

Boosting Oxidative Desulfurization of Model and Real Gasoline over Phosphotungstic Acid Encapsulated in Metal-Organic Frameworks: the Window Size Matters

Xu-Sheng Wang,^[a,b] Lan Li,^[a] Jun Liang,^[a] Yuan-Biao Huang,^{*[a]} and Rong Cao^{*[a]}

Dedication ((optional))

Abstract: The large-scale uses of fossil fuels containing organosulfur compounds lead to air pollution and other related environmental problems. Therefore, it is highly desirable to develop new materials that can efficiently reduce the sulfur contents in fossil fuels, such as gasoline, diesel oil. Particularly, metal-organic frameworks (MOFs) supported polyoxometallic acids have been proved to be an important class of heterogeneous catalysts for oxidative desulfurization. However, there was no comprehensive study on the correlation between the desulfurization activities and window sizes of MOFs. In this work, a series of robust MOFs including MIL-100(Fe), UiO-66 and ZIF-8 with different window sizes were exploited as hosts to encapsulate phosphotungstic acid by "bottle around ship" method and utilized for ultra-deep oxidative desulfurization (ODS) of model and real gasoline. Compared with UiO-66 and ZIF-8 with very small window sizes, the mesoporous MIL-100(Fe) with larger window size exhibited the best catalytic performance in ODS of refractory sulfur compounds (benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene) and in recycle experiments. The correlations between the desulfurization activity and window size of corresponding MOFs could provide deeper insights for designing new porous catalysts for ODS and other size-selective catalysis reactions in the future.

Introduction

Nowadays, new techniques for ultra-deep desulfurization of fossil fuels have become more urgent because the large-scale use of fossil fuels leads to serious air pollution and the stricter environmental regulations have been promulgated by many countries.^[1-4] Although the traditional hydrodesulfurization (HDS) technique can removes thiols, sulfides, and disulfides in the fossil fuels, it is difficult to remove the refractory sulfur-containing aromatic hydrocarbon compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyl-

 X.-S. Wang, L. Li, J. Liang, Prof. Dr. Y.-B. Huang, Prof. Dr. R. Cao State Key Laboratory of Structural Chemistry Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China 350002.
E-mail: ybhuang@fjirsm.ac.cn (Y.B. H); rcao@fjirsm.ac.cn (R. C)
X.-S. Wang University of the Chinese Academy of Sciences Beijing, 100049, China

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

dibenzothiophene (4,6-DMDBT) due to their aromaticity and steric hindrance.^[1, 4-8] In contrast, the existing d orbits of sulfur atoms enable refractory sulfur-containing compounds to be oxidated to sulfone or sulfoxide easily. Moreover, the higher electron density of sulfur atoms is more favorable for oxidative desulfurization (ODS).^[6, 7, 9] Thus, to meet the requirement of strict environmental regulations, the ODS technique is a promising way to achieve an ultra-low level of sulfur content in fossil fuels. In the biphasic oxidative desulfurization system, DBT and other refractory organosulfur compounds were transferred to polar phase and then oxidated to their corresponding sulfones (Scheme 1). So far, polyoxometallic acids (POMs) based catalysts have been intensively studied in the ODS process because of their high catalytic activity in conversion of refractory sulfur to sulfone.^[5-7, 9-18] However, these catalysts are deactivated easily in the recycled runs because a large proportion of POMs were leaching to the solutions.[10-14] Thus, the use of porous material to confine POMs into their pores to prevent them leaching out is a promising strategy to circumvent this drawback.

In recent years, metal-organic frameworks (MOFs) have been widely applied in numerous fields including molecule separation and heterogeneous catalysis owing to its high surface area/porosity, tunable pore apertures/window size, and many other outstanding properties.^[19-28] The use of highly porous MOFs as hosts to confine effective POMs (POM@MOF) is a promising strategy for ODS with high activity and good recyclability. In particular, the diverse structures and tunable sizes of both MOFs and POMs could obtain plentiful new composite materials (POM@MOFs) as highly reactive catalysts for ODS. For example, Ribeiro et al. immobilized a commercial POM compound phosphotungstic acid (PTA, H₃PW₁₂O₄₀) into the mesocages of MIL-101 for ODS with excellent catalytic performance.^[5] Nevertheless, the PTA molecules would leach out during the ODS process due to its size (10.0 Å) is smaller than the window size (16.0×16.0 Å²) of MIL-101, which led to low activity of catalysts in the recycled runs.^[12] If the size of POM is smaller than that of the nanocages but larger than the window size of MOFs. POMs could be confined in the pores of MOFs to prevent leaching. However, it should be noted that the catalytic performance might decrease with narrowing the windows of MOFs because of the slower mass transfer.^[29] Therefore, the iudicious choice of MOFs with suitable window size which not only can confine POMs into the nanocages but also maintain the mass transfer speed is a key factor to enhance the catalytic performance. However, to the best of our knowledge, there was no report about the relationship between the oxidative desulfurization activity and the window size of MOFs.

WILEY-VCH



Scheme 1. View of ODS using PTA@MOFs as heterogeneous catalysts, and the catalytic reactions of organosulfur compounds in this study.

With those considerations in mind, herein, three types of robust MOFs MIL-100(Fe), UiO-66, and ZIF-8 with different window sizes were selected as hosts to load PTA for the oxidative desulfurization of model and real gasoline. $\overset{[30-35]}{__}$ MIL-100(Fe) is an iron(III) carboxylate porous MOF with two types of mesopores cages of free apertures of ca. 25.0 Å and 29.0 Å, accessible through microporous windows of ca. 5.8×5.8 Å² and 8.6×8.6 Å², respectively (Figure 1a).^[30, 33, 34, 36] UiO-66 was constructed by Zr₆O₄(OH)₄(CO₂)₁₂ secondary building units and dicarboxylate bridging ligands, which presents an interesting three dimensional material with two types of microporous cages of free aperture of ca. 10.0 Å and 14.0 Å, accessible through microporous windows of ca. 6.0 Å (Figure 1b). $^{[31,\ 35]}$ ZIF-8 is composed of 2-methylimidazolate and zinc(II) with a sod cage ca. 12.0 Å, accessible through a narrow six-ring pore ca. 3.4 Å (Figure 1c).^[32, 36] Interestingly, the size of PTA is ca. 10.0 Å, which could be restricted to the nanocages of the above mentioned MOFs including MIL-100(Fe), UiO-66 and ZIF-8, avoiding the leaching out of the PTA from MOFs. More significantly, the comprehensively study of the relationship between window size and the activity of ODS would help pave the way not only for the design of new porous catalysts towards ultra-deep oxidative desulfurization and other catalytic reactions, especially size-selective reactions, but also for the exploration of their new applications such as gas storage/separation, drug delivery and sensing.

Results and Discussion

Catalysts preparation and characterization

To fully understand the catalytic performance influenced by the window size of porous catalysts, PTA encapsulated in the cages of MOFs including MIL-100(Fe), UiO-66, and ZIF-8 with different window sizes were successfully synthesized using the "bottle around ship" strategy. The MOFs can assemble around the PTA molecules, which could be encapsulated into their corresponding cages. The resulting materials PTA@MOF (MOF = MIL-100(Fe), UiO-66, ZIF-8) were fully characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma OES spectrometer (ICP-OES), field emission scanning electron microscope (SEM), transmission electron microscope (TEM), thermo gravimetric measurements (TG), N₂ sorption experiment etc. Due to the characterization methods of those catalysts are similar, MIL-100(Fe) and PTA@MIL-100(Fe) as the representative materials were selected to be discussed in detail, whereas the characterization of other materials were presented in the Supplementary Information.

The phase purity of MIL-100(Fe) was confirmed by PXRD (Figure 2a), and its pattern was in good agreement with the simulated one. The PTA@MIL-100(Fe) composite was prepared by a facile one-pot method via the reaction of iron powder, H₃BTC, HF, HNO₃ and required amount of PTA in deionized water. The obtained orange solids were denoted as 7%PTA@MIL-100(Fe). 16%PTA@MIL-100(Fe), and 35%PTA@MIL-100(Fe) respectively, based on the PTA weight content determined by ICP-OES. The PXRD patterns of the PTA@MIL-100(Fe) material were similar to those of the parent material MIL-100(Fe), which indicated that the crystal structure of MIL-100(Fe) was retained after incorporation of PTA (Figure 2a). The characterization peaks of PTA were not observed in the PXRD patterns of PTA@MIL-100(Fe) indicating that the PTA were uniformly dispersed in the mesocages of MIL-100(Fe), which can be employed as single active site for enhanced catalysis. In addition, the TG analysis revealed that MIL-100(Fe) and PTA@MIL-100(Fe) are thermal stable up to 400 °C (Figure S3), which are suitable for catalytic performance.

The successful incorporation of PTA was further confirmed by FT-IR spectroscopy (Figure 2b). The characterization peak at 1080 cm⁻¹ can be assigned to the asymmetric vibrations of the P-O bond of PTA, and the peak at 980, 896, 825 cm⁻¹ was attributed to the terminal W=O_a, edge share of W-O_b-W, and corner share of W-O_c-W bonds, respectively.^[7] Compared with the W-O_c-W characterization peak of pure PTA at 802 cm⁻¹, a red shift of the PTA@MIL-100(Fe) peak to 825 cm⁻¹ indicating that a strong interaction existed between PTA and MIL-100(Fe),^[9] which promoted the high loading of PTA in MIL-100(Fe) as confirmed with the ICP-OES data.

The N₂ sorption isotherms of MIL-100(Fe) and PTA@MIL-100(Fe) with different PTA loading amount are shown in Figure 3a. The parent material MIL-100(Fe) showed high BET (2055 m²/g) and pore volume (0.993 cm³/g). Interestingly, although the very high amount of PTA (35 wt%) incorporation in MIL-100(Fe), the PTA@MIL-100(Fe) exhibited high BET surface area of 1046 m²/g, and large pore volume of 0.487cm³/g (Table 1). The existence of two types of mesopores (25.0 Å and 29.0 Å) and the corresponding microporous windows (5.8×5.8 Å for

WILEY-VCH



Figure 1. Selected robust metal-organic frameworks with different sizes of windows in this study.



Figure 2. (a) PXRD and (b) FT-IR of MIL-100(Fe), 7%PTA@MIL-100(Fe), 16%PTA@MIL-100(Fe), and 35%PTA@MIL-100(Fe), (c) PXRD and (d) FT-IR of 16%PTA@MIL-100(Fe) and the recycled samples.

pentagonal windows and 8.6×8.6 Å for hexagonal windows) of MIL-100(Fe) was illustrated by pore size distribution (PSD) of MIL-100(Fe), which was calculated by nonlocal density functional theory (NLDFT) model in Figure 3b. Notably, the mesopores and microporous windows were also retained after loading large amount of PTA, especially for 7%PTA@MIL-100(Fe), 16%PTA@MIL-100(Fe). The preserved mesopores and windows of the PTA@MIL-100(Fe) could ensure that

substrates enter into the pores and contact with the active site PTA. More interestingly, due to the relatively small windows and large mesocages, the PTA (10.0 Å) were confined inside the mesopores of MIL-100(Fe), which could prevent the leaching of PTA during catalytic reactions.

SEM and TEM revealed that the octahedral shape of MIL-100(Fe) was preserved after incorporation of PTA (Figure 4 and Figure S1). The Fe, P, and W elements were clearly observed in

WILEY-VCH



Figure 3. The N₂ adsorption-desorption isotherm at 77K (a), and pore size distribution (b) of the MIL-100(Fe), 7%PTA@MIL-100(Fe), 16%PTA@MIL-100(Fe), and 35%PTA@MIL-100(Fe).

1

Table1. The BET surface area a	and pore volume of MIL-1	100(Fe) and PTA@MIL-100(Fe).
--------------------------------	--------------------------	------------------------------

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)
MIL-100(Fe)	2155	0.993
7%PTA@MIL-100(Fe)	2056	0.927
16%PTA@MIL-100(Fe)	1627	0.861
35%PTA@MIL-100(Fe)	1046	0.487



Figure 4. (a) SEM, (b) HAADF-STEM image and (c-e) the corresponding EDX mapping of 16%PTA@MIL-100(Fe).

the energy-dispersive X-ray (EDX) of 16%PTA@MIL-100(Fe) indicating that PTA have been incorporated into MIL-100(Fe) (Figure S2). The EDX elemental mapping further revealed that the elements of Fe, P, W were uniformly distributed throughout the entire structure of MIL-100(Fe) (Figure 4b).

Oxidative desulfurization performance

Optimization of oxidative desulfurization parameters

10.1002/cctc.201601450

WILEY-VCH



Figure 5. Graphs of optimizing the catalytic conditions. (a) Loading amount, (b) dosages, (c) temperature, and (d) O/S ratio over PTA@MIL-100(Fe).



Figure 6. (a) Oxidative desulfurization of DBT under different reaction time; (b) Kinetic profile for the oxidative of DBT.

Before fully understand the catalytic performance influenced by the window size of porous catalysts, the effect of the oxidative desulfurization parameters including PTA loading amount, catalyst dosage, O/S molar ratio (the molar ratio of H_2O_2 to

organosulfur compounds), reaction temperature and time were investigated to find the optimal catalytic conditions (initial reaction conditions: catalyst dosage 15 mg/0.3mol%, O/S molar ratio 2, temperature 80 $^{\circ}$ C, reaction time 1 h). As DBT is one of

WILEY-VCH



Figure 7. Molecular structures and the sizes of the representative organosulfur compounds in this study.



Figure 8. Oxidative desulfurization of refractory organosulfur compounds using catalysts with different window size.

the most refractory organosulfur compounds, it was selected as the model substrate to optimize the reaction conditions of oxidative desulfurization over PTA@MIL-100(Fe).

The PTA loading amount had a significant effect for this reaction (Figure 5a). As shown in Figure 5a, it should be noted that the parent MIL-100(Fe) exhibited no activity in ODS process, whereas PTA encapsulated in MIL-100(Fe) exhibited effective catalytic performance. The catalytic activity of 16%PTA@MIL-100(Fe) was more than twice of that of 7%PTA@MIL-100(Fe), mainly because the high loading of PTA could provide more active sites. However, further increasing the loading of PTA to 35%, the conversion of DBT decreased to 28% due to the excess PTA partially blocked the pores and the reactants were difficult to diffuse to the PTA active sites in the cages (Figure 3a and Table 1). Consequently, 16%PTA@MIL-100(Fe) was chosen as the optimized catalyst in the subsequent study for ODS process. Notably, only DBT sulfone product was detected by GC-MS. As shown in Figure 5b, increasing the catalyst

dosage can improve the catalytic performance. Interestingly, the conversion of DBT reached to 78% using only 0.6 mol% (30 mg) PTA, which can be attributed to the well dispersed PTA molecules in the nanocages and the formation of isolated active site. When the dosage increased to 1.0 mol% (50 mg), the activity was similar to that of using 0.6 mol%. The conversion rate of the oxidative desulfurization was also affected by reaction temperature. The catalytic results of 16%PTA@MIL-100(Fe) for ODS at different temperatures ranging from 323 K to 373 K are shown in Figure 5c. The conversion of DBT increased with raising temperature firstly, and reached to maximum with 84% at 70 °C due to the formation of active metallic peroxides at high temperature.^[7, 9] However, the activity decreased when the temperature continue to increase, which was ascribed to the increased decomposition rate of H₂O₂ at higher temperature. The molar ratio of O/S is a very important factor in industry. In previous reports, most of catalytic processes need high O/S molar ratio due to the side reactions involving the thermal decomposition of hydrogen peroxide.^[10, 13] Therefore, to achieve a high economic value, the use of H2O2 as small amount as possible is highly desirable.^[37] To investigate the influence of the amount of H_2O_2 on the catalytic performance, O/S ratios from 1 to 10 were studied at optimal reaction temperature (Figure 5d). With the O/S molar ratio raising, the activity increased at first, then decreased, and the highest activity when the O/S was 4. Notably, the conversion rate can reach to 70% at stoichiometric ratio of O/S = 2, and 96% at O/S = 3. Further increasing the O/S ratio to 4, the conversion rate can reach to 100%. Although the high contents of H₂O₂ can increase the catalytic activity, the produced excess water (from ODS reaction and thermal decomposition) will hinder the ODS reaction and lead to low activity. These results indicated that the balance of the two opposing factors is very important, which can be achieved by controlling of the oxidant reagent amount.^[9, 10, 13] More significantly, compared with other catalysts such as PTA-CeO₂ and V_2O_5 -TiO₂,^[10, 13] the less required H₂O₂ indicating that 16%PTA@MIL-100(Fe) is an effective catalyst for ODS. The conversion of DBT versus reaction time at optimal conditions over 16%PTA@MIL-100(Fe) was given in Figure 6a. The GC yield can achieve 90% in 40 min, and fully conversion was obtained in 1 hour. The rate constant k (0.065 min⁻¹) for the oxidation of DBT was afforded from the linear plot of $ln(C_0/C_t)$ versus reaction time t as shown in Figure 6b and the calculation procedures can be seen in supplementary information (S2.11 Calculation method of rate constant k). Moreover, control experiments summarized in Table S1 shows that all catalysts including PTA, MIL-100(Fe) and PTA@MIL-100(Fe) have no activity without the existence of H₂O₂ (Entry 2-4). Compared with PTA@MIL-100(Fe), the PTA or MIL-100(Fe) also shown negligible activity with H2O2 existing, which confirmed the synergistic effect of two components (Entry 6-8).

Exploitation of window size-activity relationship

To explore the effect of the window size, three robust catalysts PTA@MIL-100(Fe), PTA@UiO-66 and PTA@ZIF-8 were utilized for oxidative desulfurization. The structures and the sizes of the selected MOFs and three refractory organosulfur compounds DBT, BT and 4,6-DMDBT are shown in Figure 1 and Figure 7,

WILEY-VCH



Figure 9. The recyclability and reusability of 16%PTA@MIL-100(Fe) in five runs for DBT oxidative desulfurization.

respectively. As shown in Figure 8, PTA@ZIF-8 exhibited low activity for the ODS and the conversion of 4,6-DMDBT, DBT and BT was 25.7%, 28.6%, and 9.1%, respectively. The low activity was ascribed to the very narrow windows (ca. $3.4 \times 3.4 \text{ Å}^2$) of ZIF-8, which blocked the three organosulfur compounds to enter in the cages of the catalyst.

Interestingly, the catalyst PTA@UiO-66 with a large window size of 6.0x6.0 Å² gave very high activity with conversion of 94.8% and 100% for BT and DBT, respectively, which can be mainly attributed to that the two reactants can easily diffuse into the inner pores of UiO-66. In contrast, the compound 4,6-DMDBT with big size can only reacted at the external surface of the catalyst, giving a 39.1% conversion to sulfone. However, the mesoporous PTA@MIL-100(Fe) catalyst with larger window sizes (ca. 8.6x8.6 Å²) exhibited high activity for the three substrates 4,6-DMDBT, DBT and BT and gave a conversion of 92.8%, 100%, and 61.8%, respectively. The control experiments demonstrated that the large window size could facilitate the diffusion of the reactants and thus accelerated the reaction rate and gave high yield.

Besides the effect of window size of catalysts, the ODS reactions were also influenced by the physical and chemical properties of substrates including the electron density on the sulfur and the steric hindrance around the sulfur atom. The electron density on the sulfur atom of 4,6-DMDBT, DBT, and BT is 5.760, 5.758, and 5.739, respectively. It is known that lower electron density on sulfur atoms was unfavorable for ODS. Consequently, the substrate BT gave a low activity with 61.8% conversion by PTA@MIL-100(Fe). As 4,6-DMDBT and DBT have the similar electron density on sulfurs, the activity mainly affect by the steric hindrance around the sulfur atom. Thus, PTA@MIL-100(Fe) gave a higher conversion for DBT due to the less steric hindrance around the sulfur atom. The oxidative activity of refractory organosulfur compounds by PTA@MIL-100(Fe), as discussed above, decreased in the order of DBT > 4,6-DMDBT > BT, which is consistent with previous works.^[5, 7, 38]

PTA@ZIF-8 also exhibited the same ODS order for refractory organosulfur compounds. This order can be attributed to comprehensive effects of the electron density on the sulfur and the steric hindrance around the sulfur atom. However, the activities for PTA@UiO-66 followed the order of DBT > BT > 4,6-DMDBT, which is different from PTA@MIL-100(Fe). This difference can be attributed to that the big 4,6-DMDBT can only reacted at the external surface of the catalyst and led to the low activity. Moreover, the high activity of BT by PTA@UiO-66 was result from the synergistic effect of UiO-66 and PTA. The defect vacancies exist in the catalyst PTA@UiO-66 and the produced open Lewis acid active site could also increase the desulfurization activity.^[31] The control experiments demonstrated that UiO-66 showed high catalytic activity with respect to DBT, whereas MIL-100(Fe) and ZIF-8 exhibited almost no activity (Entry 7, 10, 14, Table S1). This is mainly because the formation of Zr^{IV}-peroxo groups on the surface of the UiO-66 by the interaction with H₂O₂, which is not easy to be formed on the materials of MIL-100(Fe) and ZIF-8.[31]

To evaluate the possible leaching of PTA from the three robust catalysts, the W content in gasoline were analyzed using ICP-OES after workup, respectively. Amazingly, the leaching W into gasoline were negligible from the three robust catalysts mainly due to the fact that the PTA molecules are confined in the mesoporous cages and difficult to escape through the microporous windows. Notably, a serious loss of PTA was observed in the PTA@MIL-101(Cr) catalytic system due to the window size of 1.6 nm which is larger than the size of PTA (1.0 nm), resulting low activity of catalysts in the next several runs.^[5] Therefore, the judicious choice of MOFs with suitable window size which not only can confine POMs into the nanocages but also the accessible of the reactants is a key factor for oxidative desulfurization and other catalytic reactions.

Based on our results and other reported literatures, ^[5, 14, 16-18, 38-43] a possible mechanism for this system was illustrated. The oxidative desulfurization started with the fast diffusion of DBT from oil phase to acetonitrile phase. At the same time, the highly porous MOF materials could enhance the adsorption capacity for organosulfur compounds and co-catalyst such as H_2O_2 .^{[3, 17, 44} ^{45]} Thus the PTA supported on MOF can be oxidated to W^{VI}-peroxo by the enriched H_2O_2 , following oxidized the concentrated DBT to sulfide and sulfone.^[4] Moreover, the highly dispersed POM confined in MOF cage can serve as single active site which is beneficial for accelerating the ODS process. In particular, the suitable window size of MOF could not only confine the PTA into the pores of MOF to prevent leaching, but also ensure the accessible of the DBT reactants.

Recycling of catalyst

The stability of catalysts is important for desulfurization industry. Interestingly, compared with homogeneous catalyst, the PTA@MIL-100(Fe) catalyst can be easily separated and reused for five consecutive ODS cycles without loss of activity (Figure 9). The PXRD patterns, FT-IR spectra, N₂ sorption isotherms, pore size distribution, BET and pore volume of the recycled catalyst were similar to those corresponding fresh PTA@MIL-100(Fe) catalyst, indicating that the structure of the catalyst was retained

Table	2.	ODS	performance	for	real	gasoline	by	PTA@MIL-100(Fe)	and
PTA@	UiC)-66.							

Catalyst	Run Times	S Remaining (mass ppm)	Desulfurization/%
PTA@MIL-100(Fe)	1	73	85
PTA@MIL-100(Fe)	2	36	92
PTA@UiO-66	1	120	75
PTA@UiO-66	2	98	79

Footnotes: the initial S content in the real gasoline was ca. 473 mass ppm.

(Figure 2, Figure S4 and Table S2). Furthermore, hot filtration experiment was also investigated for the stability of PTA@MIL-100(Fe). As shown in Figure 6a, the catalytic reaction stopped after the removal of catalyst. In addition, the ICP-OES analysis exhibited that the leaching of PTA into the model gasoline was negligible which can be attributed to the fact that the PTA molecules are confined in the mesoporous cages and difficult to escape through the microporous windows.

Oxidative desulfurization of real gasoline

The outstanding performance of the PTA@MIL-100(Fe) and PTA@UiO-66 in the desulfurization of the model gasoline motivated us to apply them to a real gasoline desulfurization (sulfur content ca. 473 mass ppm, Table 2). 75% organosulfur compounds in gasoline were removed by PTA@UiO-66 after one cycle, and total 79% can be achieved after two cycles. Further more, as the window size of PTA@MIL-100(Fe) facilitate all substrates accessible to active sites, the removal of organosulfur compounds in gasoline can reach to 85% and 92% respectively after one cycle and two cycles, respectively. The high efficiency of PTA@MIL-100(Fe) indicated that it is a promising candidate catalyst for future industrial desulfurization application.

Conclusions

In conclusion, PTA molecules encapsulated in three robust MOFs with different window sizes have been successfully synthesized by a facial one-pot "bottle around ship" method. The study of the relationship of window size–activity for ODS performance revealed that the activity and the leaching amount of PTA increased with the increasing of the window size. The control experiments demonstrated that PTA@MIL-100(Fe) exhibited high activity and good recyclability in the oxidative desulfurization of model gasoline and real gasoline because of its suitable window size and confined effect, which facilitates organosulfur compounds accessible to active sites (PTA). The study of the relationship between the structure and activity paves the way not only for the synthesis of new porous catalysts

and their use for applications in oxidative desulfurization, but also for the exploration of their new applications such as other catalysis, gas storage, drug delivery.

Experimental Section

Materials

The reagents phosphotungstic acid (Sinopharm, AR), iron powder (Adamas, 99%), trimesic acid (H₃BTC, Aladdin, 99%), terephthalic acid (H₂BDC, Adamas, 99%), 2-methylimidazole (Adamas, 99%), ZrCl₄ (Adamas, 99%), HNO₃ (Sinopharm, 65%wt, 15 M), HF (Sinopharm, 40%wt, 22.5 M), DBT (Adamas, 99%), acetonitrile (MeCN, Sinopharm, 99%), n-heptane (Ourchem, 97%), 30% H₂O₂ (Sinopharm, AR), n-dodecane (Aladdin, 99%), and real gasoline (TCI, reference materials of sulfur in gasoline certified by the Japan Petroleum Institute, sulfur content 500 mass ppm level) were used as received without further purification.

Catalysts preparation

Preparation of porous MIL-100(Fe)

The porous material MIL-100(Fe) was prepared according to the method described in the literature ^[30]. In a typical procedure, a mixture of iron powder (0.45g, 8 mmol), H₃BTC (1.13 g, 5.4 mmol), HF (0.71 mL, 22.5 M, 16 mmol), HNO₃ (0.32 mL, 15 M, 4.8 mmol), and deionized water (47 mL, 2.6 mol) was ultrasonicated for 20 min and heated at 160 °C for 24 h. The obtained orange solid was further washed with water and ethanol three times, respectively. The orange solid was referred as MIL-100(Fe).

Preparation of porous PTA@MIL-100(Fe)

The encapsulation of PTA in MIL-101(Fe) was prepared following the same procedure as for the pure MIL-100(Fe). Typically, a mixture of iron powder (0.45 g, 8 mmol), H₃BTC (1.13 g, 5.4 mmol), HF (0.71 mL, 22.5 M, 16 mmol), HNO₃ (0.32 mL, 15 M, 4.8 mmol), and deionized water (47 mL, 2.6 mol) were ultrasonicated for 20 min, then 1.44 g, 2.88 g, or 5.76 g of PTA was added into the above solution and stirred for further 10 min. Then, the autoclave was transferred to a stainless vial and heated at 160 °C for 24 h. The obtained orange solids were further washed with water and ethanol throughly and dried at 70 °C over night. The solids were denoted as 7%PTA@MIL-100(Fe), 16%PTA@MIL-100(Fe), and 35%PTA@MIL-100(Fe) respectively, based on the weight content of PTA determined by ICP-OES.

Preparation of porous UiO-66

The procedure of preparation of UiO-66 was similar to the method described in the literature ^[31]. In a typical procedure, 699 mg ZrCl₄ (3 mmol) and 498 mg terephthalic acid (3 mmol) were dissolved in 60 mL DMF, and then heated at 120 °C for 24 hours.

After cooling to room temperature, the obtained white colloid was filtered, and washed three times with DMF and ethanol each and dried at 70 $^{\circ}$ C overnight.

Preparation of porous PTA@UiO-66

The encapsulation of PTA in UiO-66 was prepared by one pot method following the same procedure as for the pure UiO-66, except 1.44g PTA was added in the solution during the synthesis procedure. The resulting solid was denoted as 10%PTA@UiO-66, based on the weight content of PTA determined by ICP-OES.

Preparation of porous ZIF-8

The porous material ZIF-8 was prepared according to the method described in the literature ^[32]. In a typical procedure, 810 mg (9.874 mmol) 2-methylimidazole dissolved in 25 mL of MeOH was poured into a 25 mL MeOH solution containing 734 mg (2.469 mmol) Zn(NO₃)₂·6H₂O under stirring. After 24 h, the solid was obtained by centrifugation, and washed with fresh MeOH throughly. At last, the product is dried at 70 °C overnight.

Preparation of porous PTA@ZIF-8

The encapsulation of PTA in ZIF-8 was prepared following the same procedure as for the pure ZIF-8, except 5 mL (10 mM) of predesigned PTA solution was added during the synthesis procedure. The resulting solid was denoted as 10%PTA@ZIF-8, based on the weight content of PTA determined by ICP-OES.

Catalytic test

Preparation of model gasoline and the property of real gasoline

20 mmol DBT and 2 mL dodecane (internal standard) were mixed with n-heptane to form 1000 mL model gasoline with sulfur content ca. 950 mass ppm. Other two kinds of model gasoline (BT and 4,6-DMDBT) were prepared with the similar procedure and the sulfur contents are 950 mass ppm. For the real gasoline, the sulfur content is ca. 473 mass ppm and the density is 0.8287 g/cm³ at 15 °C.

Catalytic tests using model and real gasoline

The refractory organosulfur compounds can be extracted by MeCN and readily oxidized to the corresponding sulfones in the bi-phase ODS process (Scheme 1). The bi-phase ODS system was carried out in a reaction tube (15 mL) equipped with a magnetic stirrer at different temperature. The catalytic performance of the catalysts were investigated by oxidation of refractory organosulfur compounds (DBT, BT or 4,6-DMDBT) in the presence of H₂O₂ oxidant. The volume of model gasoline is identical to MeCN. In a typical reaction, 16%PTA@MIL-100(Fe) (30 mg, 0.6 mol%), MeCN (2 mL), and model gasoline (2 mL) were placed in a reaction tube (15 mL) under stirring. Then, H₂O₂ (20 µL) was added to the mixture and the reaction started after the tube was put into an oil bath at 70 °C. Finally, the reaction stopped by putting the tube into an ice bath. The quantitative analysis of various sulfur compounds in the model gasoline and the polar solvent were performed on a gas chromatograph (Angilent G7890A) equipped with a FID detector and a gas chromatography-mass spectrometry (Varian 450-GC/240-MS). To study the oxidative desulfurization of refractory organosulfur compounds using catalysts with different window size, the reaction conditions were set as: catalyst dosage 0.6mol%, O/S molar ratio 4, temperature 70 $^{\circ}$ C, reaction time 24 h.

The desulfurization procedure of real gasoline is similar to the above model gasoline. In a typical reaction, 16%PTA@MIL-100(Fe) (30 mg), MeCN (2 mL), and real gasoline (2 mL) were placed in a reaction tube (15 mL) under stirring. Then, H₂O₂ (20 μ L) was added to the mixture and the reaction started after the tube was put into an oil bath at 70 °C. After 24 hours, the reaction stopped by putting the tube into an ice bath. The catalyst were washed throughly with ethyl acetate and dried in an 50 °C oven. Then it was used as catalyst for the second desulfurization cycle. The qualitative analysis of sulfur content in the real gasoline was determined through ultraviolet fluorescence method by Institute of Quality Inspection for Products (Fuzhou, Fujian province, China).

Hot filtration and recycling experiment

In a typical hot filtration experiment, 16%PTA@MIL-100(Fe) (30 mg), MeCN (2 mL), and model gasoline (2 mL) were placed in a reaction tube (15 mL) under stirring. Then, H_2O_2 (20 μ L) was added into the mixture. The reaction started after the reaction tube was put into an oil bath at 70 °C. After 20 min, the solid catalyst was removed by syringe filter, and the conversion rate of DBT was detected by GC. The filtrate was further treated at 70 °C, and analysed in a period of 20 min.

In the recycling experiment, the catalyst was centrifugated after two hours reaction and washed throughly with ethyl acetate To detect the leaching amount of PTA from catalysts, both of the phases of gasoline and acetonitrile were analyzed by detecting the W leaching.

Acknowledgements ((optional))

The authors gratefully acknowledge the financial support of the 973 Program (2014CB845605 and 2013CB933200), NSFC (21671188, 21273238, 21521061, and 21331006), Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000), Youth Innovation Promotion Association, CAS (2014265), and Chunmiao Project of the Haixi Institute of the Chinese Academy of Sciences (CMZX-2014-004).

Keywords: desulfurization • heterogeneous catalysis • metalorganic frameworks • phosphotungstic acid • real gasoline.

- B. Pawelec, R. M. Navarro, J. M. Campos-Martin, J. L. G. Fierro, *Catal. Sci. Technol.* 2011, *1*, 23.
- [2] A. Gómez-Paricio, A. Santiago-Portillo, S. Navalón, P. Concepción, M. Alvaro, H. Garcia, *Green Chem.* 2016, 18 508.
- [3] F. Shi, M. Hammoud, L. T. Thompson, *Appl. Catal. B:* Environ **2011**, *103*, 261.
- [4] V. Chandra Srivastava, *RSC Adv.* **2012**, *2*, 759.
- [5] S. Ribeiro, A. D. S. Barbosa, A. C. Gomes, M. Pillinger, I. S. Gonçalves, L. Cunha-Silva, S. S. Balula, *Fuel Process. Technol.* 2013, *116*, 350.

- [6] C. M. Granadeiro, L. S. Nogueira, D. Julião, F. Mirante, D. Ananias, S. S. Balula, L. Cunha-Silva, Catal. Sci. Technol. 2016, 6, 1515.
- X. S. Wang, Y. B. Huang, Z. J. Lin, R. Cao, Dalton Trans. [7] 2014, 43, 11950.
- C. S. Song, Catal. Today 2003, 86, 211. [8]
- G. Q. Luo, L. H. Kang, M. Y. Zhu, B. Dai, Fuel Process. [9] Technol. 2014, 118, 20.
- M. Zhang, W. Zhu, S. Xun, H. Li, Q. Gu, Z. Zhao, Q. [10] Wang, *Chem. Eng. J.* **2013**, *220*, 328. W. Zhu, B. Dai, P. Wu, Y. Chao, J. Xiong, S. Xun, H. Li, H.
- [11] Li, ACS Sustain. Chem. Eng. 2015, 3, 186.
- J. Zhang, A. J. Wang, Y. J. Wang, H. Y. Wang, J. Z. Gui, [12] Chem. Eng. J. 2014, 245, 65.
- L. C. Caero, E. Hernández, F. Pedraza, F. Murrieta, Catal. [13] Today 2005, 107-108, 564.
- G. Rodriguez-Gattorno, A. Galano, E. Torres-García, [14] Appl. Catal. B: Environ 2009, 92, 1.
- X.-M. Yan, P. Mei, L. Xiong, L. Gao, Q. Yang, L. Gong, [15] Catal. Sci. Technol. 2013, 3, 1985.
- [16] D. Julião, A. C. Gomes, M. Pillinger, L. Cunha-Silva, B. de Castro, I. S. Gonçalves, S. S. Balula, Fuel Process. Technol. 2015, 131, 78.
- [17] Y. Liu, S. Liu, S. Liu, D. Liang, S. Li, Q. Tang, X. Wang, J. Miao, Z. Shi, Z. Zheng, ChemCatChem 2013, 5, 3086.
- [18] X. L. Hao, Y. Y. Ma, H. Y. Zang, Y. H. Wang, Y. G. Li, E. B. Wang, Chem. Eur. J. 2015, 21, 3778.
- J. Jiang, O. M. Yaghi, Chem. Rev. 2015, 115, 6966. [19]
- Y. B. Huang, Q. Wang, J. Liang, X. Wang, R. Cao, J. Am. [20] Chem. Soc. 2016, 138, 10104.
- [21] A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D. X Xue, H. Jiang, M. Eddaoudi, Angew. Chem. Int. Ed. 2015, 54, 14353.
- [22] X. S. Wang, J. Liang, L. Li, Z. J. Lin, P. P. Bag, S. Y. Gao, Y. B. Huang, R. Cao, Inorg. Chem. 2016, 55, 2641.
- [23] L. Li, X. Wang, J. Liang, Y. Huang, H. Li, Z. Lin, R. Cao, ACS Appl. Mater. Inter. 2016, 8, 9777.
- J. S. Qin, D. Y. Du, M. Li, X. Z. Lian, L. Z. Dong, M. [24] Bosch, Z. M. Su, Q. Zhang, S. L. Li, Y. Q. Lan, S. Yuan, H. C. Zhou, J. Am. Chem. Soc. 2016, 138, 5299.
- [25] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, Science 2013, 341, 1230444.
- [26] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, Chem. Soc. Rev. 2014, 43, 6011.
- [27] W.-H. Zhang, Q. Liu, J.-P. Lang, Coord. Chem. Rev. 2015, 293-294, 187.

- [28] C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, J. Am. Chem. Soc. 2009, 131, 1883.
- [29] J. Juan-Alcañiz, J. Gascon, F. Kapteijn, J. Mater. Chem. 2012, 22, 10102.
- B. Van de Voorde, M. Boulhout, F. Vermoortele, P. [30] Horcajada, D. Cunha, J. S. Lee, J. S. Chang, E. Gibson, M. Daturi, J. C. Lavalley, A. Vimont, I. Beurroies, D. E. De Vos, *J. Am. Chem. Soc.* **2013**, *135*, 9849.
- C. M. Granadeiro, S. O. Ribeiro, M. Karmaoui, R. Valenca, [31] J. C. Ribeiro, B. de Castro, L. Cunha-Silva, S. S. Balula, Chem. Commun. 2015, 51, 13818.
- J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber, [32] M. Wiebcke, Chem. Mater. 2011, 23, 2130.
- [33] P. Horcajada, S. Surble, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki, G. Ferey, Chem. Commun. 2007, 27, 2820.
- G. Ferey, C. Serre, C. Mellot-Draznieks, F. Millange, S. [34] Surble, J. Dutour, I. Margiolaki, Angew. Chem. Int. Ed. 2004, 43, 6296.
- [35] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, J. Am. Chem. Soc. 2008, 130, 13850.
- X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew.* Chem. Int. Ed. **2006**, *45*, 1557. [36]
- J. M. Campos-Martin, M. C. Capel-Sanchez, P. Perez-[37] Presas, J. L. G. Fierro, J. Chem. Technol. Biotechnol. 2010, 85, 879.
- X. Hu, Y. Lu, F. Dai, C. Liu, Y. Liu, Microporous [38] Mesoporous Mater. 2013, 170, 36.
- S. Ribeiro, C. M. Granadeiro, P. Silva, F. A. Almeida Paz, [39] F. F. de Biani, L. Cunha-Silva, S. S. Balula, Catalysis Science & Technology 2013, 3, 2404.
- C. M. Granadeiro, A. D. S. Barbosa, S. Ribeiro, I. C. M. S. [40] Santos, B. de Castro, L. Cunha-Silva, S. S. Balula, Catalysis Science & Technology 2014, 4, 1416.
- X. Zhang, Y. Shi, G. Liu, Catal. Sci. Technol. 2016, 6, [41] 1016.
- Y. Ding, W. Zhu, H. Li, W. Jiang, M. Zhang, Y. Duan, Y. [42] Chang, Green Chem. 2011, 13, 1210.
- [43] N. Tang, Y. Zhang, F. Lin, H. Lu, Z. Jiang, C. Li, Chem. Commun. 2012, 48, 11647.
- [44] W.-W. He, S.-L. Li, W.-L. Li, J.-S. Li, G.-S. Yang, S.-R. Zhang, Y.-Q. Lan, P. Shen, Z.-M. Su, J. Mater. Chem. A 2013, 1, 11111.
- J.-X. Qin, P. Tan, Y. Jiang, X.-Q. Liu, Q.-X. He, L.-B. Sun, [45] Green Chem. 2016, 18, 3210.

WILEY-VCH

FULL PAPER



The window size to success: Compared with UiO-66 and ZIF-8 with small window size, phosphotungstic acid encapsulated in the mesoporous MIL-100(Fe) with larger window sizes exhibited efficient desulfurization performance of model and real gasoline due to the confine of the PTA into the pores of MOF and ensure the accessible of all the organic sulfurs into the confined active sites in the pores.

Xu-Sheng Wang, Lan Li, Jun Liang, Yuan-Biao Huang,* and Rong Cao*

Page No. – Page No.

Boosting Oxidative Desulfurization of Model and Real Gasoline over Phosphotungstic Acid Encapsulated in Metal-Organic Frameworks: the Window Size Matters