelerate mesoporous TiO₂-supported NiMo catalyst to carry out the complete DBT HDS conversion through direct desulfurization. The HYD pathway of DBT could be completely switched

off. Based on increased DDS selectivity, the improved reduction properties of oxidized active species could guarantee the enhanced DBT conversion of potassium-incorporated mesoporous TiO₂ supported hydrodesulfurization catalysts.

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