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# In situ implanting single tungsten site into defective UiO-66(Zr) by solvent-free route for efficient oxidative desulfurization at room temperature

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Abstract: Design of single site catalysts with catalytic sites at atomicscale and high atom utilization, provides new opportunities to gain superior catalytic performance for targeted reactions. In this contribution, we report a one-pot green approach for in-situ implanting single tungsten site (up to 12.7 wt.%) onto the nodes of defective UiO-66(Zr) structure via forming Zr-O-W bonds under solvent-free condition. The catalysts displayed extraordinary activity for the oxidative removal of sulfur compounds (1000 ppm S) at room temperature within 30 min. The turnover frequency (TOF) value can reach 44.0 h<sup>-1</sup> at 30°C, which is 109.0, 12.3 and 1.2 times higher than that of pristine UiO-66(Zr), WO<sub>3</sub>, and WCl<sub>6</sub> (homogeneous catalyst). Theoretical and experimental studies show that the anchored W sites can react with oxidant readily and generate W(VI)-peroxo intermediates that determine the reaction activity. Our work not only manifests the application of SSCs in the field of desulfurization of fuel oil but also opens a new solvent-free avenue for fabricating MOFs based SSCs.

### Introduction

With increasingly stringent environmental regulations, desulfurization of fuel oil becomes indispensable to obtain clean

energy source.<sup>[1,2]</sup> Oxidative desulfurization (ODS) is of great significance for producing fuel oil with ultra-low sulfur content due to its capability to eliminate refractory sulfur compounds with no hydrogen consumption and simple operation.<sup>[3-6]</sup> To date, considerable research has been devoted to prepare efficient ODS catalysts for obtaining clean fuel, however most of them needed high reaction temperature to meet efficient activity.<sup>[7-9]</sup> Several works have focused on the fabrication of ODS catalyst based on ionic liquid,<sup>[10,11]</sup> metal-organic frameworks (MOFs),<sup>[12,13]</sup> polyoxometalates.<sup>[4,14]</sup> metal oxide<sup>[3,15]</sup> or metal cluster<sup>[16]</sup> for removing sulfur compounds at low temperature. Unfortunately, the unevenly dispersed large pieces of active species easily block the pore of supports thus preventing contact with reactant or can only remove dibenzothiophene (DBT), which limit their ODS performance.<sup>[17,18]</sup> For this, the development of highly active ODS catalysts with rich porosity and atomic scale active sites at ambient temperature has been strongly pursued.

Single site catalysts (SSCs) with desired coordination environments and unique catalytic performance have become excellent candidates for various applications.<sup>[19-22]</sup> SSCs with catalytic sites at atomic-scale and higher atom utilization, provide new opportunities to develop rational catalyst design for targeted reactions.<sup>[23-26]</sup> Owing to the remarkable stability, large surface area and rich coordination unsaturated sites, pristine MOFs are

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the prominent candidates for synthesizing SSCs.<sup>[27-30]</sup> Importantly, defect sites on the nodes of MOFs allow for introduction of heterogeneous metal ions without protection, which is highly desirable for the systematic investigation of catalytic activity.<sup>[31,32]</sup> Therefore, the introduction of more active single-site into MOFs would be expected as a solution to enhance the ODS performance. To the best of our knowledge, no work on the use of MOFs based SSCs as ODS catalysts has been reported.

Herein, we presented a new one-pot approach to decorate W sites into UiO-66(Zr) framework without addition of solvent. The obtained SSCs exhibited extraordinarily high ODS activity for removing DBT (1000 ppm) within 30 min and 4,6dimethyldibenzothiophene (4,6-DMDBT, 500 ppm) within 20 min at room temperature, which can be ascribed to the hyperactive single W sites anchored on node of UiO-66(Zr). The experimental and theoretical results revealed that the introduction of W sites easily combine with oxidant and generate W(VI)-peroxo intermediates that efficiently oxidize sulfur compounds.

#### **Results and Discussion**

W/UiO-66(Zr) was pioneeringly prepared through a one-pot solvent-free route, where ZrOCl<sub>2</sub>·8H<sub>2</sub>O, BDC and WCl<sub>6</sub> were ground, then added into autoclave and crystallized at 130°C for 8h (Figure 1a). The powder XRD patterns of UiO-66(Zr) and W/UiO-66(Zr) are almost identical to that of the simulated one, confirming that the structure was maintained (Figure 1b). A new broad diffraction peak started to appear at  $2\theta = 6.0^{\circ}$  and became prominent with gradually introduced tungsten content, indicating that cluster missing defects could be generated in these W/UiO-66(Zr) structures.<sup>[33-35]</sup> Further increase of W content beyond 12.7 wt.% (based on ICP measurement, Table 1) led to destruction of the pristine MOF structure of UiO-66(Zr) (Figure S1). N<sub>2</sub> adsorption isotherms of W/UiO-66(Zr) display an abrupt increase in the region of  $0 < P/P_0 < 0.1$  and second jump with hysteresis loops at P/P<sub>0</sub> of 0.4~0.95 (Figure 1c), indicating that all of them possess hierarchical porosity (Figure 1c inset and Figure S2), which is consistent with the appearance of cluster missing defects as shown by XRD results. The BET surface areas for UiO-66(Zr) and W/UiO-66(Zr) gradually decrease from 1157 m<sup>2</sup>/g to 762 m<sup>2</sup>/g with the W content increased from 0% to 12.7% (Table 1 and S1). The SEM and TME images of UiO-66(Zr) present a morphology of sheet shape but of inhomogeneous particle size. The average particle size of W/UiO-66(Zr) increased with W content while the sheet-like morphology was retained (Figure 1d and S3-6). W/UiO-66(Zr)-0.12 was further investigated by HRTEM and HAADF-TEM based on its superior catalytic property, as will be shown later. There were scattered dark areas present in HRTEM image, but no lattice spacing of W-containing species were found (Figure 1e and S7). The dispersion of isolated bright dots was identified in HAADF images (Figure 1f and S8), which can be attributed to Zroxo nano-clusters formed by the destruction of UiO-66(Zr) structure under illumination of high-intensity electron beam. The element mappings display that Zr, W, O, C and Cl elements are homogeneously distributed in W/UiO-66(Zr)-0.12, which is similar to that of pristine UiO-66(Zr) (Figure 1g and S9 and S10). The exact element content of W/UiO-66(Zr)-0.12 is listed in Table S2 (Figure S11 and S12). The molar ratio of BDC, Zr and W was 0.69 : 1 : 0.094 based on calculation. The results can confirm that missing linker defects are present in W/UiO-66(Zr)-0.12.

Potentiometric acid-base titration has been confirmed to be an accurate approach to quantify the number of defects in UiO-66(Zr).<sup>[36,37]</sup> On the basis of the potentiometric acid-base titration measurement (Figure S13 and Table S3 and S4), UiO-66(Zr) was determined to exhibit a missing linker number of 1.91 per Zr-oxo cluster. Comparatively, the number of missing linkers in W/UiO-66(Zr)-0.12 was lowered to 1.65 due to the occupation of defect sites (-OH/OH<sub>2</sub>) by W (the W loading corresponds to 0.56 per Zroxo cluster).



Figure 1. (a) Schematic illustration of the synthetic process of W/UiO-66(Zr), (b) XRD patterns, (c) N<sub>2</sub> sorption isotherms and the pore size distribution curves (inset) of different samples, (d) TEM image, (e) HR-TEM image, (f) HAADF image and (g) elemental mapping images of W/UiO-66(Zr)-0.12.

Table 1. Textural properties and W, Zr contents of various samples.							
Samples	W content (wt.%) <sup>[a]</sup>	Zr content (wt.%) <sup>[a]</sup>	BET surface area (m²/g)	Micropore volume (mL/g) <sup>[b]</sup>	Mesopore volume (mL/g) <sup>[c]</sup>		
UiO-66(Zr)	0	33.1	1157	0.52	0.31		
W/UiO- 66(Zr)-0.03	2.7	32.7	967	0.43	0.35		
W/UiO- 66(Zr)-0.06	4.6	32.5	952	0.42	0.37		
W/UiO- 66(Zr)-0.12	6.1	32.3	924	0.40	0.39		
W/UiO- 66(Zr)-0.19	8.8	32.0	874	0.38	0.41		

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[a] Measured by ICP. [b] HK method. [c] BJH method.

FT-IR was conducted to monitor the bonding characteristics of the samples. The new emerging absorption band at 970 cm<sup>-1</sup> in FT-IR spectra of W/UiO-66(Zr) can be attributed to a W=O stretching vibration (Figure 2a and S14 and S15).<sup>[38-40]</sup> The broad Raman band of W/UiO-66(Zr) between 960-990 cm<sup>-1</sup> can be assigned to the starching mode of terminal W=O bands.<sup>[41]</sup> The emergent band at 910-950 cm<sup>-1</sup> is related to the weak vibrations of Zr-O-W bonds.<sup>[42,43]</sup> The additional band around 770 cm<sup>-1</sup> in the Raman spectra of W/UiO-66(Zr) compared to that of UiO-66(Zr) (Figure 2b), which is corresponding to the asymmetric stretching of the W-O bond,<sup>[41]</sup> also confirmed the presence of W-O bond. XPS spectra show that Zr in all the samples can be assigned to Zr<sup>4+</sup> oxidation state. Moreover, the Zr 3d peaks slightly shift to higher binding energies with increasing W content, which indicates the flow of electron density from Zr center to W center via the Zr-O-W linkages (Figure 2c and S16).[44-46] The charge transfer also can be confirmed by XPS spectra of O 1s, C 1s, Cl 2p and UV-vis spectroscopy (Figure S17-20). The two peaks around at 36.0 and 38.0 eV corresponded to W  $4f_{7/2}$  and W  $4f_{5/2}$ , signaling 6+ oxidation state of W in all the W/UiO-66(Zr) samples (Figure 2d and S21).[47] To further identify the atomic local structure, Fourier transform (FT) extended X-ray absorption fine structure (EXAFS) of W element was measured (Figure 2e). The FT-EXAFS spectrum of W/UiO-66(Zr)-0.12 exhibited one sharp peak at a distance that accounts for the W-O bond length and W-W coordination was not detected, which give forthright evidence for the formation of single W sites (Figure S22). The local structural parameters of W/UiO-66(Zr)-0.12 (Table S5) was obtained by fitting the EXAFS curve (Figure 2f). The fitting result indicated that the first shell coordination number of W atom was 4.<sup>[26]</sup> Combined with above structural characterization results, the atomic local structure of W in W/UiO-66(Zr)-0.12 can be ascertained, as shown in the inset in Figure 2f. Meanwhile, a good fit has been achieved between the measured XANES (X-ray absorption near edge structure) spectrum and the calculated one based on this atomic local structure model (Figure S23). According to potentiometric acid-base titration analysis, the reduction of the measured number of missing linkers in W/UiO-66(Zr)-0.12 relative to UiO-66(Zr) is 0.26 (corresponding to 1.04 -OH/OH<sub>2</sub> defect sites) per Zr-oxo cluster, in agreement with the number of W-occupied defect sites (1.12 per Zr-oxo cluster). The result further verified the identified location of single-atom W sites (See Figure S13 for details). DFT calculation results also indicate that the replacement of Zr by W is thermodynamically highly unfavorable (Figure S24). Similar to the case of W/UiO-66(Zr)-0.12, the EXAFS curve of W in W/UiO-66(Zr)-0.25 shows no W-W coordination (Figure S25), indicating a loading of single W sites up to 12.7 wt.%. All the as-prepared W/UiO-66(Zr) samples exhibits good thermal stability until 500°C, which shows the potential to act as a single-site heterogeneous catalyst for a wide range of reactions (Figure S26).



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Figure 2. (a) FT-IR spectra, (b) Raman spectroscopy, (c) and (d) XPS spectra for Zr 3d and W 4f of different materials, (e)  $k^3$ -weight FT-EXAFS curves of W/UiO-66(Zr)-0.12 at W L<sub>3</sub>-edge, (f) FT-EXAFS fitting curve of W/UiO-66(Zr)-0.12 at R space (insert, the corresponding structure model).

The catalytic activities of as-synthesized samples for ODS reactions were assessed at 30°C. UiO-66(Zr) exhibited poor activity, only 51.8% sulfur can be removed after a reaction time of 25 min. The GC-MS result further shows that only a total of 16.4% sulfur was oxidized as most of the DBT removed from the model fuel phase was in fact due to the extraction by acetonitrile. Notably, the removal of sulfur over W/UiO-66(Zr)-0.03, W/UiO-66(Zr)-0.06, W/UiO-66(Zr)-0.12, W/UiO-66(Zr)-0.19 and W/UiO-66(Zr)-0.25 reached 94.9%, 96.6%, 99.9%, 99.7% and 99.8% respectively after the same reaction time (Figure 3a). Moreover, only dibenzothiophene sulfone (DBTO<sub>2</sub>) could be detected in both the model fuel phase and the extraction phase by GC-MS after the ODS reaction over W/UiO-66(Zr)-0.12 and W/UiO-66(Zr)-0.19, confirming that DBT has been completely oxidized into DBTO<sub>2</sub>. W/UiO-66(Zr)-0.03, W/UiO-66(Zr)-0.06 and W/UiO-66(Zr)-0.25 exhibited slightly inferior oxidation performance as slight DBT could be detected in their both phases (Figure S27). Thus, among the W/UiO-66(Zr) samples, W/UiO-66(Zr)-0.12 showed the highest catalytic activity per active site for complete oxidation within 25 min at 30°C (Figure S28). It was worth noting that the DBT adsorption capacity of W/UiO-66(Zr)-0.12 is below 2% (Figure S29), and proved that the adsorption has little effect on ODS reaction. The removal efficiency of sulfur over W/UiO-66(Zr)-0.12 reached 99.0%, 99.8%, 99.8%, 97.3% and 95.6% at a reaction time 25 min when 1 mL, 2.5 mL, 5 mL, 7.5 mL and 10 mL acetonitrile were used as extraction phase (Figure 3b). The results indicated that very small amount of extractant can meet the requirement of ODS activity (Figure S30). The influence of O/S (oxidant/sulfur) molar ratio was studied. As shown in Figure 3c, the ODS performance of W/UiO-66(Zr)-0.12 increased with

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O/S molar ratio from 2 to 8. When the O/S molar ratio was 2, oxidation efficiency could reach 92.8% after a reaction time of 30 min. The removal efficiency of sulfur reached 99.2% within 30 min with the O/S molar ratio of 3, which indicated that W/UiO-66(Zr)-0.12 can offer high catalytic efficiency with exceptionally diluted oxidant. The tests with varied DBT concentration (from 250 ppm sulfur to 1500 ppm sulfur) show that DBT with a sulfur concentration of up to 1000 ppm can be removed within 30 min at 30°C (Figure S31). The influence of sulfur substrate over W/UiO-66(Zr)-0.12 was also tested by ODS of BT, DBT and 4,6-DMDBT (Sulfur content was 500 ppm for all the three tests). It is shown that 4,6-DMDBT, which is difficult to eliminate by industrial hydrodesulfurization, could be completely removed after a reaction time of 20 min at 30°C (Figure 3d), indicating that W/UiO-66(Zr)-0.12 possess great potential in future use for deep ODS of fuel oil. BT was the most difficult to oxidize due to the lower electron density on its sulfur atom (5.739) compared to DBT (5.758) and 4,6-DMDB (5.760), displaying 65.3% removal within 30 min.

The effect of reaction temperature on ODS over W/UiO-66(Zr)-0.12 is investigated with the sulfur content of DBT fixed at 1000 ppm. As shown in Figure 3e, the catalytic activity increased with reaction temperature, and the sulfur could be completely removed within 10 min at 50°C. Based on the temperature-dependent results, the activation energy (Ea) of W/UiO-66(Zr)-0.12 was calculated to be 32.4 kJ/mol, which is low compared with the data from the previous reports (Figure S32, Table S6).<sup>[11,17]</sup> The W/UiO-66(Zr)-0.12 catalyst also shows good reusability. Almost no visible efficiency decrease after four cycles was noticed (Figure 3e insert and S33. The structural stability of W/UiO-66(Zr)-0.12 after reuse was confirmed by XRD and N<sub>2</sub> sorption technique (Figure S34 and S35).



Figure 3. Influence of different (a) W content of various catalysts, (b) acetonitrile dosage, (c) the O/S molar ratio, (d) sulfur substrate, (e) reaction temperature

(reusability insert) on catalytic activities of W/UiO-66(Zr)-0.12 and (f) TOF number of different samples. Reaction conditions: 30 mg catalyst, 10 mL model fuel, 5 mL acetonitrile (except for b),  $H_2O_2$  as oxidant, O/S molar ratio of 4 (except for c), 500 ppm S (e 1000 ppm), 30°C (except for e).

To further comprehend the catalytic activity of W/UiO-66(Zr)-0.12, the ODS reactions for DBT with several representative MOF, POM/MOF and W-containing porous materials are summarized in Table S7. It is shown that most reported catalysts were active in ODS reaction of DBT when the reaction temperature was above 50°C. Ti-BDC-A,<sup>[12]</sup> W-KIT-6,<sup>[48]</sup> and W-IL-G-h-BN<sup>[49]</sup> were active at lower temperature, but need longer reaction time or organic oxidant to achieve the ideal desulfurization efficiency. Importantly, the TOF numbers of these catalysts were lower than that of W/UiO-66(Zr)-0.12. Comparatively, the TOF number over W/UiO-66(Zr)-0.12 could reach 44.0 h<sup>-1</sup> at 30°C, and is 109.0 and 12.3 and 1.2 times higher than pristine UiO-66(Zr), WO<sub>3</sub> and WCl<sub>6</sub> (Figure 3f and S36), and up to 132.0 h<sup>-1</sup> at 50°C, which is higher than most reported ODS catalysts. It is important to note that the ODS activity of W/UiO-66(Zr)-0.12 even beats that of WCI<sub>6</sub> which is a homogeneous catalyst in this reaction system.

DFT calculation was conducted to better understand the role of the implantation of W single sites in UiO-66(Zr). The optimized structures of UiO-66(Zr) and W/UiO-66(Zr) were displayed in Figure S37. To show the different reaction activity between them and H<sub>2</sub>O<sub>2</sub>, the frontier molecular orbitals (the highest occupied molecular orbital: HOMO and the lowest unoccupied molecular orbital: LUMO), which play key roles in chemical reactions, were calculated. The HOMO and LUMO of UiO-66(Zr) distributed uniformly and symmetrically throughout the whole molecule, while the HOMO of W/UiO-66(Zr) is mainly distributed on the W-O group, which is constituted by  $d_{x2-y2}$  and p orbitals of W and O atoms (Figure 4a). According to the frontier orbital theory, when UiO-66(Zr) and W/UiO-66(Zr) react with H<sub>2</sub>O<sub>2</sub>, the electrons in the HOMO of UiO-66(Zr) and W/UiO-66(Zr) flow to the LUMO of H<sub>2</sub>O<sub>2</sub>. As shown by the calculation, the HOMO of W/UiO-66(Zr) (-3.78 eV) are obviously closer to the LUMO of H<sub>2</sub>O<sub>2</sub> (-0.23 eV) compared with UiO-66(Zr) (HOMO: -6.75 eV). Therefore, W/UiO-66(Zr) has a higher tendency to react with H<sub>2</sub>O<sub>2</sub> than UiO-66(Zr), thus endowing it with superior catalytic activity.





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Figure 4. (a) Energies (in eV) and isosurfaces of HOMOs and LUMOs of UiO-66(Zr) and W/UiO-66(Zr)-0.12 at theoretical level. (b) Leaching and quenching experiments over W/UiO-66(Zr)-0.12 in the ODS reaction of DBT. (c) Proposed reaction mechanism. Reaction conditions: catalyst (30 mg), model oil (10 mL), acetonitrile (5 mL), DBT (500 ppm), oxidant (H<sub>2</sub>O<sub>2</sub>), O/S molar ratio (4:1), 30°C, p-benzoquinone (0.9 mmol) or tertiary butanol (1.8 mmol).

According to previous reports, the oxidation mechanism of sulfur compounds by H2O2 over W-based catalysts was known to execute via a peroxo-metal pathway referred to W(VI) without changing the oxidation state of W.<sup>[4,11,48,50]</sup> To confirm the above hypothesis, leaching and quenching experiments were carried out. When W/UiO-66(Zr)-0.12 was filtered out of the reaction system at a reaction time 5 min, the catalytic activity was almost completely inhibited, and confirmed that no leaching had occurred and that no plentiful radicals had been produced (Figure 4b). The catalytic performance was not strongly affected, when tertiary butanol (TBA, scavenger for HO'), p-benzoquinone (BQ, scavenger for O2-) or TBA and BQ added into the reaction system.^{[4,12]} The results suggested that HO' and  $\mathsf{O_2}^{{\scriptscriptstyle \text{\tiny \bullet}}}\text{,}$  as confirmed by EPR experiment (Figure S38),<sup>[12,13,51]</sup> play a minor role. The leaching and quenching experiments confirmed that W(VI)-peroxo intermediates should play the key role in ODS reaction. It has been reported that defective UiO-66(Zr) can catalyze the decomposition of H2O2 and generate O2- and HO. radicals.<sup>[4,13,51]</sup> Based on the above results, a plausible reaction mechanism is illustrated in Figure 4c. At first, sulfur compounds in model oil can be easily extracted into acetonitrile and adsorbed in the mesopores of catalyst with H<sub>2</sub>O<sub>2</sub>. Most H<sub>2</sub>O<sub>2</sub> reacted with W species to form W(VI)-peroxo.[11,47,50] The adsorbed sulfur compounds could be oxidized into sulfoxide, then further oxidized into sulphone, as confirmed by the mass spectrum (Figure S39). Meanwhile, H<sub>2</sub>O<sub>2</sub> was partially decomposed into O<sub>2</sub><sup>--</sup> and HO<sup>-</sup> radicals by Zr-OH sites in defective UiO-66(Zr), which also can oxidize sulfur compounds into sulphone.[4,48] The emerged mesopores in W/UiO-66(Zr), with pore size (~38.0 Å) larger than the molecular sizes of DBT and 4,6-DMDBT, also facilitate the catalytic process for providing sulfur compounds with better accessibility to single W sites.

#### Conclusion

In summary, we developed a facile one-pot approach to prepare W/UiO-66(Zr) with atomic dispersion of tungsten sites and hierarchical porosity under the solvent-free condition. The structural characterization confirmed that single W sites were anchored on the nodes of UiO-66(Zr) via forming Zr-O-W bonds. The loading content of single W sites via this approach can reach 12.7 wt.%. W/UiO-66(Zr)-0.12 with the suitable number of single W sites and mesoporosity displayed extraordinary ODS activity for the removal of DBT and 4,6-DMDBT, achieving a complete removal of sulfur (up to 1000 ppm) within 30 min at 30°C. The TOF number (132.0 h<sup>-1</sup> for DBT) at 50°C is at least 2 times higher than that of the reported catalysts. Theoretical study indicated that the introduction of single-W-sites play a vital role to determine catalytic rate. Our work demonstrated the high-efficiency desulfurization of fuel oil with W-SSCs UiO-66(Zr) at very mild conditions, and indicates that the solvent-free approach SSCs can be extended to rapid synthesis of other SSC systems for various applications.

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**Keywords:** Single site • Tungsten • UiO-66(Zr) • Solvent-free • Oxidative desulfurization

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#### **Entry for the Table of Contents**



A one-pot green approach for in-situ implanting single tungsten site (up to 12.7 wt.%) onto the nodes of defective UiO-66(Zr) structure via forming Zr-O-W bonds under solvent-free condition. The W/UiO-66(Zr) SSCs display extraordinary ODS activity under very mild condition, achieving complete oxidation of sulfur compounds (1000 ppm S) at room temperature within 30 min by using diluted  $H_2O_2$  as oxidant.