

# Ultrasound-Assisted Synthesis of Highly Dispersed Molybdophosphoric Acid on SBA-15 Catalysts for the Oxidation and Separation of 4,6-Dimethyldibenzothiopene

Mireya Villanueva Sánchez<sup>a,b</sup>, Lifang Chen<sup>a\*</sup>, Luis Enrique Noreña<sup>b,\*</sup>, Natali de la Fuente<sup>a</sup>, Elim Albiter<sup>a</sup>, Miguel Angel Valenzuela<sup>a</sup>, Jin An Wang<sup>a</sup>

<sup>a</sup>Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, Col. Zacatenco, 07738 Ciudad de México, Mexico

<sup>b</sup>Departamento de Ciencias Básicas, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas, 02200 Ciudad de México, Mexico.  
lchen@ipn.mx

In this investigation, an ultrasound-assisted synthesis method was applied to synthesize the highly dispersed 12-molybdophosphoric acid on SBA-15 catalysts. Three SBA-15-supported catalysts were obtained with varying heteropolyacid content from 10 to 20 and 30wt%. The heteropolyacid exhibited high dispersion on SBA-15, with a particle size smaller than 4 nm, as confirmed by XRD analysis and TEM observation. All catalysts possessed both Lewis (L) and Brønsted (B) acid sites, and the number of acid sites showed an almost linear increase with the heteropolyacid content. In the oxidative removal of 4,6-dimethyldibenzothiopene (4,6-DMDBT) from a model diesel, these catalysts demonstrated high catalytic activity. The 4,6-DMDBT conversion was proportional to the surface acidity, reaching the highest conversion of 98.7% on the catalyst with 30wt% heteropolyacid after a 40 min reaction at 70°C. It was proposed that the 4,6-DMDBT molecule preferentially adsorbed on the L acid sites by donating its unshared electrons in sulphur atom to the L acid sites of the catalyst via the surface acid-base reaction pathway, followed by oxidation reaction with H<sub>2</sub>O<sub>2</sub> oxidant. The resulting polar sulfone (4,6-DMDBTO<sub>2</sub>) was immediately extracted by the polar extracting agent (acetone/nitrile) and separated from the oil phase. This work has proven that adsorption, oxidation and separation of 4,6-DMDBT in a model diesel fuel can be simultaneously realized in one operation unit for ultralow sulphur diesel production.

## 1. Introduction

It is well known that heteropolyacids with *Keggin* structure contain a large number of acid sites which usually act as active centres for many catalytic reactions, such as the Friedel–Crafts alkylation of aromatic compounds [Kozhevnikov I.V., 2003], and hydroisomerization of naphtha [Chen L.F., et al, 2022]. However, heteropolyacids, such as the 12-molybdophosphoric acid, have a surface area smaller than 5 m<sup>2</sup>/g, and many active sites in them are inaccessible for surface reactions. One way to enhance their reactivity is to immobilize them on a matrix with a larger surface area and big porosity. The SBA-15 solid has a surface area greater than 500 m<sup>2</sup>/g and a pore diameter between 6 and 30 nm, depending of its synthesis route [Zhao D. et al, 2000]. When heteropolyacids are dispersed on SBA-15, the surface area of the final catalyst can reach 300-500 m<sup>2</sup>/g. The size of a single 12-molybdophosphoric acid molecule is estimated to be 1.2-1.5 nm. Theoretically, it can disperse well on the surface and the inner pores of SBA-15. However, 12-molybdophosphoric acid aggregates usually consist of several molecules, leading to pores blocking and some porosity lose.

For nanocatalysts and functional nanomaterials preparation, the ultrasound-assisted synthesis has been believed to be a simple, green, and effective method [Eycken E., Kappe C.O. 2006; Xu Z. et al. 2005]. During the sonication process, many cavitation bubbles can be formed in the mixture which may collapse in the liquid environment and inhibit the rapid growth of crystal size. During the immobilization of 12-molybdophosphoric acid on SBA-15, if the ultra-sonication is applied, the formation of large particles can be avoided [Flores Cantera J.

et al, 2024]. Hence, a highly dispersed heteropolyacid on SBA-15 nanocatalysts can be obtained via the ultrasonication assisted method.

The purpose of the current work is to synthesize highly dispersed 12-molybdophosphoric acid on SBA-15 catalysts using the ultrasonic-assisted method used for the production of ultralow sulphur diesel. The 12-molybdophosphoric acid loading varied from 10 to 20 and 30wt%. The crystalline structure and textural properties of these catalysts were characterized by X-ray diffraction and N<sub>2</sub> adsorption-desorption isotherms. Their surface acidity was quantitatively measured by means of the *in situ* FTIR of pyridine adsorption technique. The morphological features were observed by transmission electron microscopy (TEM). The catalytic activity of the catalysts was evaluated in the 4,6-dimethyldibenzothiophene (4,6-DMDBT) oxidation reaction in a model diesel using hydrogen peroxide as oxidant. The formed sulfone with higher polarity was immediately extracted by a polar agent (acetonitrile) in the designed biphasic reaction system. Thus, oxidation of an organosulfur compound in a model diesel and the separation of the formed sulfone from the oil phase can be realized in one single operation, with a high oxidative desulfurization efficiency.

## 2. Experimental

### 2.1 Chemicals

Tetraethylorthosilicate (Sigma–Aldrich, 98%); Triblock copolymer [(polyethylene oxide)–block-(polypropylene oxide)–block-(polyethylene oxide)] (Aldrich, Mn: 5800; viscosity: 350 cps at 60 °C); methanol (Aldrich, absolute, >99.9%); Phosphomolybdic acid, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (terms HPMo) (Sigma–Aldrich, 98%); 4,6-dimethyldibenzothiophene (Sigma–Aldrich, 98%). 4,6-Dimethyldibenzothiophene sulfone (Sigma–Aldrich, 98%). Hydrogen peroxide (Sigma–Aldrich, 30% H<sub>2</sub>O<sub>2</sub> in water); formic acid (Sigma–Aldrich, ≥95%); n-Hexadecane (Sigma–Aldrich, ≥99%). Acetonitrile (Sigma–Aldrich, 99.8%).

### 2.2 Synthesis of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SBA-15

The catalyst support, the SBA-15 solid, was prepared by the hydrothermal synthesis method according to that previously reported in literature [3]. For the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SBA-15 catalysts synthesis, the incipient wetness impregnation method together with an ultrasound-assisted method was applied. 5g of the SBA-15 solid were added into 50 ml methanol containing a given amount of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> for 60 min of adsorption and impregnation under ultra-sonication with potential 800 W and frequency 40 KHz for 5 min in a Branson-1516 reactor. Then, the suspended mixture was dried by removing the extra methanol at 60 °C. The obtained sample was calcined at 300 °C for 2h. These catalysts were labeled as xHPMo/SBA-15, where x corresponds to the wt% H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> loading and HPMo refers to H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>. H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> loading greater than 30wt% on SBA-15 was not reported due to their relative poorer dispersion, and the lower catalytic activity.

### 2.3 Catalyst characterization

The crystalline structures of the SBA-15 support and the HPMo/SBA-15 catalysts were analyzed by the X-ray diffraction technique employing a Bruker Model X D2 PHASER diffractometer. The Cu K $\alpha$  radiation was selected with a diffracted beam monochromator ( $\lambda = 1.5405 \text{ \AA}$ ). For the SBA-15, the low angle XRD pattern was recorded in a 2 $\theta$  region between 0 and 10°. For the HPMo/SBA-15 catalysts, XRD patterns were recorded in a two-theta range between 10 and 80°. The textural properties of the catalysts were measured by nitrogen physisorption isotherms on a 3P Instruments GmbH & Co-KG (Model Micro 100). The surface area data were calculated according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model from the data of desorption isotherms.

The SBA-15 and HPMo/SBA-15 morphological features were observed by transmission electron microscopy (TEM), (JEOL model JEM-2100) at a 200 kV accelerating voltage. The surface acidity was quantitatively measured by the *in situ* FTIR of pyridine adsorption method. The measurement was performed on a 170-SX FTIR spectrometer in a temperature range between 50 and 300 °C. The sample wafer (approximately 1 cm<sup>2</sup> with 10-20 mg) was exposed to pyridine, by breaking a capillary containing 50 $\mu$ l of liquid pyridine inside the spectrometer cell. The number of Brønsted (B) and Lewis (L) acid sites were calculated according to the integral area of the IR bands at around 1540 and 1445 cm<sup>-1</sup>, respectively. The extinction coefficients E<sub>B</sub> = 1.0086 cm/mmol for Brønsted acid sites and E<sub>L</sub> = 0.9374 cm/ mmol for Lewis acid sites were used for the acid site calculation.

### 2.4 Catalytic evaluation

The catalytic activity of the HPMo/SBA-15 catalysts was tested in the oxidative removal of 4,6-dimethyldibenzothiophene (4,6 DMDBT) in a model diesel (n-hexadecane containing 300 ppm 4,6 DMDBT). A calculated amount of catalyst was added in a glass beaker with a mixture of 30 ml model diesel and 30 ml of

acetonitrile as polar extracting agent. The oxidation reaction was performed at atmospheric pressure at 50, 60, and 70 °C reaction temperatures with magnetic agitation (750 rpm), respectively. The reaction time was set at 60 min. H<sub>2</sub>O<sub>2</sub> was selected as oxidant. Normally, the molar ratio H<sub>2</sub>O<sub>2</sub>/4,6-DMDBT was 6. The 4,6-DMDBT concentration in n-hexadecane was monitored by UV-vis spectrophotometry. The variation of the UV absorption band at 283 nm corresponding to the 4,6-DMDBT absorption was recorded during the oxidation reaction. The 4,6-DMDBT conversion was determined as a function of reaction time using the following equation (1):

$$X_{4,6\text{-DMDBT}} (\%) = (C_0 - C_t) / C_0 \quad (1)$$

Where  $X_{4,6\text{-DMDBT}}$  is the 4,6-DMDBT conversion percentage;  $C_0$  is the 4,6-DMDBT concentration in oil phase at time zero and  $C_t$  is the 4,6-DMDBT concentration in oil phase at time  $t$ . The 4,6-DMDBT conversion was reported in an average of three times of measurement under the same condition. The validation of the experimental results was indicated by the error bars in the plots of 4,6-DMDBT concentration against the reaction time.

### 3. Results and Discussion 4,6-DMDBT

#### 3.1 Textural properties

The hysteresis loops of N<sub>2</sub> adsorption-desorption isotherms of SBA-15 and H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> immobilized on SBA-15 catalysts are shown in Figure 1. The typical mesoporous features were present in all the samples. The N<sub>2</sub> adsorption in the low  $p/p_0$  region confirms the creation of some micropores within the mesoporous solid. The average pore diameters of the catalysts varied between 12.7 and 6.3 nm, depending on the heteropoly acid content. H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> grafting led to some surface area, pore diameter, and pore volume diminishing. The textural data are reported in Table 1.

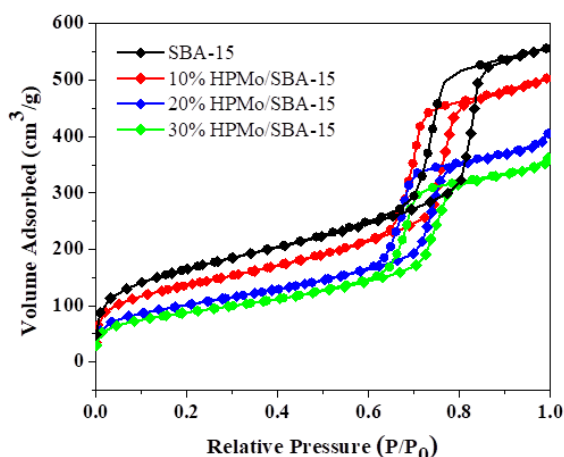


Figure 1. Hysteresis loops of N<sub>2</sub> adsorption-desorption isotherms of the different samples

Table 1: Textural properties of the SBA-15 and the H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub>/SBA-15 catalysts

Catalysts	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
SBA-15	583.6	0.860	12.7
10%HPMo/SBA-15	479.2	0.777	8.4
20%HPMo/SBA-15	360.6	0.618	7.9
30%HPMo/SBA-15	310.4	0.550	6.3

#### 3.2 X-ray diffraction analysis

The low angle XRD pattern of SBA-15 along the two-theta range from 0.5 to 6° is shown in Figure 2a. Three well-resolved peaks at 0.75, 1.05 and 1.51° were observed, corresponding to the (100), (110) and (200) planes reflections of the SBA-15 solid with a P6mm hexagonal symmetry [Zhao D. et al, 2000]. When the heteropolyacid was loaded on the surface of SBA-15, only one wide intense peak with peak maximum at 22.5° was observed between 15 and 40°, Figure 2b, corresponding to amorphous silica, herein SBA-15. This result indicates a very high dispersion of the heteropolyacid crystals on the SBA-15 surface. The ultrasonication

application during the synthesis procedure led to the high dispersion of heteropolyacid with very fine particles, smaller than 4 nm.

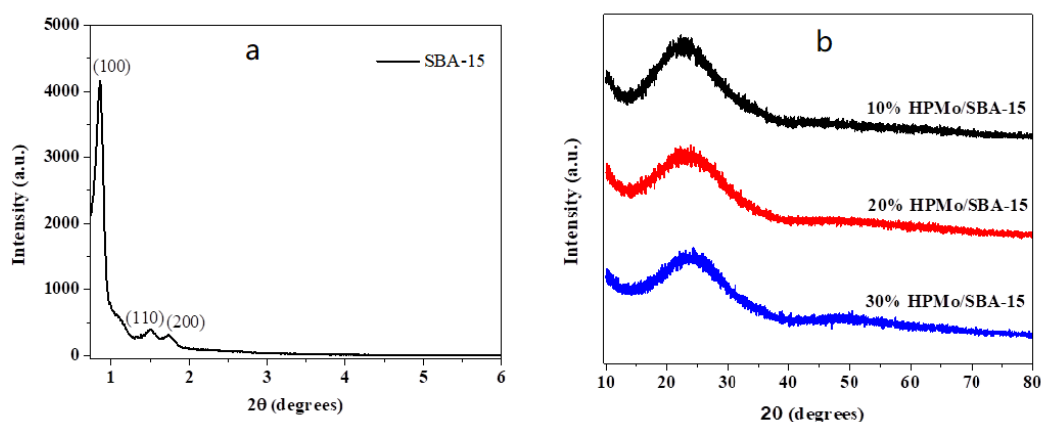


Figure 2: XRD patterns of (a) SBA-15 and (b) HPMo/SBA-15 catalysts.

### 3.3 Morphological features of SBA-15 and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SBA-15 catalysts

Figure 3 shows the TEM micrographs of SBA-15 and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SBA-15 catalysts. For the SBA-15 support, Figure 3A, many parallel channels were clearly observed. The average channel diameter was approximately 12 nm with a pore wall thickness about 4 nm. For the 10wt%HPMo/SBA-15 catalyst, Figure 3B, highly ordered hexagonal pore structures were present; while, large heteropolyacid nanoparticles on the SBA-15 support were not able to be observed, indicating their high dispersion. For the 30wt%HPMo/SBA-15 catalyst, Figure 3C, some small dark dots on the SBA-15 surface can be seen, which may correspond to dispersed 12-molybdophosphoric acid nanoparticles. In the present work, the application of ultrasonication during the catalyst synthesis resulted in a high dispersion of heteropolyacid nanoparticles. The TEM observations are in good agreement with the XRD analysis.

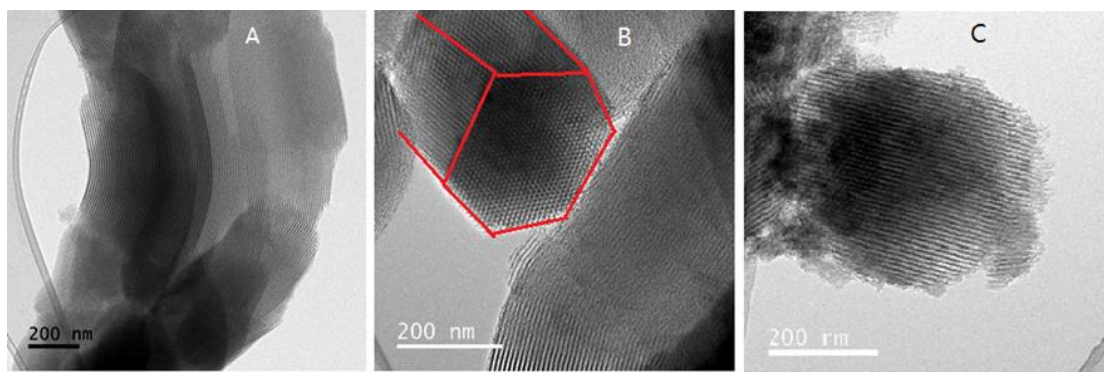


Figure 3: TEM micrographs of SBA-15 and HPMo/SBA-15 catalysts. (A): SBA-15; (B): 10%HPMo/SBA-15; (C) 30%HPMo/SBA-15.

### 3.4 Surface acidity of SBA-15 and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SBA-15 catalysts

The surface acidity of the SBA-15 and the HPMo/SBA-15 catalysts were measured by *in situ* FTIR spectroscopy (Figure 4). Generally, the IR bands at 1450, 1580 and 1595 cm<sup>-1</sup> correspond to the Lewis (L) acid sites and the IR bands at 1545, 1608 and 1637 cm<sup>-1</sup> correspond to the Brønsted (B) acid sites [Srinivas D. et al, 2004]. The absorption band at around 1490 cm<sup>-1</sup> is indicative of the pyridine molecule adsorbed on both, B and L sites [Yang X.K. et al, 2009]. The strong and asymmetrical IR band at 1450 cm<sup>-1</sup> recorded at 50 °C indicated that some pyridine was physically adsorbed on SBA-15 via hydrogen bonding. In this work, the IR spectra recorded at 100 °C were used for quantitative calculations of acidity. For the bare SBA-15 support, many L acid sites existed as confirmed by the strong IR absorption bands at 1450, 1580 and 1595 cm<sup>-1</sup>, and no Brønsted acid sites were formed because no IR band at 1540 cm<sup>-1</sup> appeared. On the other hand, for the HPMo/SBA-15

catalysts, both, L and B acid sites coexisted. Clearly, the B acid sites resulted from the 12-molybdophosphoric acid deposition on SBA-15. These acid sites were retained at 200 °C and most of them disappeared after thermal treatment at 300 °C, due to the partial decomposition of the *Keggin* structure of the dispersed heteropolyacid. The number of L and B acid sites almost linearly increased with the  $H_3PMo_{12}O_{40}$  content. The quantitative acid data are reported in Table 2. The catalyst with 30wt% of 12-molybdophosphoric acid contained a larger number of acid sites: 645  $\mu\text{mol/g}$ , which is 3.21 and 1.85 times greater than those of the 10wt%HPMo/SBA-15 and 20wt%HPMo/SBA-15 catalysts, respectively.

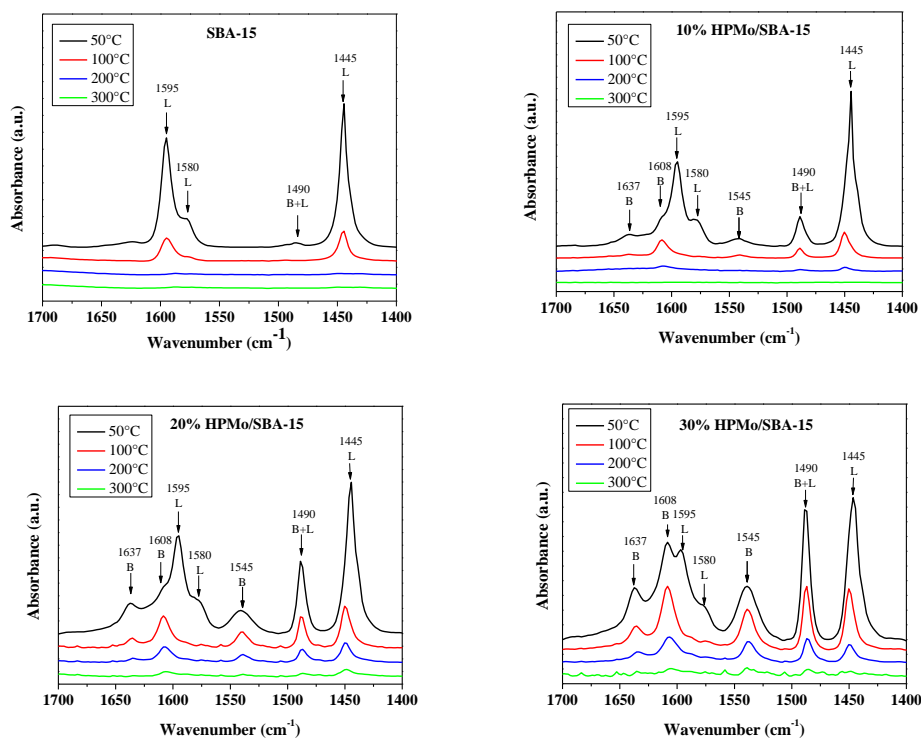


Figure 4. In situ FTIR spectra of pyridine adsorption on SBA-15 and  $H_3PMo_{12}O_{40}/SBA-15$  catalysts.

Table 2: Acidity of SBA-15 and  $H_3PMo_{12}O_{40}/SBA-15$  catalysts obtained from the IR spectra recorded at 100 °C.

Samples	Brønsted acidity ( $\mu\text{mol/g}$ )	Lewis acidity ( $\mu\text{mol/g}$ )	Total acidity ( $\mu\text{mol/g}$ )
SBA-15	0	166	166
10%HPW/SBA-15	44	157	201
20%HPW/SBA-15	105	244	349
30%HPW/SBA-15	226	419	645

### 3.5 Catalytic activity

The catalytic activity of the  $H_3PMo_{12}O_{40}/SBA-15$  catalysts was evaluated in the oxidative removal of 4,6 DMDBT in a model diesel. The results obtained at different reaction temperatures (50, 60 and 70 °C) are shown in Figure 5. At the set reaction temperature, the 4,6 DMDBT concentration rapidly decreased in the first 20 min of reaction. At the same reaction temperature, the 4,6 DMDBT conversion increased together with the heteropolyacid content or the surface acidity. At different reaction temperatures, a higher temperature favoured the 4,6 DMDBT oxidation. The highest conversion was obtained at 70 °C on the 30wt%HPMo/SBA-15 catalyst, reaching 98.7% after 40 min of reaction. The oxidative desulfurization reaction at a temperature higher than 70 °C was not performed considering the thermal stability of oxidant (hydrogen peroxide) and the possible evaporation of the extracting agent (acetonitrile evaporation temperature: 82.2 °C). It is noteworthy that the sulphur atom in the 4,6 DMDBT molecule has two pairs of unshared electrons, and thus it may act as an electron donor; on the other hand, many L acid sites distributed on the catalyst surface and they possess capacity for accepting electrons. As a result, when the 4,6 DMDBT molecule contacts the catalyst surface, it can

preferentially adsorb on the Lewis acid sites by offering its isolated electron pairs, forming peroxophomolybdate species. Because the sulphur compound adsorption on the catalyst is the crucial step, 4,6 DMDBT conversion was proportional to the Lewis acidity content over the HPMo/SBA-15 catalyst. When a B acid site locates close to the L acid site, forming combined B-L centres, the H<sup>+</sup> in peroxophomolybdate species may also participate in the O atom transferring from the oxidant to the S atom in 4,6-DMDBT, inducing cleavage of the O–O bond, this favours the formation of sulfone (4,6-DMDBT<sub>2</sub>) [Chen L.F., et al, 2022].

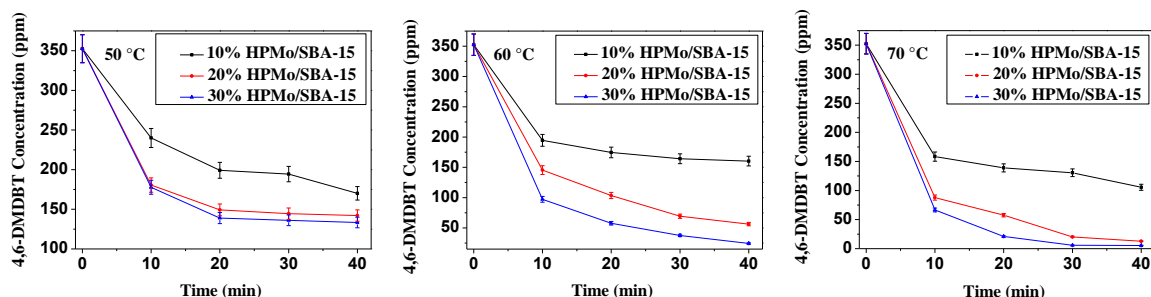


Figure 5. Oxidative removal of 4,6 DMDBT in a model diesel. Reaction conditions: reaction time: 60 min; catalyst concentration: 2g/L; H<sub>2</sub>O<sub>2</sub>/4,6 DMDBT: 6; Initial 4,6 DMDBT in *n*-hexadecane 300 ppm; *n*-hexadecane/acetonitrile volume ratio: 1:1.

#### 4. Conclusions

The ultrasound-assisted synthesis method has demonstrated remarkable efficacy in preparing highly dispersed 12-molybdophosphoric acid on SBA-15 catalysts. These catalysts showed extremely fine particles, measuring smaller than 4 nm, distributed on the surface and inside the pores of SBA-15. All three catalysts revealed a considerable presence of L and B acid sites, and the quantity of these acid sites exhibited an upward trend corresponding to the increasing heteropolyacid content. In the context of 4,6-DMDBT oxidation in a model diesel, the pivotal role of surface acidity in the catalysts became apparent, with the 4,6-DMDBT conversion directly correlating with the Lewis acidity of the catalysts. The highest conversion (98.7%) was achieved with the 30wt% HPMo/SBA-15 catalyst. Our proposed mechanism suggests that 4,6-DMDBT molecules are selectively adsorbed onto the Lewis acid sites through a surface acid-base reaction, followed by surface oxidation facilitated by H<sub>2</sub>O<sub>2</sub>, forming a polar sulfone. This work has confirmed that oxidation and separation of refractory organosulfur compounds 4,6-DMDBT in a model diesel fuel can be simultaneously realized in one operation unit to produce near zero-sulphur diesel fuel.

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