

Oxidative Desulfurization of Dibenzothiophene Using Cobalt (II) Complexes with Substituted Salen-Type Ligands as Catalysts in Model Fuel Oil

Deependra Tripathi^{1,2} · Raj K. Singh²

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Abstract

Three cobalt(II)-salen complexes (CoL1, CoL2 and CoL3) were synthesized via the reaction of the three tetradentate ligands as N,N'-ethylenebis(salicylimine) L1, N,N'-ethylenebis(3-*tert*-butylsalicylimine) L2 and N,N'-ethylenebis(3,5-di-*tert*-butylsalicylimine) L3, with a stoichiometric amount of cobalt(II) acetate tetrahydrate, respectively. All the three complexes were studied as oxidative desulfurization catalyst on dibenzothiophene taken in model fuel oil n-dodecane. The acetonitrile used as an extracting solvent and H_2O_2 as an oxidant. Comparatively CoL3 proved to be the best catalyst which showed the 76% DBT removal at the optimized conditions. The nth-order kinetic model is the best way to represent oxidation kinetics of complexes.

Graphic Abstract



This cobalt(II) Schiffs base complexes were studied as catalyst for oxidative desulfurization of dibenzothiphene (DBT) taken as model sulphur compounds in fuel model oil (n-dodecane) using H_2O_2 as oxidant and acetonitrile as extracting solvent for DBT sulfone in a batch experiment.

Keywords Cobalt (II) complexes · Salen · Oxidative desulfurization · Kinetics · Dibenzothiophene · Model fuel

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Extended author information available on the last page of the article

1 Introduction

Due to the growing environmental problems and adverse effects on the health of living organisms, many federal agencies are imposing the stringent fuel standards with respect to sulfur content. Considering this, deep desulfurization of liquid fuels is a subject of current interest in spite of the fact that the crude is getting high in sulfur levels [1]. Hydrodesulfurization (HDS) is widely used process in the refinery for lowering the sulfur levels however, it has limitations like inefficiency to remove dibenzothiophene (DBT) and its derivatives, and higher operational costs [2]. The HDS removes the sulphur in the form of H_2S from the sulphur species like alkyl and aromatic mercaptans, diphenyl sulphide, sulphur heterocyclic's like thiophene, dibenzothiophene etc. existing in fuel oils. This process was less efficient for desulfurization of aromatic thiols, and thiophenes derivatives although several efforts were made to increase the efficiency of HDS on these species involving transition metal mediated cleavage of the C-S bonds. Among the several other metals Mo [3-5], Co [6]and Fe [7] were found to be studied extensively.

Attempts have been made in the recent past to develop other processes like extractive desulfurization, adsorptive desulfurization [8], biodesulfurization [9], photocatalytic oxidation [10], electrochemical oxidation [11] and oxidative desulfurization (ODS) [12]. Some integrated processes were also tried like extraction coupled catalytic oxidative desulfurization system (ECODS). An interesting ECODS based study was done using air and isobutylaldehyde (IBA) as metal-free photochemical oxidative systems and using deep eutectic solvents (DESs) of choline chloride (ChCl) and series of straight-chain monobasic acids for liquid-liquid extraction. The sustainable and green process was found to be effective for dibenzothiphene (DBT) removal up to 98.6% [13]. The 3D carbon spheres (3D-CSs) supported phosphotungstic acid (HPW/3D-CSs) were synthesized by carbonization of 3D printed spheres (3D-PSs) and then studied as deep oxidative desulfurization catalyst in comparison to conventional catalyst powder form. The performance was observed to be excellent at optimized conditions in removing almost~100% DBT (dibenzothiophene), 4-MDBT (4-methyldibenzothiophene) and 4, 6-DMDBT (4, 6-Dimethyldibenzothiophene) from fuel oil [14]. In another interesting study, the well-dispersed Pt NPs supported catalyst on hexagonal boron nitride (Pt/h-BN) was studies as aerobic catalytic desulfurization activity. The charge transfer from B atoms of h-BN makes the Pt NPs positively charged enabling the boosted activity and the removal of 98.3%, 96.5%, 93.7% and 85.9% was observed for dibenzothiophene, 4, 6-dimethyldibenzothiophene, 4-methyl-benzothiophene, and benzothiophene respectively [15].

Among these, the ODS has an advantage of simple operating conditions without the requirement of sophisticated utilities. In ODS, the sulfur species like DBT get oxidised into respective sulphone (DBTO₂) with the help of the oxidising agents like hydrogen peroxide, molecular oxygen and sometime aldehydes in the presence of the catalyst [16, 17]. Several catalysts like organic acid [18], polyoxometalates [19], polymolybdates [20] and transition metal salts, oxides and complexes [17] have been used in ODS. Among the transition metals, vanadium oxides and complexes have been widely investigated e.g. $VO(acac)_2$ to oxidize DBT by hydrogen peroxide [21]. Similarly V₂O₅ [22], V-Mo oxides [23], vanadium peroxocomplexes [24] and polymer-bound oxidovanadium(IV) and dioxidovanadium(V) complexes [25] have been used as ODS catalyst. Molybdenum, tungsten and titanium metal oxides have also been used as a catalyst with oxidants including hydrogen peroxide [26, 27]. In other studies, it was also noticed that the iron porphyrin and phthalocyanines complexes also have impressive catalytic activity in the ODS process [28, 29].

Cobalt (II) is an important metal that is widely utilized for catalyzing various oxidation reactions either in the form of its salts or complexes. It has also been utilized for the ODS of model sulfur compounds in fuels [30]. Cobalt phthalocyaninetetrasulfonamide was found to be very efficient catalyst for the oxidation of model sulfur compounds present in diesel using aldehyde and molecular oxygen [31]. Co(II) Schiff base complexes have been studied for the desulfurization in the past too e.g. ultra-deep desulfurization of fuel with Co(II) and Ni(II) complexes with chitosan Schiff base assisted by ultraviolet [32]. Recently we have also used N-benzylated cobalt phthalocyaninetetrasulfonamide as catalyst for oxidation of dibenzothiophene (DBT) in a middle distillate model compound (*n*-dodecane) using H_2O_2 as an oxidant. The results showed that it has better catalytic activity than cobalt phthalocyanine and cobalt phthalocyaninetetrasulfonamide [33]. Despite these efforts, there is a need to develop the new high efficiency, economical and environmentally benign catalytic ODS technologies with low catalyst loading requirements [17].

In order to develop a new type of highly active catalyst for ODS, three cobalt(II) complexes with substituted and unsubstituted salen-type ligands were synthesized and their catalytic activity was studied in a batch experiments for the oxidation of the model sulfur compound (DBT) taken in fuel model oil using hydrogen peroxide as sacrificial oxidant. The formed DBT sulfone (DBTO₂) was removed by in situ extraction by acetonitrile. The optimization experiment were done with respect to the dose of the catalyst, oxidant amount, volume of the acetonitrile, reaction time and temperature. Oxidation kinetics has been modelled by lumped power law model.

2 Materials and Methods

2.1 Chemicals and Materials

Cobalt(II) acetate tetrahydrate, ethylenediamine, dibenzothiophene, n-dodecane, ethanol, acetonitrile, salicylaldehyde, 3-*tert*-butyl-2-hydroxybenzaldehyde and 3,5-di-*tert*butyl-2-hydroxybenzaldehyde were procured from Merck Millipore. All the chemicals and solvents were of highest available grade and used as received without any further purification.

2.2 Synthesis

2.2.1 Synthesis of L1, L2 and L3 Ligands

For the synthesis of L1, 1.4 mL ethylenediamine (20 mmol) was added to a solution of 4.5 mL salicylaldehyde (41 mmol) with 50 mL ethanol in a round bottom flask. The reaction mixture was thoroughly stirred at refluxing temperature for 3–4 h, or until flaky yellow crystals were formed, and the solution was then left to cool in an ice-bath. The crystals were filtered and washed, then air-dried. Yield of L1 was found to be 5.2 g. For the synthesis of L2, 7.31 g 3-*tert*-butyl-2-hydroxybenzaldehyde; and for L3, 9.6 g 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was taken in place of salicylaldehyde. The yield of L2 and L3 were obtained 8.23 g and 10.12 g, respectively.

2.2.2 Synthesis of CoL1, CoL2 and CoL3 Complexes

Three cobalt(II)-salen complexes (CoL1, CoL2 and CoL3) have been synthesized using ethanol as solvent for ligands and water for metal salt then refluxing this mixture [34]. In this typical procedure, 4.02 g (15 mmol) L1 was taken in a round-bottom flask containing a stirring-bar, and fitted with a reflux condenser and 100 mL of ethanol was added under nitrogen. In a separate flask, 3.73 g (15 mmol) cobalt(II) acetate tetrahydrate was dissolved in 20 mL water with stirring at room temperature under nitrogen. The ligand solution was added with the help of a syringe, and swirled at the refluxing temperature for 3 h. The dark colour precipitate formed which was filtered and dried in an oven at 70 °C. The yield of N,N-bis(salicylidene)ethylenediaminocobalt(II) (CoL1) obtained was 7.54 g. Similarly, the N,N-bis(3-tertbutyl-2-hydroxybenzaldene) ethylenediaminocobalt(II) (CoL2) and N,N-bis (3,5-di-tert-butyl-2-hydroxybenzaldene) ethylenediaminocobalt(II) (CoL3) were synthesized by taking 5.71 g of L2 and 7.39 g of L3 respectively with obtained yield as 7.83 g and 10.04 g, respectively.

2.3 Characterization

The structures of all synthesized complexes were confirmed by various analytical techniques. Firstly, CHNS analysis was done by Perkin Elmer Series II CHNS/O 2400 analyzer. The Fourier transform infrared (FT-IR) spectra were recorded on a Thermo-Nicolet 8700 research spectrophotometer with a range between 450 and 4000 cm⁻¹ (KBr pellets). ¹H and ¹³C NMR have recorded on Bruker Avance 500 spectrometer, in the proton noise-decoupling mode with a standard 5 mm probe, with CDCl₃ as the solvent for synthesized ligands. Optical absorption spectra in the region between 190 and 800 nm were recorded in DMSO with a UV-2600 Shimadzu UV-Vis spectrophotometer using 1 cm path length cuvettes at 25 °C. The thermogravimetry curves were obtained on PerkinElmer EXSTAR TG/DTA 6300 with aluminium pans under continuous 200 mL min⁻¹ nitrogen flow. The mass loss was recorded from 30 to 800 °C. MALDI-TOF-MS spectra were recorded by using Bruker UltrafleXtreme-TN MALDI-TOF-MS spectrometer and 2-(4-hydroxyphenylazo) benzoic acid (HABA) matrix.

2.4 Catalytic Activity Study

The catalytic activity of the synthesized complexes was tested for the oxidation of DBT, a heterocyclic model sulfur compound. A liquid phase glass batch reactor operated at atmospheric pressure under stirring was employed. The H₂O₂ was used as the oxidant in different concentrations combining with different mixtures of acetonitrile and the metal complexes in the reactor containing 100 mL of n-dodecane that was taken as model fuel for the optimization studies. Acetonitrile works as the extractant for the polar sulfoxide and sulfone formed. At first, the dose of the catalysts was optimized by taking 100 mL of acetonitrile keeping the 0.05 mmol concentration of DBT in model fuel. Thereafter, the sulfur mass proportion to oxidant and the extractant amount were studied. Volumes of acetonitrile ranging from 100 to 200 mL were investigated for a mixture of 100 mL of model fuel and the previously optimized mass of metal complexes. The effect of different temperatures and time was studied under the selected conditions. All the experiments were carried out at ambient atmospheric pressure. Using the optimized conditions, the comparative catalytic potential was estimated for the three synthesized complexes CoL1, CoL2 and CoL3. Total sulfur content in the model oil was estimated using the XRF analysis with the Lab-X3500, Oxford Instruments, UK as per ASTM D4294 [35].

3 Results and Discussion

Since the metal like Cu complexes with salen (N,N'bis(salicylidene)ethylenediamine) and substituted salen ligands have been reported to be used as oxidation catalysts [36] so this study was undertaken using the cobalt salen and substituted salen complexes as the ODS catalysts. Unsubstituted salen complexes are poorly soluble in organic solvents. Side chains attached to the ethylene bridge or the benzene rings may increase the solubility. The presence of bulky groups near the coordination site is generally desirable, as it enhances catalytic activity and prevents dimerization. Salen ligands derived from 3,5-di-tert-butylsalicylaldehyde will be useful because they fulfill both criteria, and tend to be soluble even in non-polar solvents like dodecane.

The complexes, cobalt(II)-N,N'-ethylenebis(salicylimine) CoL1, cobalt(II)-N,N'-ethylenebis(3-*tert*-butylsalicylimine) CoL2 and cobalt(II)-N,N'-ethylenebis(3,5-di-*tert*butylsalicylimine) CoL3 were synthesized via reaction of the three tetradentate ligands L1, L2 and L3 with the cobalt(II) acetate tetrahydrate. All the ligands and complexes were characterized by using the elemental analysis, FT-IR, NMR, UV–Vis, MALDI-TOF-MS and thermogravimetric analysis and details are given in the supplementary information.

Cobalt complexes were reported to be employed as oxidative desulfurization catalyst in several papers for DBT oxidation [30-33] while acetonitrile was reported to be the best solvent for extracting the polar sulfoxide and sulfone from the model fuel oil [17]. Therefore, the same reaction (Scheme 1) was used in order to perform the comparative catalytic activity study of the synthesized complexes. The experiments were performed on a DBT solution in n-dodecane (a model fuel compound). The H₂O₂ was taken as oxidant. First, in order to screen the complex for the optimization experiments among the three CoL1, CoL2 and CoL3, n-dodecane solutions (100 mL) containing the 0.05 mmol complexes, 5.0 mmol H₂O₂ and 0.5 mmol DBT was stirred at 40 °C for 2 h under the ambient atmospheric pressure. The 100 mL acetonitrile was added insitu as extractant too. It was found that the complex CoL3 performed best followed

Scheme 1 Oxidation of DBT by H_2O_2 in the presence of synthesized cobalt complexes

by the CoL2 and CoL1 showing the 71, 56 and 53% DBT removal, respectively. Therefore, CoL3 was chosen for further optimization studies.

Now the catalyst to sulfur and the oxidant (H_2O_2) to sulfur mass proportion was optimized by doing the oxidation experiments with different catalyst:DBT molar ratio (Fig. 1A). It was observed that catalyst:DBT molar ratio of 1:15 gave the best result with 74% DBT oxidation while other parameters were kept constant (DBT:H₂O₂ molar ratio was kept at 1:10 and reaction temperature, 40 °C; reaction time, 2 h; acetonitrile:n-dodecane volume ratio = 1:1). Agglomeration and clogging of catalyst at higher catalyst dose didn't allow DBT molecules to reach the active sites which decreased the DBT oxidation efficiency [37].

In the catalytic oxidative desulfurization, the employed oxidant H_2O_2 produces the strong pro-oxidant species like



Fig. 1 Effect of various parameters on DBT oxidation efficiency in presence of CoL3 as catalyst. **A** catalyst:DBT molar ratio; DBT:H₂O₂ molar ratio=1:10, acetonitrile:n-dodecane volume ratio=1:1, temperature=40 °C, time=120 min. **B** DBT:H₂O₂ molar ratio; catalyst:DBT molar ratio=1:15; acetonitrile:n-dodecane volume ratio=1:1, temperature=40 °C, time=120 min. **C** Acetonitrile:n-dodecane volume ratio=1:5; DBT:H₂O₂ molar ratio=1:10; catalyst:DBT molar ratio=1:10; DBT:H₂O₂ molar ratio=1:10; catalyst:DBT molar ratio=1:10; DBT:H₂O₂ molar ratio=1:10; catalyst:DBT molar ratio=1:10; DBT:H₂O₂ molar rati

hydroxyl (·OH) and peroxyl (HOO·) radicals. These radicals oxidizes the DBT and convert it in to the polar DBTsulfoxide or DBT-sulfone species. Further, the increased solubility of these oxidized species in the used polar solvent like acetonitrile, they get extracted and removed. Some undesirable reaction also exists like decomposition of H_2O_2 to form oxygen and water. But these reactions become favourable only at high catalyst dose so must be avoided.

So further, keeping the catalyst:DBT molar ratio of 1:15, the optimization of the oxidant to sulfur proportion was done by performing the experiments varying the DBT:H₂O₂ molar ratios as 1:3, 1:5; 1:10 and 1:15 keeping the other parameters same as above (Fig. 1B). It was found that DBT:H₂O₂ molar ratio of 1:5 gave the best results and no further increase was observed on increasing the H₂O₂ amount at DBT:H₂O₂ molar ratios of 1:10 and 1:15. At higher H₂O₂ dose, recombination of H₂O₂ with hydroxyl radical (\cdot OH) is a high possibility by following sequence of reaction to form peroxyl radical (HOO·), water and oxygen [28]:

$$H_2O_2 + OH \xrightarrow{-H_2O} HOO \rightarrow O_2 + H_2O$$
 (1)

Now keeping the catalyst:DBT molar ratio at 1:15 and DBT: H_2O_2 molar ratio at 1:5, different volume ratio of extractant (acetonirile) relative to the n-dodecane was also tried while the temperature was maintained at 40 °C and stirring was done for 2 h. The best results were observed by using the 1:1 volume ration of acetonitrile:n-dodecane. At higher extractant ration (as 2:1) the increase in the DBT removal was insignificant while at low extractant volume ratios (as 1:2 and 1:1.5) the DBT oxidation was reduced substantially (Fig. 1C).

Further experiments were performed at different reaction temperatures ranging from 30 to 60 °C. It was observed that the maximum DBT removal was achieved at 50 °C (Fig. 1D). At higher temperatures > 50 °C, H_2O_2 gets decomposed to form oxygen in place of hydroxyl radicals [37], thus, reducing the availability of hydroxyl radical (·OH) to oxidize DBT to DBT-sulfoxide or DBT-sulfone.

After optimization of various parameters like catalyst:DBT molar ratio, DBT:H₂O₂ molar ratio, acetonitrile:n-dodecane volume ratio and temperature, the comparative catalytic potential for DBT oxidation in n-dodecane was evaluated for all the synthesized complexes CoL1, CoL2, and CoL3 with respect to time. The experiments were also conducted without catalyst and using cobalt acetate as reference compound. Results are shown in Fig. 2 by data points. Under the optimized conditions, the order of the catalytic activity was observed to be CoL3 > CoL2 > CoL1 with a maximum DBT oxidation



Fig. 2 Effect of time on DBT removal efficiency by different catalysts for DBT present in n-dodecane along with H_2O_2 at optimized conditions. Experimental data shown by points and lines represent fitting of the nth order kinetic model. Experimental conditions: catalyst:DBT molar ratio=1:15, DBT: H_2O_2 molar ratio=1:5, acetonitrile:n-dodecane volume ratio=1:1, temperature=50 °C, time=30 min

efficiency of 76, 66 and 63% for CoL3, CoL2 and CoL1 respectively. The reference metal salt (cobalt acetate) shows very low activity as the DBT oxidation was found to be very low. The DBT removal rate was also found to be high for CoL3, as 64% DBT oxidation occurs in first 15 min only which reached to 76% in 30 min and does not exceeds further from this maximum limit. Therefore, 30 min is the optimum time to get the maximum oxidation.

During the DBT oxidation, catalyst is not lost and also excess of H_2O_2 was used. Therefore the kinetic expression can be represented by a simple power law rate equation avoiding the catalyst and H_2O_2 dependence [38, 39]:

$$-\frac{dC_t}{dt} = k_n C_t^n \tag{2}$$

where, C_t is the residual concentration of DBT at time t (mmol/L), n is the order of reaction and k_n is reaction constant for the nth order reaction. Considering, C_o as the initial concentration of DBT (mmol/L) at time t = 0 min, Eq. 2 can be integrated to obtain the following equation [40]:

$$C_t^{1-n} - C_0^{1-n} = (1-n)k_n t$$
(3)

Many authors reported ODS reaction to follow the pseudofirst-order kinetic model. Equation 2 can be integrated for n = 1 to yield:

$$C_t = C_o \exp\left(-k_1 t\right) \tag{4}$$

 Table 1
 Percentage DBT oxidation and kinetics by different catalysts for DBT present in n-dodecane along with H₂O₂ at optimized conditions

Catalyst	DBT removal efficiency (%)	nth order kinetics				1st order kinetics		
		Reaction Order	k _n ((mmol/L) ⁽¹⁻ⁿ⁾ /min))	R ²	ARE (%)	$k_1 (min^{-1})$	R ²	ARE (%)
Without Catalyst	38	6.8	1.760	0.930	3.91	0.0053	0.686	12.92
Cobalt acetate	51	7.1	13.441	0.968	4.73	0.0118	0.653	25.29
CoL1	64	5.1	13.068	0.763	14.37	0.0170	0.844	19.45
CoL2	66	3.7	0.946	0.962	7.63	0.0179	0.776	28.43
CoL3	76	3.3	1.982	0.977	9.56	0.0464	0.867	38.83

Experimental conditions: catalyst:DBT molar ratio=1:15, DBT:H₂O₂ molar ratio=1:5, acetonitrile:n-dodecane volume ratio=1:1, temperature=50 °C, time=30 min

ARE average relative error

where, k_1 is the first-order rate constant. Average relative error function given by Eq. 5 was used to find the values of n, k_n and k_1 by non-linear regression method.

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{\left(C_{t,\exp,i} - C_{t,cal,i} \right)}{C_{t,\exp,i}} \right|$$
(5)

where, $C_{t,exp}$ and $C_{t,cal}$ are the experimental and calculated value of DBT concentrations in mmol/L. Values of n, k1 and k_n along with coefficient of determination (R^2) and ARE values for both nth order and 1st order reaction models for different catalysts are shown in Table 1. Values of R^2 are found to be closer to 1 and that the ARE values are lower for nth-order kinetic model in comparison to 1st order kinetic model. Thus, the nth-order kinetic model better represented the kinetic data. The first-order rate constant was highest for CoL3 catalyst in comparison to other catalyst indicating its effectiveness over other tested catalysts. The higher dispensability of the complex CoL3 in the n-dodecane due to the presence of four tertiary butyl substituent's is the reason for the higher activity along with the formation of suitable electronic density around the active catalytic metal centre. Since the synthesized cobalt complexes CoL1, CoL2 and CoL3 were used as homogeneous ODS catalyst so catalyst recovery and recyclability was not studied.

As far as the comparison of our CoL3 catalyst with the other oxidation system is concerned, although high catalytic activity is reported to be achieved but with complex systems e.g. high sulfur removal of 97% was achieved from diesel fuel oil using cobalt acetate or chloride salt and molecular oxygen as oxidant but aldehydes were also used as sacrificial materials [30]. In a similar system, 91.5% sulfur removal was achieved using cobalt phthalocyaninetetrasulfonamide as catalyst [31]. The ultravioletassisted oxidative desulfurization (UODS) using metal complex of chitosan salicylal Schiffs base, sulfur removal of 98.34% and 97.17% was achieved from real gasoline and diesel samples respectively [32]. The maximum DBT removal was also observed to be 85% from n-dodecane (model fuel oil) using an oil soluble N-benzylated cobalt phthalocyaninetetrasulfonamide but the catalyst's multi-step synthesis is complicated [33].

4 Conclusions

Three cobalt(II)-salen complexes (CoL1, CoL2 and CoL3) were synthesized and studied as catalyst for the oxidative desulfurization (ODS) reaction performed on DBT (dibenzothiophene) taken in the fuel reference oil i.e. n-dodecane using H₂O₂ as oxidant. The acetonitrile was taken as in-situ extractant for oxidised DBT compounds i.e. sulfoxides and sulfone. The reaction conditions were optimized and it was found that best oxidation occurs at catalyst:DBT molar ratio of 1:15, DBT:H₂O₂ molar ratio of 1:5, acetonitrile:n-dodecane volume ratio of 1:1, reaction temperature of 50 °C and reaction time of 30 min. Among the three, CoL3 was found to be the most active catalyst as at the optimized conditions with 76% DBT removal. The presence of bulky tertiary butyl groups near the coordination site enhances catalytic activity and prevents dimerization and also increases solubility in the organic solvent like dodecane. Kinetics of the removal process was found to follow power law kinetic model. The study indicated that this new ODS process with the help of simple cobalt(II) complex having tertiary butyl substituted salen type ligand has the potential to meet a future directives of sulfur content in the fuel.

Author contributions DT carried out the experiment and drafted the manuscript; RKS helped in conceiving the idea and data interpretation.

Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflict of interest.

References

- 1. Ali MF, Al-Malki A, Ahmed S (2009) Fuel Process Technol 90:536–544
- Yang RT, Hernández-Maldonado AJ, Yang FH (2003) Science 301:79–81
- Churchill DG, Bridgewater BM, Parkin G (2000) J Am Chem Soc 122:178–179
- Janak KE, Tanski JM, Churchill DG, Parkin G (2002) J Am Chem Soc 124:4182–4183
- 5. Buccella D, Janak KE, Parkin G (2008) J Am Chem Soc 130:16187–16189
- Ganguly T, Das A, Jana M, Majumdar A (2018) Inorg Chem 57:11306–11309
- 7. Ganguly T, Majumdar A (2020) Inorg Chem 59:4037-4048
- Guchhait S, Biswas D, Bhattacharya P, Chowdhury R (2005) Chem Eng J 112:145–151
- Zhang J, Zhao DS, Yang LY, Li YB (2010) Chem Eng J 156:528–531
- Lam V, Li GC, Song CJ, Chen JW, Fairbridge C, Hui R, Zhang J (2012) Fuel Process Technol 98:30–38
- 11. Babich IV, Moulijn JA (2003) Fuel 82:607-631
- 12. Srivastava VC (2012) RSC Adv 2:759-783
- Zhu W, Wang C, Li H, Wu P, Xun S, Jiang W, Chen Z, Zhao Z, Li H (2015) Green Chem 17:2464–2472
- Zhu J, Wu P, Chen L, He J, Wu Y, Wang C, Chao Y, Lu L, He M, Zhu W, Li H (2020) J Energy Chem 45:91–97
- Wu P, Wu Y, Chen L, He J, Hua M, Zhu F, Chu X, Xiong J, He M, Zhu W, Li H (2020) Chem Eng J 380:122526
- Rajendran A, Cui TY, Fan HX, Yang ZF, Feng J, Li WY (2020) J Mater Chem A 8:2246–2285
- Otsuki S, Nonaka T, Takashima N, Qian W, Ishihara A, Imai T, Kabe T (2000) Energ Fuel 14:1232–1239
- Komintarachat C, Trakarnpruk W (2006) Ind Eng Chem Res 45:1853–1856
- Garcia-Gutierrez JL, Fuentes GA, Hernandez-Teran ME, Murrieta F, Garcia P, Murrieta-Guevara F, Jiménez-Cruz F (2008) Appl Catal Gen 334:336–373
- Silva G, Voth S, Szymanski P, Prokopchuk EM (2011) Fuel Process Technol 92:1656–1661

Affiliations

Deependra Tripathi^{1,2} · Raj K. Singh²

- Deependra Tripathi dtripathichem@gmail.com; dtripathi@cy.iitr.ac.in
- ¹ Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

- 21. Xu D, Zhu W, Li H, Zhang J, Zou F, Shi H, Yan Y (2009) Energy Fuels 23:5929–5933
- 22. González-García O, Cedeño-Caero L (2009) Catal Today 148:42–48
- Anisimov AV, Fedorova EV, Lesnugin AZ, Senyavin VM, Aslanov LA, Rybakov VB, Tarakanova AV (2003) Catal Today 78:319–325
- Maurya MR, Arya A, Kumar A, Kuznetsov ML, Avecilla F, Pessoa JC (2010) Inorg Chem 49:6586–6600
- Maciuca A, Ciocan C, Dumitriu E, Fajula F, Hulea V (2008) Catal Today 138:33–37
- Ramírez-Verduzco LF, De los Reyes JA, Torres-Garcia E (2008) Ind Eng Chem Res 47:5353–5361
- 27. Zhu W, Li H, Jiang X, Yan Y, Lu J, Xia J (2007) Energy Fuels 21:2514–2516
- Zhou XR, Chen X, Jin YQ, Markó EI (2012) Chem Asian J 7:2253–2257
- Zhou XR, Li J, WangN X, Jin K, Ma W (2009) Fuel Process Technol 90:317–323
- Murata S, Murata K, Kidena K, Nomura M (2004) Energy Fuels 18:116–121
- Rao TV, Krishna PM, Paul D, Nautiyal BR, Kumar J, Sharma YK, Nanoti SM, Sain B, Garg MO (2011) Pet Sci Technol 29:626–632
- 32. Wang L, Li S, Cai H, Xu Y, Wu X, Chen Y (2012) Fuel 94:165–169
- Tripathi D, Negi H, Singh RK, Singh UP, Srivastava VC (2019) J Coord Chem 72(17):2982–2996
- Shankar G, Premkumar RR, Ramalingam SK (1986) Polyhedron 5:991–994
- ASTM D4294 (2016) Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry, ASTM International, West Conshohocken PA
- 36. Wu X, Gorden AE (2009) Eur J Org Chem 2009:503-509
- Kumar S, Srivastava VC, Badoni RP (2014) Int J Chem React Eng 12:1–8
- Subbaramaiah V, Srivastava VC, Mall ID (2013) Ind Eng Chem Res 52(26):9021–9029
- Singh S, Srivastava VC, Gautam S (2016) Int J Chem React Eng 14:539–545
- 40. Pandey S, Srivastava VC (2018) Pet Sci Technol 36:40-47

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² Analytical Science Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, Uttarakhand, India