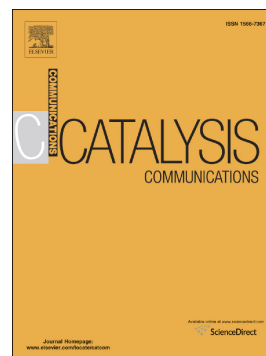


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Dichlorodioxomolybdenum(VI) complexes bearing oxygen-donor ligands as catalysts for oxidative desulfurization of simulated and real diesel

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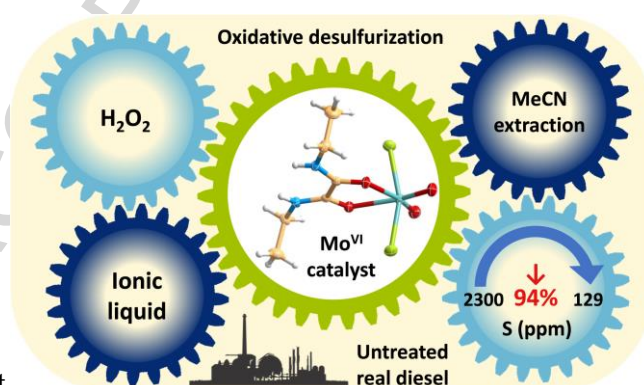
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Graphical Abstract



Abstract

The complexes $[\text{MoO}_2\text{Cl}_2(\text{DMB})_2]$ (**1**) and $[\text{MoO}_2\text{Cl}_2(\text{DEO})]$ (**2**) (DMB = *N,N*-dimethylbenzamide, DEO = *N,N'*-diethyloxamide) have been evaluated as catalysts in extractive-catalytic oxidative desulfurization (ECOD) of a simulated diesel fuel. Using the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}]\text{PF}_6$) as extraction solvent and H_2O_2 as oxidant, ultra-deep desulfurization (S-content from 3000 ppm to less than 10 ppm) was possible within a reaction time of 1-3 h, and the systems **Cat**/ $[\text{BMIM}]\text{PF}_6$ could be recycled for five times without significant decrease in activity. The S-content of a real untreated diesel was lowered by 94.4% from 2300 ppm to 129 ppm after only 2 h of reaction using the ECOD process with **2** as catalyst.

Keywords: Oxidative desulfurization; Dioxomolybdenum catalysts; Hydrogen peroxide; Ionic liquids; Optimization; Real diesel.

1. Introduction

Homogeneous catalysts with oxomolybdenum(VI) active centers have been shown to be effective for a broad range of organic transformations such as oxidation, deoxygenation, carbon-carbon and carbon-heteroatom bond forming reactions, X-H (X = Si, B, P and H) bond activation and organic reductions [1-7]. The commercial availability of the simplest molybdenyl derivative, MoO_2Cl_2 , has led to its extensive use in many reactions [2-7]. In the presence of a coordinating solvent, addition compounds of the type $[\text{MoO}_2\text{Cl}_2(\text{L})_2]$ (L = DMF, THF, DMSO, MeCN) are formed. The complex $[\text{MoO}_2\text{Cl}_2(\text{THF})_2]$ is often used to prepare $[\text{MoO}_2\text{Cl}_2(\text{L})_n]$ complexes by displacement of the THF with O- or N-donor ligands. An alternative route to these complexes is based on the addition of the ligand to a diethyl ether solution of $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]$, which can be prepared by extraction of an aqueous solution of sodium molybdate in concentrated HCl [2,3]. Readily available solvent adducts such as $[\text{MoO}_2\text{Cl}_2(\text{DMF})_2]$ and $[\text{MoO}_2\text{Cl}_2(\text{DMSO})_2]$ have been very successfully used as catalysts for many organic reactions [2-11].

A recent review by Thiruvengadam and Chand [12] highlights the application of oxomolybdenum(VI) complexes for the oxidation of sulfides using aqueous hydrogen

peroxide as oxidant. Sulfoxidation is an important reaction not only from the point of view of organic synthesis (for the selective preparation of sulfoxides or sulfones) but also for the oxidative desulfurization (ODS) of transportation fuels. Regulations on the permissible levels of sulfur in fuels are becoming more and more strict, with a global shift towards “zero sulfur” fuels, and the revamp of existing hydrodesulfurization (HDS) facilities to meet these lower caps is cost-prohibitive since elevated temperatures and hydrogen pressures are required, as well as higher catalyst amounts and/or improvements in catalyst performance[13]. Sulfoxidation chemistry is seen as an economically viable alternative route to diesel desulfurization that could complement conventional HDS technology. In ODS, organosulfur compounds are oxidized to the corresponding sulfoxides and/or sulfones, which can then be removed by adsorption, distillation, or solvent extraction[14,15]. An important variant of ODS is extractive-catalytic ODS (ECOD), in which the extraction of sulfur-containing compounds/products and catalytic oxidation take place simultaneously in a one-pot biphasic system. We recently showed that the complex $[\text{MoO}_2\text{Cl}_2(4,4'\text{-di-}i\text{-tert-butyl-2,2'\text{-bipyridine})]$ could be used successfully in an ECOD process for the desulfurization of model and real diesel fuel[16].

In previous work carried out by some of us, the complexes $[\text{MoO}_2\text{Cl}_2(\text{DMB})_2]$ (**1**) and $[\text{MoO}_2\text{Cl}_2(\text{DEO})]$ (**2**) (DMB = *N,N*-dimethylbenzamide, DEO = *N,N'*-diethyloxamide) (Fig. 1) were found to be extremely active catalysts for the epoxidation of olefins with *tert*-butylhydroperoxide[17]. We hypothesized that these complexes could be promising catalysts for ODS. In the present work, ECODS systems containing complexes **1** and **2** have been optimized for the desulfurization of a multicomponent model diesel. The optimized ECOD system, using complex **2** entrapped in the ionic liquid $[\text{BMIM}]\text{PF}_6$, was used for the near-complete removal of sulfur from an untreated real diesel fuel.

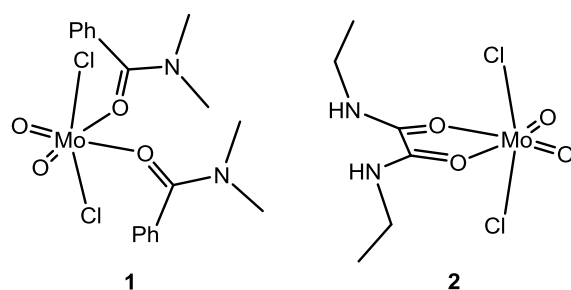


Fig. 1. Structures of complexes $[\text{MoO}_2\text{Cl}_2(\text{DMB})_2]$ (**1**) and $[\text{MoO}_2\text{Cl}_2(\text{DEO})]$ (**2**).

2. Experimental

2.1. Catalyst synthesis and characterization

Complexes **1** and **2** were prepared as described previously by treatment of the solvent adduct $[\text{MoO}_2\text{Cl}_2(\text{THF})_2]$ with either two equivalents of DMB or one equivalent of DEO[17]. In the course of preparing complex **2**, single-crystals of a THF solvate, **2**·THF, were obtained and found to be of suitable quality for structure determination by X-ray diffraction. Full details are provided in the Electronic Supporting Information (ESI).

2.2. ODS studies

2.2.1. Materials and methods

The chemicals dibenzothiophene (98%), 4-methyldibenzothiophene (96%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), *n*-octane (98%), 1-butyl-3-methylimidazolium hexafluorophosphate (97%), 1-butyl-3-methylimidazolium tetrafluoroborate ($\geq 98\%$), tetradecane (99%), acetonitrile (Fisher Chemical), dimethylformamide, and 30% w/w hydrogen peroxide were purchased from Sigma-Aldrich unless otherwise indicated, and used as received. The untreated real diesel fuel with a sulfur content of 2300 ppm was supplied by Galp.

The desulfurization of the model diesel was monitored using a Bruker 430-GC-FID gas chromatograph fitted with a Supelco SPB-5 capillary column (30 m \times 250 μm i.d.; 25 μm film thickness) and using hydrogen as the carrier gas (55 $\text{cm}^3 \text{s}^{-1}$). The analysis of the sulfur content in the treated diesel samples was performed at Galp by ultraviolet fluorescence using a Thermo Scientific instrument, with a TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

2.2.2. Model diesel

The desulfurization studies were performed in 5 mL borosilicate flasks which were loaded with a magnetic stirring bar and a model diesel fuel solution (0.75 mL) prepared by dissolving equal amounts (1000 ppm each) of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in *n*-

octane. In a typical procedure, the catalyst **1** or **2** and an extraction solvent were added to the reaction vessel and the biphasic mixture was stirred vigorously for 10 min at 50 or 70 °C to perform an initial extraction. After this step, the oxidant was added to the system to initiate the catalytic oxidative stage. The reference (starting) conditions were 10 µmol of catalyst, 0.75 mL of extraction solvent and 0.60 mmol of oxidant, which correspond to $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2)$ molar ratio of 1:7:60. An optimization study was performed for each catalyst in which several reaction parameters were systematically varied, namely the effect of the absence or presence of different extraction solvents ([BMIM]PF₆, [BMIM]BF₄ and MeCN), the amount of 30% aq. H₂O₂ (0.13, 0.26 or 0.60 mmol) and catalyst (5, 10 or 20 µmol), the model diesel/extraction solvent volume ratio (1:1, 1:0.5 or 1:0.3), and the reaction temperature (50 or 70 °C).

The quantification of sulfur was performed by periodically taking aliquots from the model diesel phase, which were then diluted with tetradecane. For selected reactions the extent of non-productive oxidant decomposition was studied by titrating residual H₂O₂ with standardized ceric sulfate (full details are given in the ESI).

Catalyst recycling (for a total of five consecutive cycles) was performed by removal of the desulfurized model diesel from the ODS reactor, followed by addition of a fresh portion of model diesel and (after the 10 min initial extraction) a fresh portion of oxidant. The same reaction conditions were applied from one cycle to the next.

2.2.3. Untreated real diesel

The real diesel was treated by application of the optimized ODS conditions determined for the model diesel in the presence of catalysts **1** or **2**. To reach the best diesel desulfurization, some diesel samples were first desulfurized by liquid-liquid extractions with polar solvents, namely MeCN and DMF. After the oxidative catalytic process, all the diesel samples were washed with MeCN or DMF to remove the oxidized sulfur species still present.

3. Results and Discussion

3.1. Desulfurization of model diesel

3.1.1. Optimization studies

Complexes **1** and **2** were applied as catalysts for the ODS of a high-sulfur (3000 ppm) model diesel containing DBT, 4-MDBT and 4,6-DMDBT. With [BMIM]PF₆ as extraction

solvent, a sulfur removal of ca. 41% was obtained at the end of the initial extraction step performed at 50 °C in the absence of oxidant (with a model diesel/IL volume ratio of 1:1). After addition of the oxidant H₂O₂, sulfur removal continued to increase during the catalytic oxidative stage, leading to ultra-deep desulfurization (S < 10 ppm) within 3 h for **1** and 2 h for **2**. The ODS process with **1** or **2** was subsequently optimized by varying, in this order, the nature of the extraction solvent ([BMIM]PF₆, [BMIM]BF₄ or MeCN, or solvent-free), the amount of H₂O₂, the amount of catalyst, the model diesel/solvent volume ratio, and finally the reaction temperature. A compromise was sought between the desulfurization efficiency (preferably achieving values greater than 99.5% within 1-3 h) and the desire to use the minimum amounts of extraction solvent, oxidant and catalyst. The oxidant/S molar ratio should be as small as possible to avoid the oxidation of fuel components responsible for fuel quality[18]. The results of these optimization experiments are given in the ESI, whereas Fig. 2 presents the desulfurization profiles obtained under the final optimal conditions.

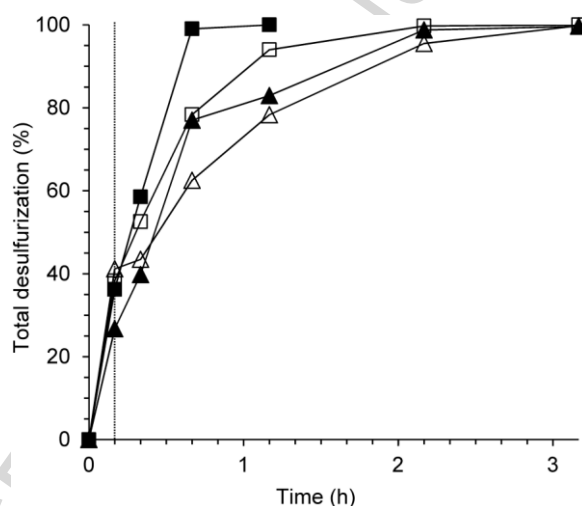


Fig. 2 Desulfurization of a model diesel (3000 ppm S) using complexes **1** (△,▲) or **2** (□,■) as catalyst, and the ionic liquid [BMIM]PF₆ as extractant and reaction medium, under the initial (unfilled symbols) and optimized (filled symbols) conditions: (△/□) $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:7:60$, $V(\text{oil})/V(\text{IL}) = 0.75/0.75$, 50 °C; (▲) $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:7:13$, $V(\text{oil})/V(\text{IL}) = 0.75/0.375$, 50 °C; (■) $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:14:52$, $V(\text{oil})/V(\text{IL}) = 0.75/0.75$, 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by the addition of oxidant.

For both **1** and **2**, the desulfurization efficiency was higher in water-immiscible [BMIM]PF₆ than in water-miscible [BMIM]BF₄ and MeCN. This suggests that any benefit of

having the oxidant in the same liquid phase as the catalyst may be offset by catalyst deactivation or alteration caused by the presence of water. While increasing the reaction temperature from 50 to 70 °C was very beneficial for the ODS process with **2** (allowing 99% sulfur removal after 40 min, and complete desulfurization after 1 h), the higher temperature could not be used with **1** since it promoted a perceptible increase in miscibility between the model diesel and IL phases. Nevertheless, it is remarkable that an ultra-low sulfur model diesel (< 10 ppm S) could be obtained using **1** as catalyst under the optimized conditions with a H₂O₂/sulfur (O/S) molar ratio of 1.85, which is slightly lower than the molar ratio of **2** for the stoichiometric oxidation of the dibenzothiophene compounds to the corresponding sulfones. A higher H₂O₂/sulfur ratio of 3.7 was required for **2**, which may be indicative of an enhanced non-productive decomposition of the oxidant, probably caused by the higher reaction temperature used in the catalyst **2** system (70 °C) than the reaction temperature used in catalyst **1** system (50 °C). Accordingly, titration analysis of the reaction mixture after 2 h showed that all the oxidant had been consumed.

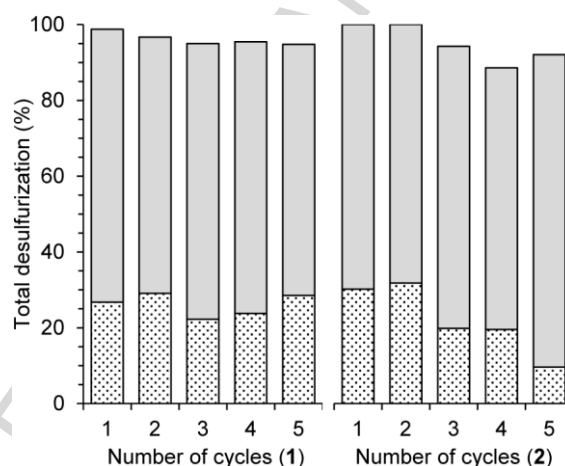


Fig. 3 Desulfurization data for five consecutive ODS cycles with complexes **1** or **2** as catalyst. The dotted bars indicate the sulfur removal values after the initial extraction stage. Reaction conditions for **1**: $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:7:13$, $V(\text{oil})/V([\text{BMIM}]\text{PF}_6) = 0.75/0.375$, 50 °C, 2 h. Reaction conditions for **2**: $n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:14:52$, $V(\text{oil})/V([\text{BMIM}]\text{PF}_6) = 0.75/0.75$, 70 °C, 2 h.

3.1.2. Catalyst recycling

After ODS cycles performed under the optimized conditions with the model diesel (2 h reaction time), the IL ([BMIM]PF₆) phase containing the dissolved catalysts was recycled

(Fig. 3). The desulfurized model diesel phase was removed and then the next cycle was initiated simply by adding a fresh portion of model diesel, performing the extraction stage as usual during 10 min, and then adding a fresh portion of H_2O_2 to start the catalytic stage. The disadvantage of this procedure is that the concentration of oxidized sulfur compounds (sulfones) in the IL phase increases with the number of ODS cycles performed and may eventually reach the saturation point. Indeed, a white precipitate typically appeared after performing four cycles. Nevertheless, the desulfurization performances of the systems **1**/[BMIM]PF₆ and **2**/[BMIM]PF₆ were practically maintained across five ODS cycles (Fig. 3). The similarity of the initial extraction results (22-29%) for the system **1**/[BMIM]PF₆, with no obvious decrease in sulfur removal capacity upon recycling, indicates that the accumulation of oxidized sulfur compounds in the IL phase over the various ODS cycles did not have a negative impact on the transfer of sulfur compounds from the model diesel to the IL medium, even though the volume of the latter was only half that of the model diesel.

3.2. Desulfurization of untreated real diesel

The ODS systems using catalysts **1** and **2** were investigated for the treatment of a high sulfur real diesel (2300 ppm S). In addition to the ODS step performed with the catalyst/[BMIM]PF₆ system under the optimized conditions determined previously, initial and/or final extractions with MeCN or DMF were performed. In agreement with the results obtained with the model diesel, the ODS system with catalyst **2** proved to be more efficient than that with catalyst **1** in the desulfurization of the untreated real diesel (Table 1). When the final extraction was performed with MeCN, the application of an initial extraction with the same solvent (before the oxidative catalytic stage) improved the overall desulfurization efficiency for both catalysts, albeit only slightly for **2**. On the other hand, for DMF, the application of an initial extraction was not beneficial, and in fact led to a significantly lower desulfurization efficiency in the case of **2**. The exceptional results obtained for the ODS system using **2**, without an initial extraction, i.e. 93.1% and 89.7%, demonstrate that the initial extraction step can be omitted due to the high efficiency of **2** for the oxidative treatment of the real diesel.

In an effort to improve the performance of the ODS system **1**/[BMIM]PF₆ in the treatment of the real diesel, further experiments were performed (without any initial extraction treatment) in which the oxidant amount and/or diesel/IL volume ratio were varied (Table 2). With the lower amount of oxidant [$n(H_2O_2)/n(S) = 1.85$], similar desulfurization

efficiencies were obtained for diesel/IL volume ratios of 1:1 and 1:0.5. We surmised that the failure to observe an increase in sulfur removal upon increasing the volume of IL might be due to sulfur oxidation being restricted by the low amount of oxidant, inhibiting a continuous transfer of sulfur compounds from the diesel to the IL. However, when the amount of oxidant was doubled [$n(\text{H}_2\text{O}_2)/n(\text{S}) = 3.7$], using equal volumes of IL and diesel, only a minor improvement in the desulfurization efficiency was obtained (from 49.8 to 53.4%). A remarkable increase in the sulfur removal from the real diesel, to 83.4%, was observed when the higher amount of oxidant was used but with lower amount of IL, i.e. a diesel/IL volume ratio of 1:0.5. This behavior must be related with the two-fold increase in the concentration of the catalyst entrapped in the IL phase, which will result in a higher catalyst concentration at the interface of the immiscible aqueous and IL phases, thus promoting an increase in the reaction rate between the non-oxidized sulfur compounds (extracted from the diesel phase) and H_2O_2 over the catalyst.

Table 1. Experiments performed for ODS of an untreated real diesel, under the optimal model diesel ODS system conditions, using catalysts **1** and **2**.

Catalyst	Extraction process ^a	ODS process	S content (ppm)	Desulfurization efficiency (%)
1	---	MeCN ^b	1176	48.9
	---	DMF ^b	1000	56.5
	MeCN	MeCN ^b	657	71.4
	DMF	DMF ^b	1014	55.9
2	---	MeCN ^c	158	93.1
	---	DMF ^c	237	89.7
	MeCN	MeCN ^c	129	94.4
	DMF	DMF ^c	402	82.5

^a Liquid-liquid diesel/organic solvent extraction of non-oxidized sulfur compounds during 10 min at 70 °C.

^b Oxidative desulfurization in a biphasic diesel/[BMIM]PF₆ system during 2 h using the optimal experimental conditions [$n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:7:13$, $V(\text{oil})/V(\text{IL}) = 0.75/0.375$, 50 °C] obtained from model diesel desulfurization, with a final extraction with an organic solvent (MeCN or DMF) for 30 min at 50 °C.

^c Oxidative desulfurization in a biphasic diesel/[BMIM]PF₆ system during 2 h using the optimal experimental conditions [$n(\text{cat}):n(\text{S}):n(\text{H}_2\text{O}_2) = 1:14:52$, $V(\text{oil})/V(\text{IL}) = 0.75/0.75$, 70

°C] obtained from model diesel desulfurization, with a final extraction with an organic solvent (MeCN or DMF) for 30 min at 70 °C.

Table 2. Experiments performed for ODS of an untreated real diesel using catalyst **1** and different oxidant amounts and diesel/IL volume ratios.^a

$n(\text{H}_2\text{O}_2)/n(\text{S})$	Diesel/IL volume ratio	S content (ppm)	Desulfurization efficiency (%)
1.85	1:0.5	1176	48.9
1.85	1:1	1162	49.8
3.7	1:0.5	381	83.4
3.7	1:1	1071	53.4

^a Oxidative desulfurization with a biphasic diesel/[BMIM]PF₆ system for 2 h at 50 °C, $n(\text{S})/n(\text{cat}) = 7$, with a final extraction with MeCN for 30 min at 50 °C.

4. Conclusions

In summary, two dioxomolybdenum(VI) complexes bearing O-donor monodentate and bidentate ligands were effectively used as catalysts for the oxidative desulfurization of model and real diesel fuels with high sulfur contents. The different ligands, *N,N*-dimethylbenzamide (DMB) and *N,N'*-diethyloxamide (DEO), coordinated to the molybdenyl derivative MoO₂Cl₂ resulted in distinct optimal operating conditions to achieve the highest catalytic performance for desulfurization of a multicomponent model diesel and an untreated real diesel supplied by Galp. The catalyst **2** is one of the most effective ODS catalysts reported to date for removing sulfur from a real diesel, allowing under optimized conditions a reduction in the sulfur content from 2300 to 129 ppm, which corresponds to a desulfurization efficiency of 94.4%.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2019.xx.xxx>.

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Highlights

- Active Dichlorodioxomolybdenum(VI) catalysts for oxidative desulfurization of diesel.
- Deep extractive/oxidative desulfurization of diesel using low $\text{H}_2\text{O}_2/\text{S}$ ratio (< 4).
- The systems $[\text{MoO}_2\text{Cl}_2\text{L}]/[\text{BMIM}]\text{PF}_6$ were recycled repeatedly without loss of activity.
- The presence of N,N'-diethyloxamide ligand enhances the catalyst activity to treat real diesel.
- The S-content of real diesel was lowered by 94.4%, from 2300 ppm to 129 ppm after 2h.