Removal of Organic Sulphur in Coal by the Use of Anhydrous HF and Superacid HF/BF$_3$

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Anhydrous hydrogen fluoride (HF) and HF combined with a small amount of boron trifluoride(BF$_3$) desulphurized high-sulphur coal in the presence of hydrocarbons without H$_2$ in mild reaction conditions. HF removed mainly sulphidic and oxidized sulphur. HF/BF$_3$ decreased thiophenic sulphur as well as sulphidic and oxidized sulphur although the extent of desulphurization was almost the same as that with HF alone.

Organic sulphur in coal is difficult to remove by physical means or conventional chemical process because it is firmly linked with the organic units of coal. We previously reported that a liquid Bronsted superacid, trifluoromethanesulphonic acid(TFMS), desulphurized high-sulphur lignite coal, producing H$_2$S in the presence of aromatic hydrocarbon without H$_2$ at 150-200°C 1). Sulphidic and sulphoxide sulphur, but not thiophenic sulphur, were removed. In highly superacidic media such as HF combined with Lewis acid (SbF$_5$, TaF$_5$) ionic hydrogenation of aromatic compounds took place at comparatively lower reaction temperatures under hydrogen pressure or alkane without a transition metal catalyst 2,3). The hydrogenation ability of such superacid seems to be due to their acidity. The acidity of the mixture of HF/7 mol% BF$_3$ (H_0=-16.6) is much higher than that of TFMS(H_0=-14.6), leading to higher activity of the former as an acid catalyst 4). And HF/BF$_3$ are fully recoverable from product by distilation only, and can be reused, because their boiling point are very low(HF: 19.9°C, BF$_3$: -101°C). Here, we examine the ability of anhydrous HF and HF/BF$_3$ to remove organic sulphur in high-sulphur coal through ionic reactions. Sulphur forms in the treated coals were characterized by XPS in order to describe their behaviors in the highly superacidic media by identifying the remaining sulphur species.

A lignite, Mequinenza coal (MQ) was used, ground to 0.25 mm under. The MQ was treated with an aqueous nitric acid solution (25 vol%) for 24 h at room temperature to remove inorganic sulphur (FeS$_2$ and FeSO$_4$). The organic sulphur content in the coal was determined according to the JIS M8813-1976 method in a Heraeus CHN-O-PAPID. HNO$_3$ -treated MQ coal (sample coal) almost free of inorganic sulphur (SO$_4^{2-}$: 2% in total sulphur), and toluene or isopentane (20 mL) were placed in a dry ice-methanol cooled hastelloy-C micro-autoclave of 100 mL capacity. HF and BF$_3$ were introduced into the coal-solvent slurry. The autoclave was then heated to 200°C at a heating rate of 3 °C/min for 3 h under autogenous pressure with stirring (1000 rpm). The solid product obtained was vacuum-dried at 110 °C for 24 h. For comparison, the coal was also heat treated in tetrahydronaphthalene (tetraline) at 420 °C for 30 min under autogenous pressure. The reaction conditions are shown in Table 1. XPS was measured using the microfocused monochromatic Al Kalpha radiation from an ESCALAB 220i-XL (VG Scientific). Bonding energy was corrected to the carbon (1s) peak at 284.6 eV. The spectra were obtained at a pass energy of 20 eV. The full width at half maximum (FWHM) of the silver metal 3d5/2 signal was <0.5 eV under these condition. The XPS spectra were curve - resolved, using peak values at 169.4, 167.3, 165.8, 163.8 and 163.1 eV for sulphate(SO$_4^{2-}$), sulphoxide (C-SO$_2$-C), sulphone (C-SO-C), thiophenes and alkylsulphides, respectively.

Elemental analyses of the treated coals and their desulphurization products are shown in Table 2. Heat treatment at 200°C in the presence of toluene as solvent without acid catalyst (MQ-1) showed only 6 % desulphurization. The reaction with HF in the presence of isopentane (MQ-2) increased desulphurization to 22 % in the same reaction condition, indicating that HF activates and partially cleaves a portion of the S - C bonds in the coal molecules. The addition of toluene increased desulphurization markedly to 52 % (MQ-3). Treatment with the conjugate Brönsted-Lewis superacid HF/7 mol% BF$_3$ (MQ-4) produced only slightly more desulphurization. The extent of desulphurization of MQ-3 and MQ-4 was almost the same as that of the thermally treated coal (MQ-5).

Distribution of organic sulphur in the sample MQ and treated coals as determined by XPS is shown in Figure 1. The organic

Table 1. Reaction conditions of the treated coals

Run	Reaction condition HF (g)	BF$_3$ (g)	Solvent (reactant)	Temp (°C)	Pressure (MPa)
MQ-1	-	-	toluene	200	1.1
MQ-2	5.46	-	isopentane	200	4.5
MQ-3	5.46	-	toluene	200	5.5
MQ-4	5.46	1.22	toluene	200	5.7
MQ-5	-	-	tetraline	420	7.1

Amount of HF and BF$_3$ was g/g-coal.

Table 2. Elemental analyses and desulphurization

Run	Elemental analyses (wt%, daf) C	H	N	Odiff	S	Ash (wt%)	WI (%)	Desul. (%)
Original MQ	63.2	6.1	0.9	17.8	12.0	12.5	-	-
Sample MQ	53.8	4.9	4.1	28.8	8.7	10.5	-	-
MQ-1	61.5	5.0	3.9	20.7	8.9	11.3	92	6
MQ-2	70.8	5.6	2.6	13.5	7.5	3.8	90	22
MQ-3	79.5	5.7	1.7	9.9	3.2	4.5	131	52
MQ-4	83.5	5.9	1.0	7.8	1.8	1.6	210	57
MQ-5	71.0	5.9	2.2	16.1	4.8	10.4	83	54

WI: Weight increase, Desul: Desulphurization

The solvent, toluene, is incorporated into the subsequent carbonium ions from cleavage of coal molecules, resulting in a weight increase of feed coal. However, polymerization of toluene itself in the presence of HF and HF/BF$_3$ was not significant (only 0.7 - 2.3 wt% in the products). Desulphurization is calculated by considering weight increase and demineralization as follow :

Desulphurization (%) ={1 - S x (WI / 100) /8.7} x 100

WI={(treated coal - ash in the treated coal) / (sample coal - ash in the sample coal)} x 100

8.7: sulphur content of sample coal (%)

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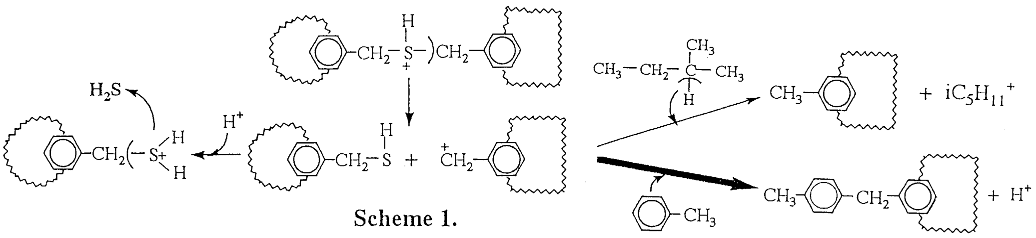


Scheme 1.

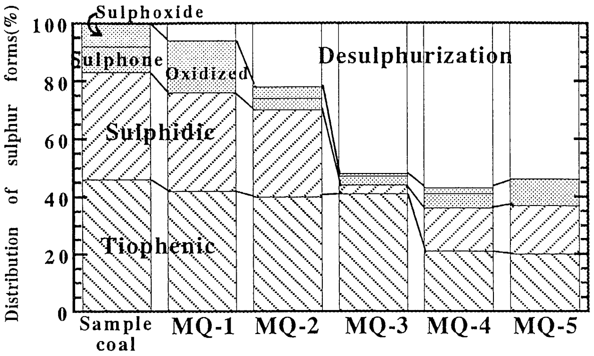
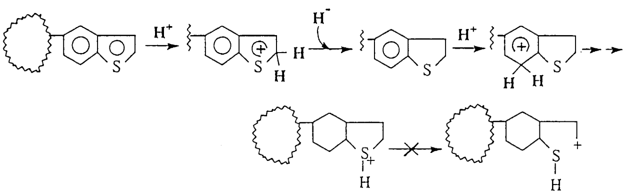


Figure 1 Distribution of organic sulphur forms in the sample coal and treated coals.



Scheme 2.

sulphur of the sample coal consisted of 20% oxidized sulphur, 35 % sulphidic sulphur and 45 % thiophenic sulphur. No significant decrease of any sulphur forms was observed by heat treatment at 200°C in toluene. However, the treatment with HF in the presence of isopentane (MQ-2) clearly decreased both oxidized and sulphidic sulphur. The decrease in the sulphidic sulphur content in the reaction with HF and toluene (MQ-3) was marked. The reaction with HF/BF$_3$ produced less thiophenic sulphur than did the reaction with HF alone although the extent of desulphurization in each was almost the same, and the distribution of organic sulphur in MQ-4 was almost same as that of thermally treated coal (MQ-5).

The present letter reports that a Brönsted acid, anhydrous HF, and superacid HF/BF$_3$ desulphurized coal without gaseous hydrogen at 200°C. The extent of desulphurization (55 - 60%) of coal using the acids was higher than that (35 - 41%) from the reaction of coal with TFMS which we reported previously, and was almost the same or slightly higher than that by thermally treating coal at 420°C with a sophisticated hydrogen donor solvent, tetraline, and high hydrogen pressure. HF activated the cleavage of sulphur - carbon bonds, but its extent depended on solvent. Toluene with HF significantly decreased sulphidic sulphur, whereas isopentane partly reduced both sulphidic and oxidized sulphur. Protonation of the sulphur containing coal molecules would easily take place in acidic conditions at the lone pair electron of sulphur, protonated sulphide would then decompose into a benzyl - like carbenium ion and a thiol. The carbenium ion would be stabilized by toluene through electrophilic reaction or by the abstraction of hydride from isopentane. Simultaneously, the thiol - like component would be also protonated and liberate its sulphur as H_2S. However, the carbenium ion produced would recombine with the thiol - like component under unstable conditions. We previously reported that the extent of depolymerization of treated coal using toluene and HF/BF$_3$ was higher than using isopentane$^{5)}$. It was assumed that transalkylation of coal with toluene occured preferentially to hydride transfer from isopentane to produced a carbenium ion, reflecting cleavage of S - C bond and desulphurization. The desulphurization reaction mechanism of sulphidic sulphur in coal with hydrocarbon is shown in Scheme 1.

HF as well as TFMS reduced sulphidic and oxidized sulphur significantly but thiophenic sulphur only slightly. In contrast, HF/BF$_3$ reduced thiophenic sulphur also. The difference in activity of these superacids seems to be one of acidity (HF=-15.1, TFMS=-14.6, HF/BF$_3$=-16.6). HF/BF$_3$ would be protonate aromatic hydrocarbon directly and produce carbonium ion. This carbonium ion is crucial intermediate for hydrogenation of aromatic hydrocarbon and hydrogenated by abstraction of hydride ion from highly branched alkane or branched alkyl groups in the coal (Scheme 2). These results showed aromatic components of coal would be hydrogenated through ionic reaction in the highly superacid media and some thiophenic sulphur would be converted to alkyl sulphidic sulphur. The sulphidic sulphur would not become alkyl sulphidic sulphur but alicyclic sulphur. The cleavage of the S - C bond of alicyclic sulphur containing compounds is not easy because the very unstable primary carbenium ion is produced (Scheme 2). Consequently, the extent of desulphurization by MQ-3 and MQ-4 was almost the same, indicating that it dose not significantly depend on the superacidity. However, HF/BF$_3$ shows the possibility of further desulphurization if it is subsequently treated at the thermal stage because sulphidic (alicyclic) sulphur is not thermally stable andeasily activated by the desulphurization catalyst.

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