

Alberto de Angelis, Daniele Molinari,
Paolo Pollesel, Carlo Perego
Eni SpA Refining & Marketing Division
San Donato Milanese (MI)
Susie C. Martins
UOP - Des Plaines (IL, USA)
carlo.perego@enitecnologie.eni.it



TOWARDS ZERO SULPHUR DIESEL

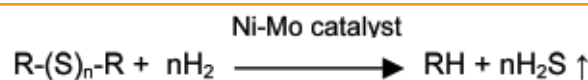
Hydrodesulphurization is an expensive route to reduce sulphur content in diesel to less than 10 ppm. Eni-UOP have developed a new oxidative-desulphurization process, which lowers sulphur using directly-produced peroxides. In the present paper the performances of different heteropolyacids as effective catalysts in S-oxidation reaction are discussed.

Diesel deep desulphurization

The sulphur content in the fuels is required by regulations to be lowered year by year, in order to reduce air pollution due to SO₂ production. Sulphur content in the diesel will have to be reduced to less than 15 ppm in U.S. and less than 10 in E.U., by the year 2009. Diesel with a sulphur content lower than 10 ppm is commonly described as Ultra Low Sulphur Diesel (ULSD).

Conventional process to obtain sulphur removal from diesel consists of a catalytic hydrogenation, so called hydro-desulphurization, where sulphur containing compounds are reduced to H₂S

Devoted to prof. Elio Santacesaria in honour of his 65th birthday and of his constant contribution to innovative new processes development in industrial chemistry.



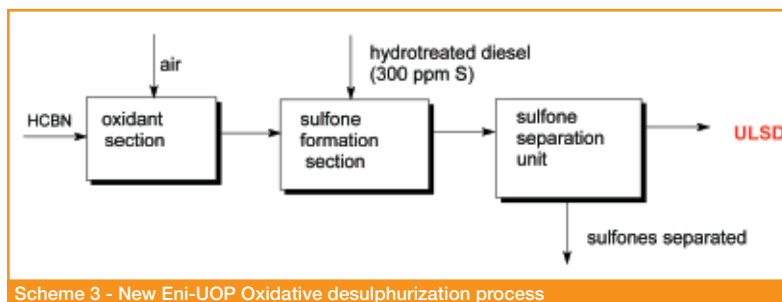
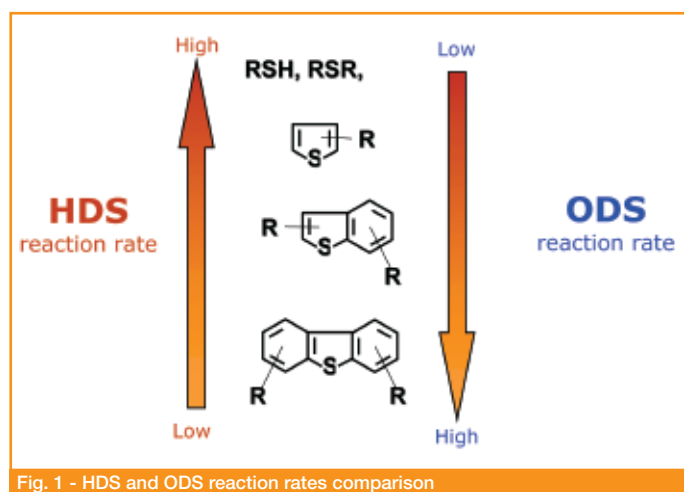
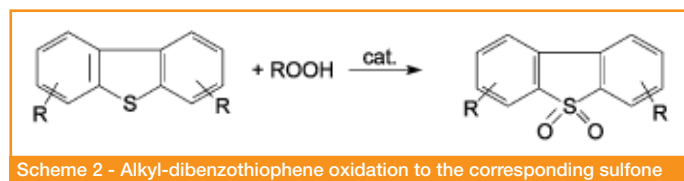
Scheme 1 - Hydrodesulphurization reaction

and therefore removed from the liquid phase (Scheme 1). Conventional hydro-desulphurization process can easily remove many kind of organic sulphur compounds such as mercaptans, sulphides, disulphides, usually obtaining a residual sulphur content of about 300 ppm. Higher molecular weight sulphur compounds, such as dibenzothiophenes, can not be removed at standard conditions and in most cases, either a new high pressure hydrotreating unit or a major revamp of 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 (higher catalyst costs). An alternative route to meet ULSD requirement is oxidative desulphurization technology. This technology removes the most refractory dibenzothiophenes oxidising them to the corresponding sulfones (Scheme 2), which are highly polar compounds and are easily removed from the diesel either by extraction or by adsorption.

The chemistry of the oxidative desulphurization is complementary to the hydrodesulphurization one. In fact, considering the most common sulphur-compounds usually present in a diesel cut, the reaction rate for the hydrodesulphurisation decreases from the mercaptans and the organic disulfides to the alkyl-dibenzothiophenes sulphur compounds. The 4,6 dimethyl-dibenzo-thiophene (4,6 DMDBT) is one of the most refractory compounds to the hydrodesulphurisation. On the contrary, the reaction rate for the oxidative desulphurisation increases the same way from mercaptans to the dibenzothiophene sulphur compounds. The 4,6 DMDBT is one of the most reactive compounds despite the hindrance around the sulphur atom [1]. In the picture below (Fig. 1) is shown the relative reaction rate for common sulphur compounds found in the diesel cut.

Oxidative desulphurization is not a new concept and it has been discussed for several years in previous publications [2, 3]. The



oxidants used in this reaction are either hydrogen peroxide, peracid or organic peroxides [4]. This process is efficient and very low sulphur content can be obtained (<10 ppm), but the high cost of either H_2O_2 or organic hydroperoxide makes economics comparison with traditional hydro-desulphurization process unfavourable for the oxidative desulphurization.

In order to overcome this limitation, Eni and UOP, have jointly developed a new oxidative desulphurization process, represented in Scheme 3, in which the hydroperoxide is produced in situ, therefore reducing ULSD production costs.

In this process scheme the first step is an auto-oxidation reactor in which a suitable hydrocarbon refinery stream (HCBN) is oxidised with atmospheric air obtaining the organic hydro-peroxide. This auto-oxidation is carried out under mild conditions ($T < 200^\circ C$) and at low contact time in order to avoid non-selective oxidation reactions (formation of ketones, aldehydes, and acids) and excessive hydroperoxide production. In the second stage a proprietary oxidation catalyst oxidises dibenzothiophenes to the corresponding sulfones using as oxidant the pre-formed hydroperoxide, this reaction is performed at low pressure and mild temperature ($T < 180^\circ C$). In the next unit the formed sulfones are removed from the diesel, usually by adsorption, obtaining ULSD (S content <10 ppm).

The main advantages of new Eni-UOP process may be summarized a:

- It does not use hydrogen to produce ULSD
- It operates under mild conditions
- It does not require expensive chemicals (such as H_2O_2 or peroxides)
- It uses conventional reaction and separation refinery equipments
- It can treat a wide range of hydrotreated diesel.

In addition to the state-of-the-art catalyst developed for the process, new catalytic systems have been considered to improve the performances especially with particular feeds. One of the best class of materials tested are heteropolyacid compounds.

Heteropolyacids

Heteropolyacids (HPA) are very stable crystal compounds of general formula $[X_xM_mO_y]^{q-}$, where $x < m$, X is a heteroatom such as P, As, B, etc and M is usually molybdenum or tungsten and less frequently vanadium, niobium or mixture of these elements [5]. Heteropolyacids are characterised by different stable structures: most common are Keggin's $[XM_{12}O_{40}]^{n-}$, Dawson's $[X_2M_{18}O_{62}]^{n-}$, Anderson's $[X(OH)_6M_6O_{18}]^{n-}$ and Dexter-Silverton's $[XM_{12}O_{42}]^{n-}$, but many other structures were identified and characterised. Heteropolyacids proved to give excellent performances both as solid acid [6] and redox catalysts [7], and there are many industrial processes in which heteropolyacids are currently used.

On the contrary heteropolyacids have not been thoroughly investigated as catalysts in diesel deep desulphurization. In fact, in the literature only $H_3PW_{12}O_{40}$ [8, 9, 10] was studied in this reaction, using H_2O_2 as oxidant in a two phase system in the presence of a transfer phase agent.

Even if this system proved to be quite efficient, it presents some evident drawbacks: it is difficult to handle at large scale, catalyst productivity is low referred to HPA, H_2O_2 is an expensive chemical to perform this reaction and its selectivity is not very high.

Catalysts preparation and characterisation

Several heteropolyacids have been synthesised with different structures: four of them possess Keggin's structure ($H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_3PMo_{10}W_2O_{40}$, $H_5PMo_{10}V_2O_{40}$), two Anderson's ($(NH_4)_3TeMo_6O_{24}$, $(NH_4)_3[Co(OH)_6Mo_6O_{18}]$), one heteropolyacid with Wells-Dawson structure ($H_6P_2Mo_{18}O_{62}$) and one with Dexter-Silverton ($(NH_4)_8CeMo_{12}O_{42}$). Their structures and purity were confirmed with ^{31}P NMR, for Keggin's and Dawson's heteropolyacids, Raman and IR spectroscopy for Anderson's heteropolyacids, ^{125}Te NMR for $(NH_4)_3TeMo_6O_{24}$ and ^{95}Mo for $(NH_4)_8CeMo_{12}O_{42}$. Since heteropolyacids have a very low surface area, usually about 3 m²/g as free acids, the heteropolyacids have been supported on alumina, previously pre-treated with HNO_3 , in order to remove the basic sites, which can modify heteropolyacids structure.

Catalysts screening

The screening of the previously described catalysts was performed in a batch reactor, completely mixed by a mechanical impeller, at the pressure of 5 bar and at the temperature of 80 °C. The reaction lasted for two hours, samples were taken and

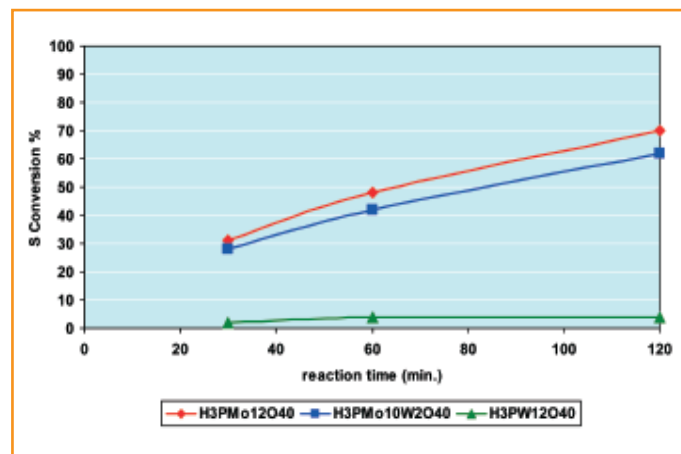


Fig. 2 - Influence of different metal in the heteropolyacid

analysed through GC.

Catalysts were used as fine solid particles (>120 mesh size), and 600 mg of catalyst were loaded in 200 g of synthetic diesel (80% wt n-hexadecane and 20 wt% tetraline). Ter-buthyl hydro peroxide was used as the oxidant, and 10.6 mmols of t-ButOOH were added.

4,6 DMDBT was used as a sulphur model compound at a concentration of 6.25 mmols/kg. Initial molar ratio t-ButOOH/4,6 DMDBT was equal to 8.5.

First of all it has been investigated the influence of the different metals on the external shell of the heteropolyacids. In fact even though tungsten and molybdenum belong to the same chemical group VI B and therefore their chemical behaviour is quite similar, the catalytic properties of their heteropolyacids are often very different.

For this reason two heteropolyacids with the same Keggin structure but different metal $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$ and the one containing both molybdenum and tungsten ($H_3PMo_{10}W_2O_{40}$) were tested.

From the graph in Fig. 2 it is evident that while tungsten based heteropolyacid ($H_3PW_{12}O_{40}$) proved to be a very poor catalyst in the oxidation of dibenzothiophene to the corresponding sulphone with t-butyl hydroperoxide, on the contrary molybdenum heteropolyacid ($H_3PMo_{12}O_{40}$) demonstrated to be quite active obtaining sulphur conversion higher than 70%. As expected the activity of the heteropolyacid containing both molybdenum and tungsten ($H_3PMo_{10}W_2O_{40}$) lies between the two and having 10 atoms of molybdenum out of 12 its behaviour it is more similar to the phosphomolybdic acid, with catalytic performances only slightly lower.

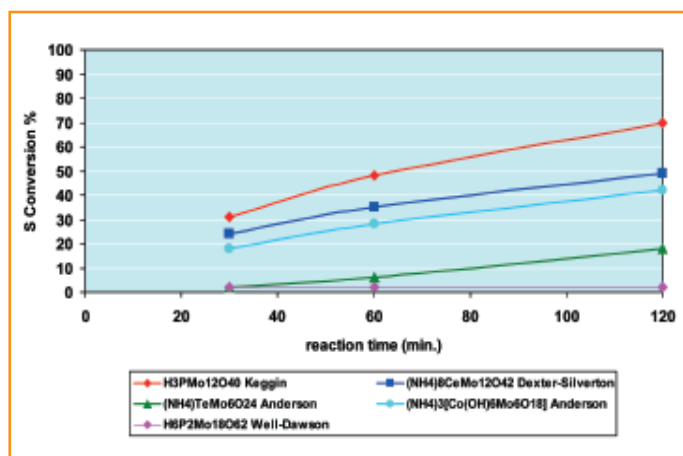


Fig. 3 - Influence of different structure with molybdenum heteropolyacids

Since molybdenum based heteropolyacid proved to be the best one, all molybdenum heteropolyacids with different structures were tested.

From Fig. 3 it is evident that the heteropolyacid with the Keggin structure was the one that showed the best catalytic properties, with Dexter-Silverton one following Keggin.

It is interesting to note that the Keggin heteropolyacid is more active than the Dexter-Silverton one, even though the redox potential is higher for the Dexter-Silverton ($E^0=1.6$ EV vs 0.6 [11, 12]). This can be reasonably attributed to the fact that Keggin $H_3PMo_{12}O_{40}$ is able to stabilize the hydroperoxide giving the corresponding peroxy-heteropolyacid [5], while Dexter-Silverton heteropolyacid is not able to do the same.

Anderson heteropolyacids possess intermediate activity, while Dawson heteropolyacid was not able to catalyse the reaction, which is not completely surprising since it is well known that Dawson heteropolyacids are usually efficient oxidation catalysts with oxygen rather than with peroxides.

It is well known from the literature [11] that the redox properties of $H_3PMo_{12}O_{40}$ can be greatly enhanced with a partial substitution of vanadium to molybdenum in the structure obtaining the iso-structural series $H_3PMo_{(12-n)}V_nO_{40}$, where n is comprised

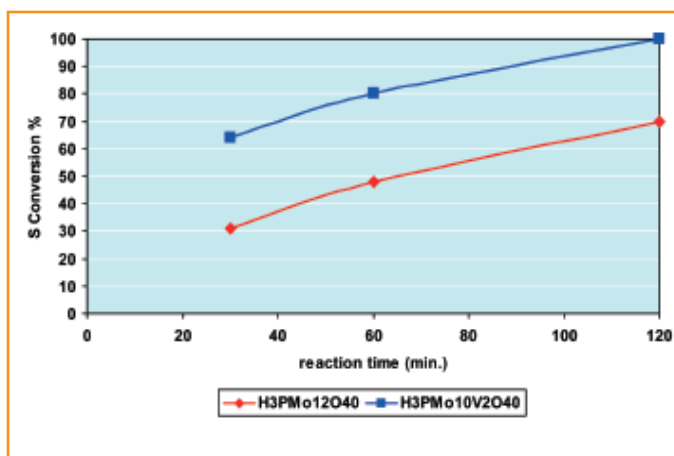


Fig. 4 - Influence of vanadium substitution in molybdenum heteropolyacids

between 1 and 3.

Therefore it has been synthesised and tested under the same reaction conditions the compound $H_3PMo_{10}V_2O_{40}$, which within the heteropolyacids $H_3PMo_{(12-n)}V_nO_{40}$ is the one with the highest redox potential.

The increase of the sulphur conversion with vanadium substituted heteropolyacid was really relevant reaching complete sulphur conversion within the two hours (Fig. 4).

Continuous fixed bed reactor tests

Since $H_3PMo_{10}V_2O_{40}$ and $H_3PMo_{12}O_{40}$ proved to be the best catalysts in batch tests, the next step was the study of their life and productivity through fixed bed tests.

Fixed bed tests were carried out with the best heteropolyacid catalysts in an up-flow tubular glass reactor in the same ranges of operating conditions as batch tests (standard reaction temperature 110 °C, WHSV 2 h⁻¹). Catalyst particle size was in the 20-40 mesh range, 3.0 g of catalyst were loaded in the reactor. TBHP was used as the oxidant and fed at the concentration of 30 mmoles/kg.

To test sulphur oxidation performances, hydrotreated diesel with slightly less than 500 wt ppm S was fed to the reactor.

Verso un diesel a contenuto nullo di zolfo

La legislazione richiede limiti molto bassi per il contenuto di zolfo nel diesel e raggiungerli tramite la idrodesolforazione può essere troppo oneroso. Eni e UOP hanno sviluppato un nuovo processo di desolforazione ossidativa, basato sull'ossidazione dei composti solforati mediante perossidi generati all'interno del processo. In questo articolo viene descritta l'efficacia di diversi eteropoliacidi come catalizzatori in questo nuovo processo.

RIASSUNTO 

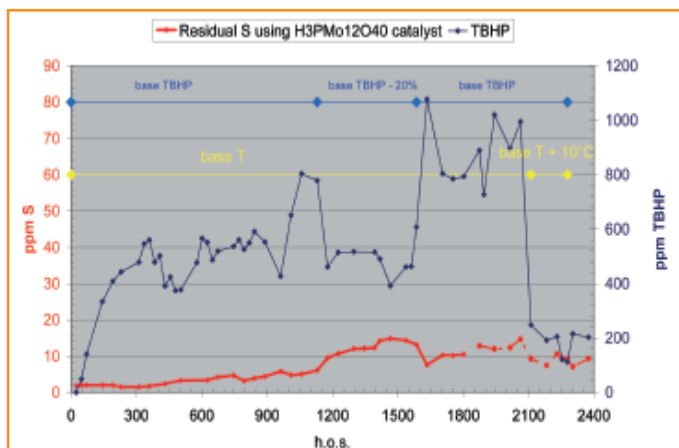


Fig. 5 - Fixed bed tests with $\text{H}_3\text{PMo}_{12}\text{O}_{40}\text{-Al}_2\text{O}_3$

Sulphonates were removed through adsorption on silica gel column. Residual sulphur in the diesel fuel and peroxide concentration during the run are displayed in Fig. 5.

From the previous figure it is evident that $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was active for more than 2,000 hours t.o.s with an average residual sulphur content lower than 10 ppm.

This heteropolyacid therefore proved to be an excellent catalysts in sulphur-containing molecules oxidation process for obtaining ULSD. The high quantity of non converted hydroperoxide proved that this catalyst is also very selective and a lower concentration of hydroperoxide can be used as well, reducing the cost of the process.

Also $\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ tested in a fixed bed reactor (Fig. 6) proved to be a stable catalyst with a life exceeding 1,600 hours t.o.s., even if it was less selective than $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, catalysing not only the DMDBT oxidation to the corresponding sulphone but also hydroperoxide decomposition. In fact residual hydroperoxide content was always under 10 ppm.

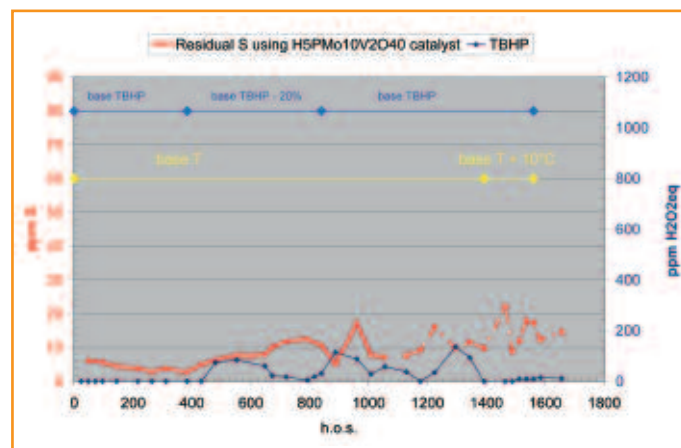


Fig. 6 - Fixed bed tests with $\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}\text{-Al}_2\text{O}_3$

These two heteropolyacids can be easily regenerated at the end of their catalytic life for heat treatment under air flow at mild condition (250 °C).

Conclusions

Eni and UOP have developed a process for the oxidative desulphurisation of diesel fraction for the production of Ultra Low Sulphur Diesel. The process is divided in three main sections: oxidant generation, sulphur compounds oxidation to sulphonates and sulphonates separation. The sulphonate generation by peroxidation reaction is based on a proprietary catalyst. Heteropolyacid-based catalysts have been considered as possible catalyst for improving reaction performances. Several heteropolyacids have been prepared and tested. Two of them ($\text{H}_3\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ supported on Al_2O_3) have showed the best performances in terms of sulphur conversion, peroxide consumption and stability.

References

- [1] D. Wang *et al.*, *Appl. Cat. A*, 2003, **253**, 1.
- [2] F.J. Liota, Z.H. Yuan, Production of ultra-low sulphur fuels by selective hydroperoxide oxidation, AM-03-23, NPRA 2003 Annual meeting.
- [3] R.E. Levy *et al.*, Unipare ASR-2 Diesel desulfurization process: a novel cost effective process for ultra-low sulphur diesel fuel, AM-01-10, NPRA 2001 Annual meeting.
- [4] C.D. Gosling *et al.*, The role of oxidative desulfurization in an effective ULSD strategy, AM-04-48, NPRA 2004 Annual meeting.
- [5] M.T. Pope, *Heteropoly and Isopoly Oxometallates*, Springer- Verlag, Heidelberg, Germany, 1983.
- [6] M.N. Timofeeva, *Appl. Cat. A*, 2003, **256**, 19.
- [7] T. Okuhara *et al.*, *Appl. Cat. A*, 2001, **222**, 63.
- [8] K. Yazu *et al.*, *Energy & Fuels*, 2001, **15**, 1535.
- [9] F.M. Collins *et al.*, *J. of Mol. Catal. A*, 1997, **117**, 397.
- [10] C. Li *et al.*, *Chem. Eur. J.*, 2004, **10**, 2277.
- [11] I.K. Song, M.A. Barteau, *J. of Mol. Catal. A*, 2004, **212**, 229.
- [12] J.J. Borrás-Almenar *et al.*, *Polyoxometalate Molecular Science*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.