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Oxidative Desulphurization Of North-East Indian Coals By Using Different Metal Ions/Oxides As Catalyst

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Abstract:

The present communication reports a simple oxidative desulphurization technique for high sulphur coal by using performic acid in presence of various metal ions/oxides. This simple oxidation by per acids gave the desulphurization of Tirap coal up to 22.58 wt%, while in presence of various metal ions as catalysts, the oxidative desulphurization is found to be increased. Desulphurization is achieved up to the extent 24.59-39.51 % using various metal catalysts. Physico-chemical characteristics of raw and oxidized coal samples are determined and FT-IR and XRD studies of raw and treated samples have been reported. Formation of oxidized sulphur species (S=O and -SO_2) is detected in FT-IR spectroscopy. The reaction mechanism of sulphur removal by metal ions/oxides have been also been discussed.

Introduction

The Indian coals are high Sulphur in nature. Thus, desulphurization is essential for commercial utilization of high S coals. One of the major problems with direct utilization of coal is the emission of sulphur containing gases (mainly sulphur dioxide and sulphur trioxide) in to atmosphere [1]. In view of world energy crisis and with the gradual depletion of superior high quality low sulphur coal reserves, attention is being given to desulphurise the low grade high sulphur coal from relatively large reserves to obtain environmentally acceptable clean fuels. Hence, the pretreatment processes for sulphur removal from coal to be effective in order to remove the inorganic and organic sulphur forms.

The desulphurization of coal is being carried out either by physical, chemical or biological methods. Physical methods are only capable of removing large pyritic particles. The biological techniques, however, are time consuming with some of bacteria specifically remove only certain types of sulphur forms. Most of the effective coal desulphurization techniques are based on chemical methods whereby almost al pyritic sulphur and substantial amount of organic being removed from coal. Chemical processes are promising desulphurization methods by which all pyritic S can effectively be removed, however, in case of organic S, removal is achieved to reasonable extent only.NE Indian coals was found to be having 75-90% of organic sulphur which makes it difficult to remove.

A number of oxidative desulphurization methods have been used for removal of organic-S. Typical oxidizing agents that have been applied to coal include hydrogen peroxide [2], potassium permanganate [3].chlorine [4], and a number of other chemical oxidants. Although both potassium permanganate,cholrine are efficient desulphurizing agents,however,these these treatments were found to effect severally on coal microstructure and coking properties, respectively. Baruah et al.[5] showed significant extent of desulphurization by using H_2O_2-HCOOOH as an oxidant and Borah et al.[6] studied the effect of few metal ions in H_2O_2 solution towards desulphurization.

In our present investigation, oxidation by H_2O_2-HCOOOH in presence of different metal ions/oxide has been reported for the desulphurization of some North East Indian coals.

Experimental

Hydrogen peroxide (30%), formic acid (85%), aluminum oxide, stannous chloride of Merck grades were used for the study. The coal samples of Assam are collected and ground to 72 BS. The proximate analysis of coal samples are done by TGA 701 Thermogravimetric Analyser (M/S Leco Corporation USA). The carbon, hydrogen and nitrogen are estimated by Perkin-Elmer (model 2400) elemental analyzer and total sulphur by sulphur determinator (LECO CORP, USA). The forms of pyritic sulphur and sulphate sulphur are determined by standard method [ASTM D 2492].The percent organic sulphur is calculated by difference. The FTIR of the coals and treated samples are done by Perkin Elmer system 2000, Model 640B using KBr pellet with same weight of dried coal samples and KBr.

Oxidation Of Coal Samples

30 gm of the coal sample is mixed with 0.5 gm of the metal ion/oxide, and then 8.8 ml of 20% formic acid is added. To this mixture 75 ml 20% hydrogen peroxide is added drop by drop for in situ formation of performic acid. This mixture is refluxed for one hour at atmospheric pressure. The oxidized coal samples are filtered and dried and preserved for further analysis.

Results And Discussion

Table 1 demonstrates the extent desulphurization on the coal sample. The Al_2O_3 and $SnCl_2$ observed to be act as the enhancer in extent of oxidative desulphurization (ODS) as well as in deashing of the coal sample. The extent of deashing and desulphurization in presence of these two catalysts were increased by 2.48-16.13%. The possible reactions taking place during oxidation of the sulphur functionalities in coal are consisting of following steps:

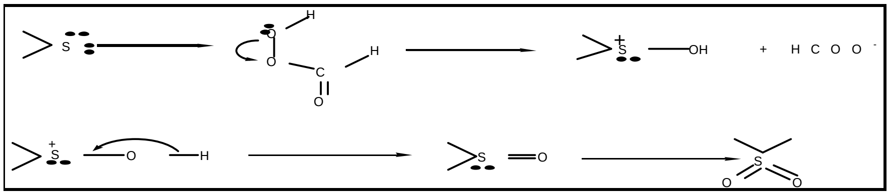
- Formation of performic acid

$$HCOOH + H_2O_2 \rightarrow HCO_3H + H_2O$$

- Oxidation of pyrites by performic acid to form hematite iron and sulphuric acid.

$$FeS_2 + 15\ O_2 + 8H_2O \rightarrow 4Fe_2O_3 + 8H_2SO_4$$

- Organic sulphur compounds are oxidized to sulphoxides, sulphonic acid and sulphones by electrophonic addition reactions[7]



The principle behind the attack of the electrophilic oxygen of performic acid with the nucleophilic sulphur centre is that the overlap of the highly populated highest occupied molecular orbital (HOMO) of the nucleophile i.e. sulphur centre with the lowest unoccupied molecular orbital and sulphur can expand its valence electrons more than eight.

Chemistry Of Oxidative Desulphurization In Presence Of Sn And Al Oxides/Ions

The reduction potential of Sn^{4+}/Sn^{2+} system (0.15V) is less than that of SO_4^{2-}/SO_2 system (0.17V) showing its preference for reducing SO_4^{2-} to SO_2.[7]

$$Sn^{4+} + 2e \rightarrow Sn^{2+}$$

$$SO_4^{2-} + 4H^+ + 2e \rightarrow SO_2 + 2H_2O$$

The produced SO_2 may react as follows,

$$SO_2 + H_2O \rightarrow H_2SO_3 + H_2O_2 \rightarrow H_2SO_4$$

Parameters	Raw coal	Oxidized coal	Oxidized with Al2O3	Oxidized with SnCl2
M	3.51	0.98	3.77	4.61
VM	43.17	42.10	41.70	40.5
Ash	2.01	1.53	1.48	1.34
FC	51.31	55.3	53.0	53.5
PS	0.48	0.17	0.1	0.32
SS	0.45	0.11	0.03	0.02
SS	1.55	1.64	1.74	1.63
TS	2.48	1.92	1.87	1.97
C	80.9	80.3	77.4	75.4
H	5.83	6.27	6.13	6.14
Deashing	-	23.88	26.36	33.33
Desulphurization	-	22.58	24.59	39.51

Table 1: Physicochemical characterization of different oxidized coals (as received wt %)

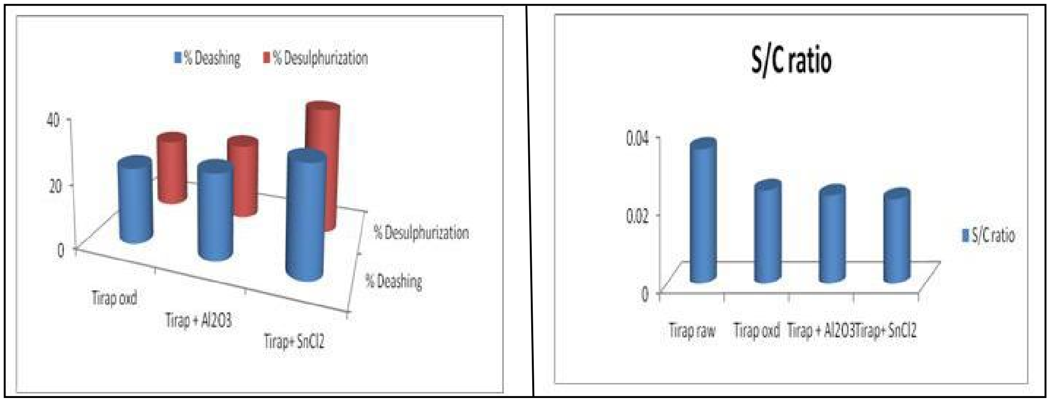


Figure 1: wt% of Desulphurization, deashing and S/C ratio of the coal and oxidized samples

The following reaction was occurs with liberation of OH^+ ion.

$$HCOOOH + H^+ \leftrightarrow HCOOH + OH^+$$

Thus, consumption of H^+ enhance the production OH^+ which in turn facilitates the oxidation of organic sulphur in coals because OH^+ is potentially strong electrophile which selectively attacks nucleophilic sulphur rather than carbon leading to shortening of the S-O bond with consequent elongation of the O-O bond. Now, consumption of H^+ is possible by the following reactions, on account of which there is considerable increase in desulphurization in presence Al_2O_3 as

$$Al^{3+} + 3e^- \leftrightarrow Al$$

$$Al_2O_3 + 6H^+ \leftrightarrow 2Al + 3H_2O$$

FTIR Study Of Coal Samples

Absorption bands close to 520,610 and 640 cm^{-1} shown are due to stretching vibration of S-S bonds of sulphides and C-S bonds in primary and secondary thiols.[9] It has been found that organically bound sulphur has been converted to sulphoxides and sulphones. Peaks for organic sulphates occur in the region of 1415-1385 cm^{-1} [10] .The stretching vibration in sulphoxides generally occur in the region 1070-1030cm- .Absorption bands for $-SO_2$ group in sulphones occur at 1350-1300 cm^{-1} for asymmetrical vibration and 1160-1120 cm^{-1} for symmetrical vibration[13]. Peaks appearing at 1368 and 1090 cm^{-1} in oxidized coal samples belong to $-SO_2$ vibration.

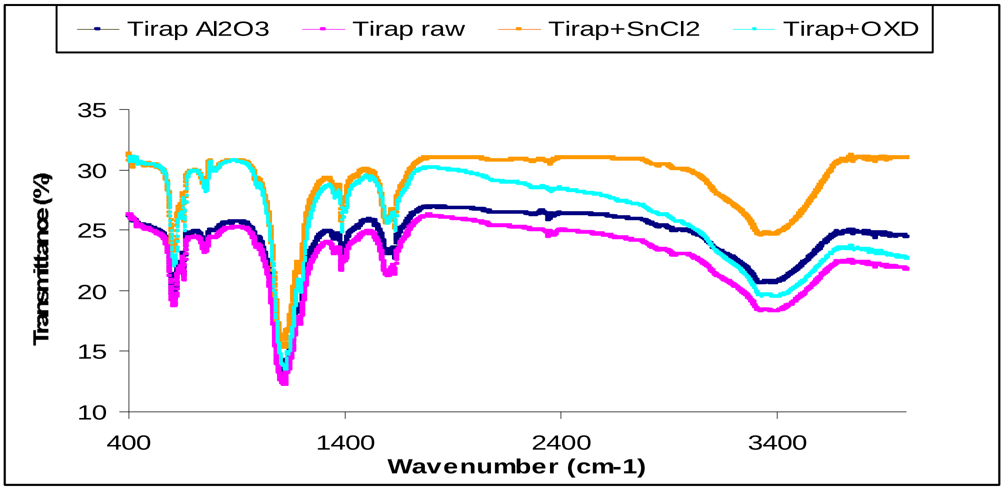


Figure 2: FT-IR spectra of different raw and oxidized samples

Conclusion

Performic acid was found to be a promising oxidant for desulphurization of NER coals. It is observed that oxidized sulphur species formation is an important prerequisite for formation of sulphur. The varying degree of desulphurization was observed in the systems with externally added metal ion/oxide, which suggested that proper metal ion/oxide can enhance desulphurization of coal.

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