Heteropolyacids as effective catalysts to obtain zero sulfur diesel*

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Abstract: This paper deals with the catalytic properties of different supported heteropolyacids (HPAs), both molybdenum- and tungsten-based, in the oxidative desulfurization process of diesel. We are jointly developing a new oxidative desulfurization process, aimed at reducing the sulfur content in diesel to less than 10 ppm (parts per million) using in situ produced peroxides. In this new process, high-molecular-weight organosulfur compounds, such as 4,6-di-methyl-dibenzothiophene (DMDBT), difficult to be eliminated by conventional hydro-desulfurization, are oxidized to the corresponding sulfones and subsequently removed by adsorption. Molybdenum-based HPAs, with Keggin structure, proved to be the most active and selective catalysts for oxidizing DMDBT with on-stream lifetimes exceeding 1500 h time on stream (t.o.s.).

Keywords: heteropolyacids; desulfurization; diesel; air pollution; molybdenum.

INTRODUCTION

The sulfur content in fuels is required, by regulations, to be progressively lowered. In diesel, it will have to be reduced to a value lower than 15 ppm (parts per million) in the United States, and to a value lower than 10 ppm in the European Union within the year 2009. Conventional processes to obtain sulfur removal from diesel consist of catalytic hydrogenation (hydro-desulfurization), where sulfur-containing compounds are reduced to H_2S and then separated from the liquid phase. The hydro-desulfurization process can easily remove many kinds of organic sulfur compounds such as mercaptans, sulfides, and disulfides. However, higher-molecular-weight sulfur compounds, such as dibenzothiophenes, cannot be removed under standard conditions and in most cases, either a new high-pressure hydrotreating unit or a major revamp of a low/moderate-pressure hydrotreating unit is required. The installation of a new pressure unit is very expensive, and it is avoided unless there is no other option, but also the revamping of low/moderate pressure causes an increased hydrogen consumption, new reactor, and shorter catalyst cycle (i.e., higher catalyst costs). An interesting new way to reduce the sulfur content in diesel below 10 ppm (ULSD, ultra low sulfur diesel) is oxidative desulfurization technology, which can be applied to pre-hydrotreated diesel. This technology removes the most refractory dibenzothiophenes, oxidizing them to the corresponding sulfones (Scheme 1), which are highly polar compounds easily removed by extraction or adsorption chromatography.
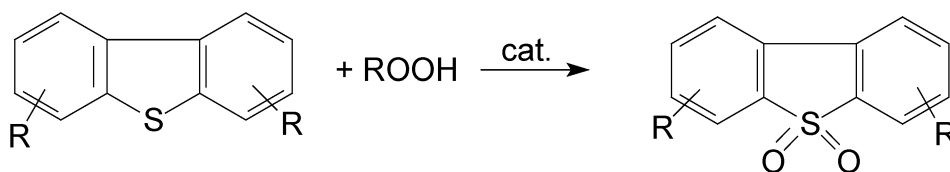
Scheme 1 Alkyl-dibenzothiophene oxidation to the corresponding sulfone.

Oxidative desulfurization is not a new concept. It has been discussed recently [1,2]. The oxidants used in this reaction are either hydrogen peroxide, peracid, or organic peroxides [3]. This process is efficient, and very low sulfur content can be obtained. But the high cost of H_2O_2 or organic hydroperoxide makes the economics unfavorable in comparison with the traditional hydro-desulfurization process.

In order to overcome this limitation, we have jointly developed a new oxidative desulfurization process in which the hydroperoxide is directly produced in the reaction medium. ULSD process can become economically convenient. Various oxidation catalysts proved to be effective in this new process. The activities and stabilities of different heteropolyacids (HPAs) will be illustrated here.

EXPERIMENTAL

Heteropolyacid syntheses and characterization

Ten HPAs were prepared, six of them with Keggin structure ($H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_5PMo_{10}V_2O_{40}$, $H_3PMo_{10}W_2O_{40}$, $H_4PMo_9W_2VO_{40}$), two with Anderson structure [$(NH_4)_3TeMo_6O_{24}$, $(NH_4)_3Co(OH)_6Mo_6O_{18}$], one with Dawson structure [$(NH_4)_6P_2Mo_{18}O_{62}$], and one with Dexter–Silverton structure [$(NH_4)_8CeMo_{12}O_{42}$]. HPA syntheses were performed according to literature, references were cited in Table 1.

Table 1 Literature references used for HPA synthesis and NMR data from which the purities were estimated.

HPA	Syn. ref.	^{31}P shift (ppm)	^{95}Mo shift (ppm)	^{29}Si, ^{125}Te shift (ppm)	Purity (% mol)
$H_3PMo_{12}O_{40}$	[4]	−3.2 [11]	15 [14]		93
$H_3PW_{12}O_{40}$	[4]	−14.3 [12]			95
$H_4SiMo_{12}O_{40}$	[4]		17 [14]	−74.5 [16]	95
$H_5PMo_{10}V_2O_{40}$	[5]	−3.0 to −3.4 [13]	15		90
$H_3PMo_{10}W_2O_{40}$	[4]	−5 to −8	17		89
$H_4PMo_9W_2VO_{40}$	[6]	−4 to −9	12		90
$(NH_4)_3TeMo_6O_{24}$	[7]		5 [14]	662 [17]	95
$(NH_4)_3Co(OH)_6Mo_6O_{18}$	[8]		43 149 [15]		90
$(NH_4)_6P_2Mo_{18}O_{62}$	[9]	−2.4 [11]	−26 [15]		97
$(NH_4)_8CeMo_{12}O_{42}$	[10]		2 [14]		95

NMR signals were assigned as in previous works, which are indicated after the chemical shift values in the same table. Crystalline solids (ca. 100 mg) were dissolved in 1 ml of deuterated water. Spectra were collected on a Varian VXR-400 at 25 °C with resonance frequencies of 161.9 (^{31}P) and 79.5 MHz (^{29}Si) using 85 % H_3PO_4 and $Si(CH_3)_4$ as external chemical shift references. Spectra for ^{95}Mo (50 °C) and ^{129}Te (25 °C) were collected on a Bruker AMX-300 (10-mm tubes) at 19.5 and 94.8 MHz with 1 M aq. Na_2MoO_4 and 2 M $TeCl_4$ in HCl (at 1237 ppm) as external shift references, respectively.

Structures of $(NH_4)_3TeMo_6O_{24}$ and $(NH_4)_3[Co(OH)_6Mo_6O_{18}]$ were confirmed by Raman and IR spectroscopy.

Catalyst preparation

The HPAs were supported on alumina pretreated with HNO_3 to remove all the basic sites, which can modify the crystal structure of the HPAs. The HPAs were supported through wetness imbibition with aqueous solution and then dried under air flow at 100 °C for 5 h. Mo content (or molar equivalent content of W or V) on alumina was 12 mass %.

Catalyst testing: Batch reactor

The screening was performed in a batch reactor, thoroughly mixed by a mechanical impeller, at a pressure of 5 bar, 80 °C for 2 h. Samples of the reacting mixture (1 ml) were withdrawn from the reactor at desired reaction time using a tube dipped in the liquid phase. The product samples were analyzed by Perkin Elmer AutoSystem XL GC equipped with flame ionization detector (FID) and flame photometric detector (FPD) to determine the concentration of sulfur compounds. 600 mg of finely powdered catalyst was mixed with 200 g of synthetic diesel (80 % wt *n*-hexadecane and 20 wt % tetraline). Subsequently, 10.6 mmol of *tert*-butyl hydroperoxide (TBHP) was added, as oxidant, followed by 90 mmol of 4,6-dimethyl-dibenzothiophene (DMDBT), used as a model organosulfur compound.

Catalyst testing: Fixed-bed reactor

Fixed-bed tests were carried out in an up-flow tubular reactor with the same ranges of operating conditions as for the batch tests (standard reaction temperature 110 °C, weight hour space velocity [WHSV] 2 h^{-1}).

Catalyst particle size was in the 20–40 mesh range. 3.0 g of catalyst was loaded into the reactor. TBHP was fed at a concentration of 30 mmol/kg diesel. To test performance, hydrotreated diesel with less than 300 wt ppm sulfur was fed to the reactor. Total sulfur content analysis was performed as described in ASTM D5453-06 method. The initial TBHP/sulfur molar ratio was greater than 8.5. Samples were collected using an automated multi-sampling valve, placed at the reactor outlet, every hour on stream. Before total sulfur analysis, the sulfones, formed during the reaction, were removed through adsorption on a silica gel column.

RESULTS AND DISCUSSION

Influence of molybdenum and tungsten on HPA activity

It is well known from the literature that even though molybdenum and tungsten belong to the same group in the periodic table, often the catalytic behavior of their HPAs is very different. For this reason, three different Keggin HPAs were tested: the first containing only molybdenum ($H_3PMo_{12}O_{40}$), the second containing only tungsten ($H_3PW_{12}O_{40}$), and the third containing both molybdenum and tungsten ($H_3PMo_{10}W_2O_{40}$).

From the graph reported in Fig. 1, a large difference in the catalytic activity of molybdenum- and tungsten-based HPAs is evident. The tungsten-based HPA ($H_3PW_{12}O_{40}$) was a very poor catalyst; on the contrary, the molybdenum HPA ($H_3PMo_{12}O_{40}$) was quite active obtaining a sulfur conversion higher than 70 %. As expected, the activity of the HPA containing both molybdenum and tungsten ($H_3PMo_{10}W_2O_{40}$) was between the other two. Since it has 10 molybdenum nuclei, its behavior is similar to phosphomolybdic acid.
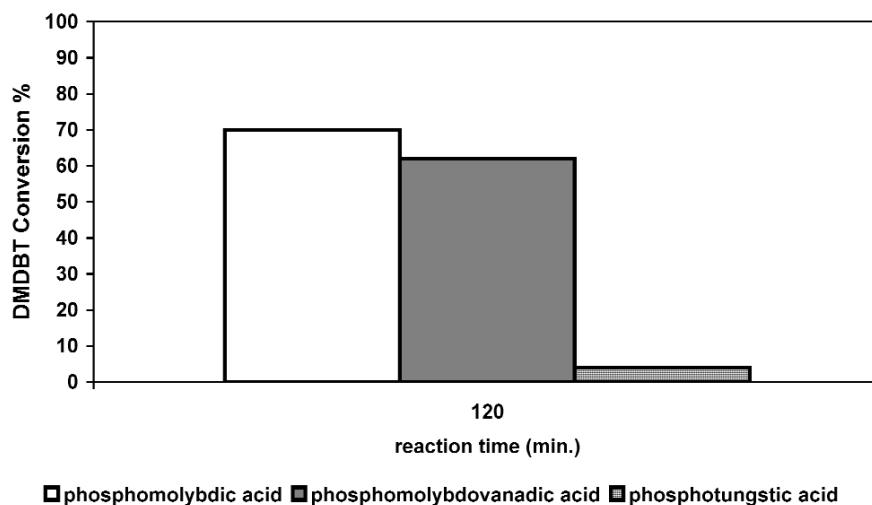
Fig. 1 Catalyst activity for DMDBT oxidation: influence of the metal in the HPA (Keggin) structure.

Influence of different crystal structure on HPA activity

Since the molybdenum-based HPA proved to be most active, molybdenum HPAs with different crystal structures were compared: Keggin ($H_3PMo_{12}O_{40}$), Anderson $\{(NH_4)_3TeMo_6O_{24}$ and $(NH_4)_3[Co(OH)_6Mo_6O_{18}]\}$, Well–Dawson ($H_6P_2Mo_{18}O_{62}$) and Dexter–Silverton $[(NH_4)_8CeMo_{12}O_{42}]$.

From Fig. 2, it is evident that the HPA with Keggin structure showed the best catalytic properties followed by the Dexter–Silverton HPA.
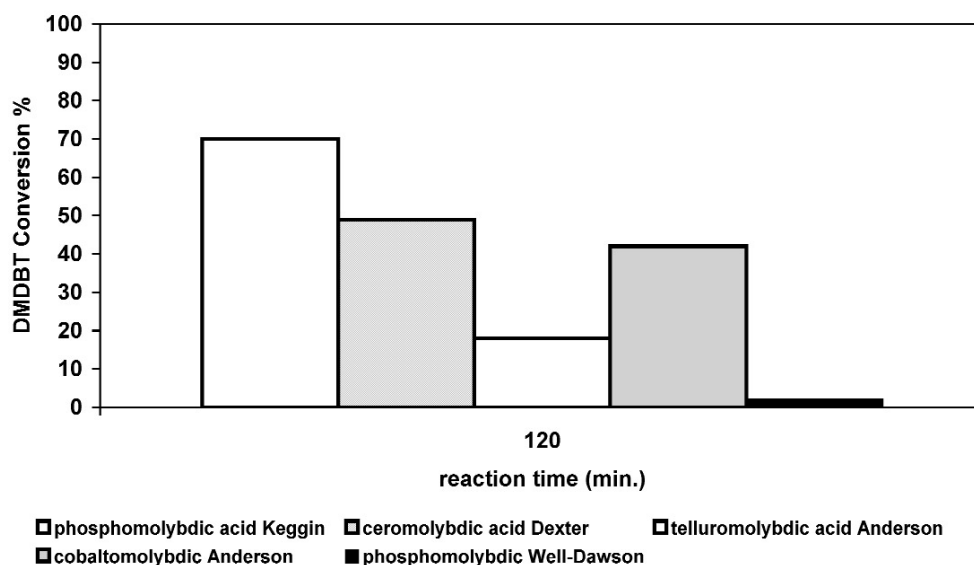

Fig. 2 Catalyst activity: influence of different crystal structure (molybdenum HPAs).

It is interesting to note that the Keggin HPA is more active even though the redox potential of the Dexter–Silverton HPA is higher ($E°$ = 1.6 V (NHE) vs. 0.6 [18,19]). This is attributed to $H_3PMo_{12}O_{40}$ being able to form the peroxo-HPA complex [20], while the Dexter–Silverton HPA cannot.

Anderson HPAs possess intermediate activity, while the Dawson HPA did not catalyze the reaction. This is not surprising since it is well known that Dawson HPAs are usually effective oxidation catalysts with oxygen rather than with peroxides.

Influence of vanadium on HPA activity

It is well known from the literature [11] that the redox properties of $H_3PMo_{12}O_{40}$ can be greatly increased with a partial substitution of vanadium into the structure, obtaining the iso-structural series $H_3PMo_{(12-n)}V_nO_{40}$, where n is between 1 and 3.

$H_5PMo_{10}V_2O_{40}$ was synthesized and tested since it has the highest redox potential of this series.

The substitution of vanadium into a molybdenum HPA in fact increases (Fig. 3) the catalytic performance in the DMDBT oxidation reaction. $H_5PMo_{10}V_2O_{40}$ gave complete sulfur conversion within 2 h, demonstrating to be the most active catalyst. This increased activity was confirmed by comparison with $H_4PMo_9W_2VO_{40}$, another HPA with Keggin structure (Fig. 4).

The introduction of vanadium in this HPA sharply increased its catalytic properties, even though $H_4PMo_9W_2VO_{40}$ proved to be less active than $H_5PMo_{10}V_2O_{40}$, presumably due to the presence of two inactive tungsten nuclei within the Keggin unit.
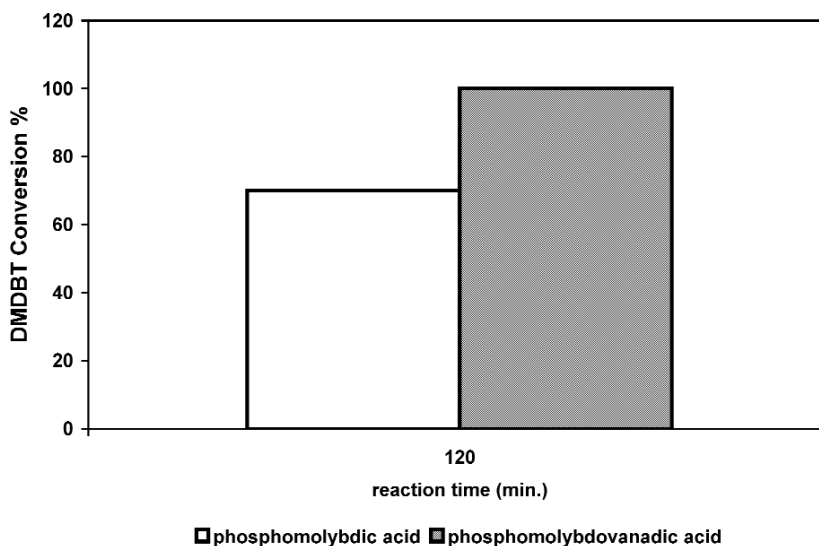

Fig. 3 Catalyst activity: influence of vanadium substitution [$H_{(3+n)}PMo_{(12-n)}V_nO_{40}$].
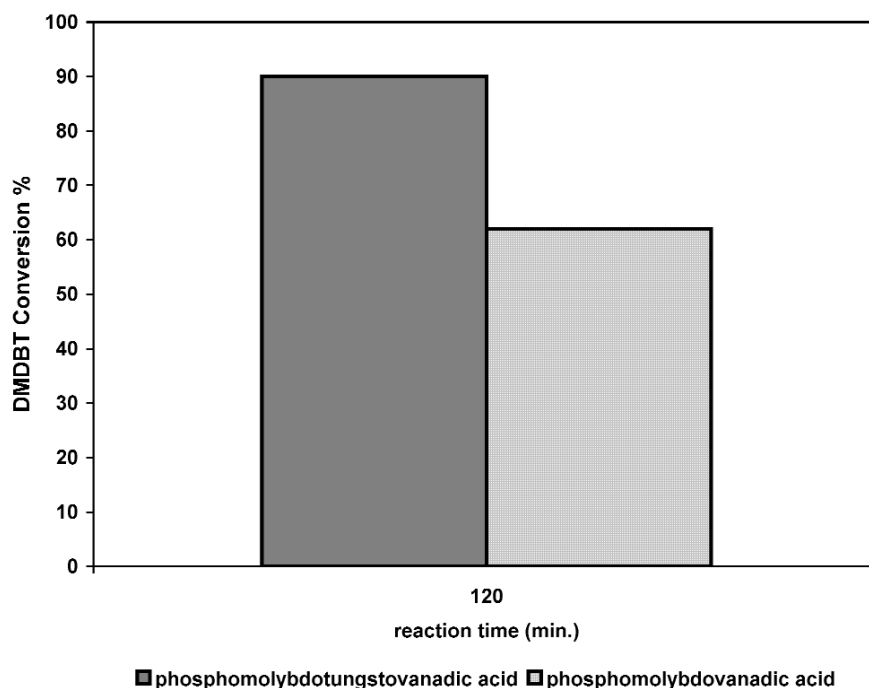
Fig. 4 Catalyst activity: influence of vanadium substitution [$H_{(3+n)}PMo_{(10-n)}W_2V_nO_{40}$].

Fixed-bed reactor tests

These tests were performed to evaluate the stability and activity of HPA-based catalysts using a real diesel feed, which contains basic compounds potentially able to cause deactivation. Tests were performed using $H_5PMo_{10}V_2O_{40}$ or $H_3PMo_{12}O_{40}$ supported on alumina as catalyst. The first one was more active in batch tests. The second one was highly active, and as a commercial product may be more economically appealing in an industrial development.

$H_3PMo_{12}O_{40}$ was active for more than 2000 h time on stream (t.o.s.) and provided ULSD with an average residual sulfur content lower than 10 ppm (Fig. 5). The high quantity of non-converted TBHP demonstrated that this catalyst was also very selective, allowing a lower concentration of hydroperoxide and reducing process costs.

$H_3PMo_{10}V_2O_{40}$ also proved to be a stable catalyst with a lifetime exceeding 1600 h t.o.s. (Fig. 6). However, it was less selective than $H_3PMo_{12}O_{40}$ since it catalyzed TBHP decomposition in addition to DMDBT oxidation. In fact, the residual hydroperoxide content was always under 10 ppm.

$H_3PMo_{12}O_{40}$ and $H_3PMo_{10}V_2O_{40}$ can be easily regenerated at the end of their catalytic lives by heat treatment under mild condition (250 °C) under air flow.
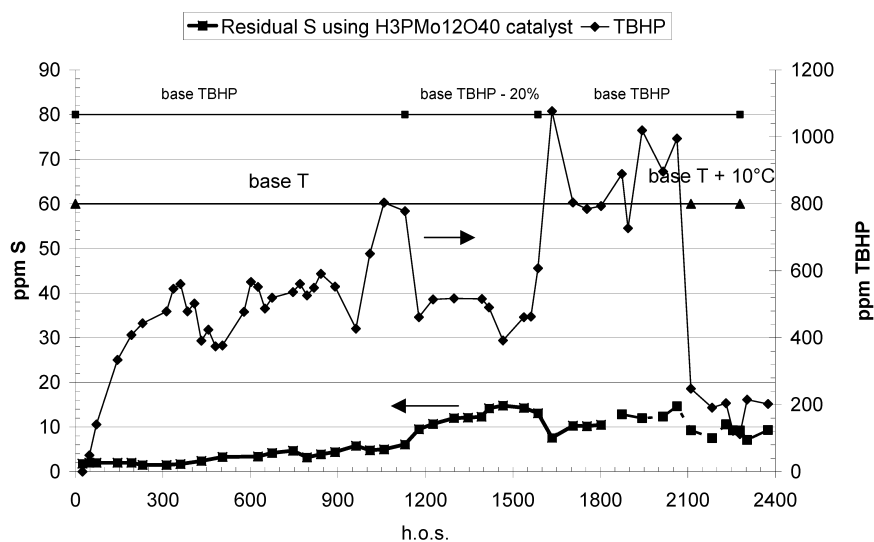
Fig. 5 Fixed-bed reactor test with $H_3PMo_{12}O_{40}$.

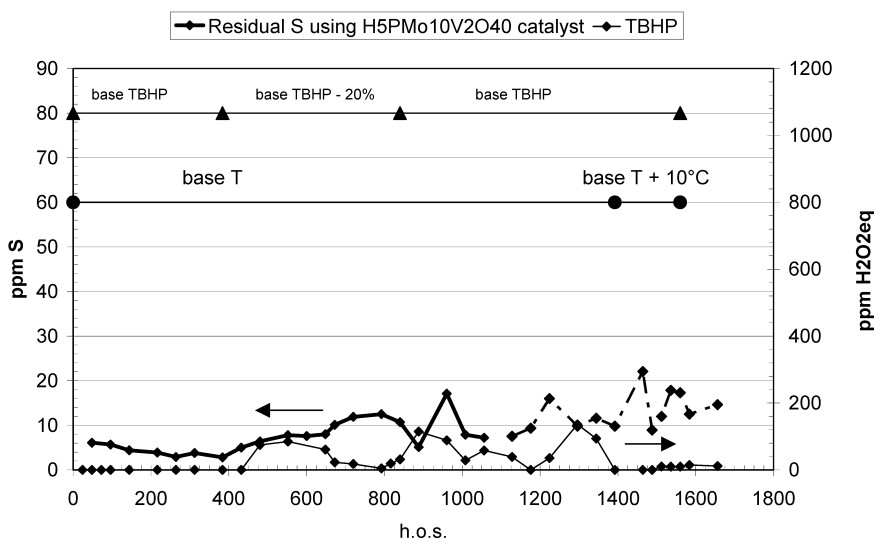**Fig. 6** Fixed-bed reactor test with $H_3PMo_{10}V_2O_{40}$.

CONCLUSIONS

Supported HPAs were investigated as catalysts in organosulfur oxidation, which is the core unit of the new Eni-UOP technology to obtain ULSD.

HPAs containing molybdenum and/or tungsten were synthesized and tested. Molybdenum-based HPAs proved to be most active catalysts using TBHP as oxidant, while tungsten-based HPAs exhibit poorer performances. Mixed molybdenum–tungsten HPAs showed intermediate behavior.

Since molybdenum was the most active metal, several molybdenum HPAs with different structures (Keggin, Anderson, Well–Dawson, and Dexter–Silverton) were synthesized and tested. The $H_3PMo_{12}O_{40}$ HPA, with Keggin structure, was the most active of all, and its activity was increased further by substitution of one or more vanadium atoms into the structure.

The two HPA-based catalysts which showed the highest activity in batch screening ($H_3PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$ supported on Al_2O_3) were also tested in a fixed-bed reactor. Pre-hydrotreated real diesel was fed in order to evaluate catalysts stability and resistance to basic poisons. Both catalysts proved to be active and stable for more than 1500 h t.o.s.. The $H_3PMo_{10}V_2O_{40}$-based catalyst was most active with a very low residual sulfur content, while $H_3PMo_{12}O_{40}$ was the most selective with a lower TBHP consumption.

In conclusion, HPA-based catalysts demonstrated to be active and selective in the new Eni-UOP process to obtain diesel with less than 10 ppm of sulfur (ULSD).

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