

BEHAVIOR OF ALUMINUM COMPLEXES IN THE ALTERED COAL AND LOW TEMPERATURE COAL ASHES

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ABSTRACT

An occurrence of tetra-coordinated aluminum in altered coal and low temperature coal ashes was investigated. As altered coal a sample from the Lazy mine (Upper Silesian Coal Basin) was tested, further, low-temperature ashes from different coals were prepared and measured. During preparation the selected coal samples were intensively air-oxidized; ^{27}Al MAS NMR spectra of obtained ashes were then acquired and compared against those for initial coals. A reference wood ash and Al standards were used for identification of Al-forms. It was found that chemical shift at 4 ppm with coals corresponds to that for triaquo-hydroxo-diphenoxido-aluminum(III) complex (THDA), further, the shift at 72 ppm with altered coal and resulting ashes agrees with that for Al tetra-coordinated with oxygen. So, in the presence of coal organics the tetra-coordinated Al is formed under low temperature conditions, because during low temperature ashing the THDA complex is transformed to Al tetra-coordinated with oxygen only at 350 °C. A similar process occurred in the case of oxidation of coal substance under low temperature conditions in the nature at temperatures below 150 °C.

KEYWORDS: aluminum complexes, altered coal, low temperature ashes

INTRODUCTION

Due to a huge ash production, these substances are currently considered as a mineral resource rather than as a residual waste. For this reason, they are presently intensively studied both in terms of composition and use. As a part of this effort is to study the low temperature ashes originating e.g. from the catalytic processes, certain combustion techniques, a thermal treatment of coal mines dust etc. In our case, the low temperature ashes from different bituminous coals have been studied in terms of behavior of Al compounds in the temperature changes up to 350 °C.

The aim of this study is to describe formation of aluminum tetra-coordinated with oxygen during low temperature coal oxidation, as this structure is generally crucial for the further utilization of ashes.

EXPERIMENTAL

Materials. For measurements, ashes of bituminous coals from the Czech Republic were chosen. Crushed (1–2 mm) and air-dried samples from the Paskov, the Staříč and the Lazy mines (the Czech part of the Upper Silesian Coal Basin) were used. Coal samples were intensively air-oxidized at 350 °C for 160 hours in a muffle kiln (Klika, 1999); then, ^{27}Al MAS NMR spectra of obtained ashes were acquired and compared to those with the original coals and Al-standards. As standards following minerals and reference compounds were chosen for a) an

evidence of sensitivity of ^{27}Al MAS NMR method to chemical environment of Al atom, b) identification of Al compounds in tested ashes and coals:

- $\alpha\text{-Al}_2\text{O}_3$ (Korund Benátky, SRO, Czech Rep.); $\gamma\text{-Al}(\text{OH})_3$, gibbsite (Lachema Brno Comp., proven by XRD method); kaolinite (Kaolin Sedlec IA Standard, Sedlecký kaolin AS, Czech Rep.); aluminum phenoxide $\text{Al}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_5\text{O})_3$ (Sigma Aldrich, elemental analysis see Table 1); as polyphenolic complex, Al-catechin complex prepared according to (Chen, Wang and Huang, 2006) was chosen. Further:
- triaquo-hydroxo-diphenoxido-aluminum(III) complex (THDA), with the formula $\text{Al}(\text{H}_2\text{O})_3(\text{OH})(\text{C}_6\text{H}_5\text{O})_2$, prepared by a long-term reaction of gibbsite powder with phenol (1:1) in water as follows. 25 g of gibbsite was blended with the same amount of phenol and 110 ml water. The suspension was kept in capped flasks at room temperature for 15 months; then conc. NaOH was added for the removal of the unreacted phenol. Then, the formed precipitate was washed and air-dried. Subsequently, 500 ml of ethanol was added for leaching; after the ethanol evaporation, a solid phase of leach was obtained as ruby/violet powder. The yield was 1-2 %. Elemental analysis of the complex is shown in Table 1;

Table 1 Elemental analyses of the reference Al complexes (wt.%).

Complex	C	H	O	Al
Al phenoxide	56.56	6.25	29.02	8.17
THDA	49.68	5.70	35.16	9.46
TTA	0.00	6.55	74.57	18.88

Table 2 ^{27}Al MAS NMR signals of reference minerals and complexes.

Reference compounds	[ppm]	Description
Aluminum phenoxide	20.90	Al atom surrounded by 3 phenoxide anions and 3 water molecules.
$\alpha\text{-Al}_2\text{O}_3$	14.16	Corundum – distorted octahedra.
Al-catechin complex	13.85	Al-complex with irregularly arranged phenolic molecules.
$\gamma\text{-Al(OH)}_3$	8.86	Gibbsite – distorted octahedral.
kaolinite	4.82	Kaolinite – distorted octahedra.
$\text{Al(H}_2\text{O)}_3\text{(OH)(C}_6\text{H}_5\text{O)}_2$ (THDA)	4.15	Al-complex with octahedral molecules.
$\text{Al(OH)}_3\text{(H}_2\text{O)}_3$	-1.10	Al-complex with symmetrically arranged OH and water ligands.

- triaquo-trihydroxo-aluminum(III) complex (TTA), with the formula $\text{Al(H}_2\text{O)}_3\text{(OH)}_3$ prepared by a long-term hydrolysis (20 months) of AlCl_3 (25 g) in water (110 ml) at pH 5.5. After addition of small quantities of NaOH to increase pH a white precipitate was obtained. After drying the complex as a white powder was obtained, further purified by 1M HCl. The yield was about 20 %. Elemental analysis of this complex is shown in Table 1;
- wood ash, prepared in an industrial incinerator (with a recycling of unburned fuel) at the temperature of 400–500 °C. The main signal of aluminum tetra-coordinated with oxygen in ^{27}Al MAS NMR spectrum was of 58 ppm.

Methods. For the organic elemental analyses of the reference compounds the Flash 1112 EA analyzer (Thermo Finnigan, Rodano) was used; the analysis of the aluminum was carried out on an XRF spectrometer EDS Spectro X-Lab (SPECTRO Analytical Instruments, Kleve). The aluminum complexes/structures both in the mentioned coals/ashes and the reference compounds were analyzed by solid-state nuclear magnetic resonance measurements of ^{27}Al on a Bruker Avance 500 spectrometer (Bruker, Rheinstetten) which is an extra sensitive instrument. FTIR spectra of THDA komplex were acquired on a FTIR spectrometer Bruker IFS 66. A KBr pressed disk technique was applied. 64 scans were collected for each measurement over the spectral

range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} . Spectra were deconvoluted using an Omnic 7.3 software (Thermo Electron Corporation).

Important question was the sensitivity of ^{27}Al MAS NMR to chemical environment of Al atom. The considerable sensitivity of this method is evident from different chemical shifts of three Al minerals (Table 2, corundum, gibbsite and kaolinite, see below). In corundum $\alpha\text{-Al}_2\text{O}_3$, Al^{3+} ions are surrounded by their six nearest oxygen neighbors at 1.849 and 1.980 Å (Ildefonse et al., 1998) (or at 1.855 and 1.972 Å (Lewis and Schwarzenbach, 1982)), and the four nearest Al^{3+} neighbors at 2.65 and 2.79 Å (Newham and de Haan, 1962); as the result of which, a distinct NMR signal is expected because of these Al–O distances. Since further reference compounds, gibbsite, $\gamma\text{-Al(OH)}_3$, consist of octahedral layers with two Al sites with the Al–O distances spread over 1.832 to 1.947 Å (Saalfeld and Wedde, 1974), a different NMR signal than in corundum is expected. The third reference mineral, kaolinite, has two Al sites like gibbsite, but the Al–O distances are between 1.880 and 1.969 Å (Bish and von Drelle, 1989) without a resolved mode. In kaolinite, a gibbsite-like layer is associated to a tetrahedral Si layer; therefore, a different NMR signal is expected again. The measured significant differences between obtained ^{27}Al MAS NMR signals are clearly demonstrated in Table 2. These results prove that ^{27}Al MAS NMR method is very sensitive to chemical environment of Al atom.

RESULTS AND DISCUSSION

Given the low concentration of Al complexes in coal, their isolation is very difficult. It is therefore feasible to use the sensitive solid-state ^{27}Al MAS NMR method, create a comparative scale of complexes and to identify complexes in question *in situ* in coals on the basis of the same or similar chemical shifts (an allowable difference of $\pm 1\text{--}2$ ppm in the range of about 0–20 ppm). The same method can be used for ashes and altered coals (an allowable difference of ± 15 ppm in the range of 50–80 ppm). Firstly, signals in ^{27}Al MAS NMR spectra of the obtained ashes were evaluated. Generally, the signals in the range of 50–80 ppm belong to the Al tetra-coordinated with oxygen (further {4Al}). In all the cases the signal at 72 ppm was found (71.78 ppm at the Paskov, 71.74 ppm at the Stařič and 71.95 ppm at the Lazy coal ashes). These values correspond well to those found with the reference wood ash (Fig. 1). In Figure 1, after deconvolution, the main signal at 58 ppm, peak area 76.94 %, proves that {4Al} is present; further, the minor signals at 67.85 (4.42 %), 61.89 (2.07 %), and 50.98 (16.58 %) ppm were detected. These signals can be attributed to different chemical environments of {4Al} in the wood ash. All these findings prove that the {4Al} structure was present in ashes in question. Further, the ^{27}Al MAS NMR signals of original coals were investigated. In all cases, the signal at 4 ppm was found: 3.96 ppm at the Paskov, 4.16 ppm at the Stařič and 4.98 ppm at the Lazy coals. These values were compared with those obtained at reference compounds (Table 2). From Table 2 it follows that mentioned signals agree well with that found at THDA complex. Regarding the signal at 72 ppm at ashes this means that THDA existing in coals was during low temperature oxidation converted into {4Al}. In this connection, the oxidative altered coal from the Upper Silesian Coal Basin was tested (volatiles 30.8 wt.%, dry ash free basis; ash 3.8 wt.%, dry basis). This coal comes from the vicinity of red beds bodies (oxidative and thermally altered claystones, siltstones and sandstones); during its history this coal was naturally altered by oxidation under low temperature conditions at temperatures below 150 °C (Klika, 1999a, b). Due to this, both the structures THDA and {4Al} were expected in the sample. As the acquired ^{27}Al MAS NMR spectrum shows (Fig. 2), two signals both at 72 ppm (23.65 %) and 5 ppm (61.03 %) were recorded, thus, the two mentioned structures were present, as expected. Therefore, under low temperature conditions the THDA complex changes into {4Al}. Moreover, after deconvolution of the spectra a signal at 15.9 ppm was discovered (Fig. 2), which is assigned to Al-catechin (Nagata et al., 1992) or, rather, Al-catechin-like complex (see Table 2). Probably, this complex is also changed into {4Al} during low temperature conversion. Shortly, at least two, maybe three complexes are present in the coal substance of altered coal. In any case, the THDA

complex is generally present in the coal substance, i.e. in the organic mass of coal, and in the case of thermally and oxidative altered coal, beside the THDA complex also the {4Al} complex structure is present in coal substance (in our case, the ash content was only 3.8 wt.% (dry basis), as mentioned).

It seems that THDA complex originated from a gibbsite layer of kaolinite, which is very frequent in coals (Thomas, 2007). At first, the delamination of kaolinitic layers to octahedral gibbsite and tetrahedral silicite layers occurred due to long-term exposure of water and coal organics. Subsequently, reactions of gibbsite with phenols led to Al-tetrahydroxodiphenoxide complex ion, further stabilized in a water environment (i.e. in a weakly acidic environment) as $\text{Al}(\text{H}_2\text{O})_3(\text{OH})(\text{C}_6\text{H}_5\text{O})_2$ complex (THDA). During low temperature ashing this complex is transformed to {4Al} only at 350 °C. This hypothesis was further tested.

In our considerations the key compound is THDA. Therefore, this complex was studied using FTIR spectroscopy. Obtained FTIR spectrum is pictured in Figure 3. By referring to different previous spectral studies the major vibrational bands are assigned (peaks with very weak intensities at 2718, 2604, 2493 and 1776 cm^{-1} are not assigned). Figure 3 displays, beside peaks with medium intensities, three dominant bands: a broad strong band at 3433 cm^{-1} , a band with three maxima at 1624, 1607 and 1598 cm^{-1} , and a broad band at 1446 cm^{-1} ; further, three regions of 1165–1024, 880–693 and 618–512 cm^{-1} , and two expected stretch bands at 1335 and 1242 cm^{-1} (phenoxide CO) were recorded.

The broad strong band at 3433 cm^{-1} is due to O–H stretching vibrations of H_2O and OH groups (Beran et al., 2001). The band with mentioned three maxima is due to bending vibrations HOH (1624 cm^{-1}) (Beran et al., 2001) and aromatic in-ring C–C stretches (1607 and 1598 cm^{-1}) (Silverstein and Webster, 1998). The broad peak at 1446 cm^{-1} probably reflects an important phenomenon of Al–O–C linkage (see later). Further vibrations, CCH bend (1385 cm^{-1}) (Kubicky et al., 1997), phenoxide CO stretches (1335 and 1242 cm^{-1}) and C–H out of plane bends (880–693 cm^{-1}) (Silverstein and Webster, 1998) again prove an aromatic part of complex. Finally, vibrations in two regions, 1165–1024 and 618–512 cm^{-1} , are assigned to AlO–H vibrations (1165–1024 cm^{-1}) (Sinkó et al., 1999) and Al–O stretches (618–512 cm^{-1}) (Beran et al., 2001; Sinkó et al., 1999).

It seems that the mentioned broad band at 1446 cm^{-1} is composed of at least two components; an overlapping of both covalent Al–O–C and in-ring CC stretch vibrations is suggested. Probably, it reflects an important phenomenon of Al–O–C group predicted in the work (Kubicky et al., 1997). Therefore, this high-intensity band and the above-mentioned band with three maxima at 1624, 1607 and 1598 cm^{-1} were further deconvoluted (Fig. 4). Deconvolution in Figure 4 shows 7 main peaks at 1434, 1468, 1504,

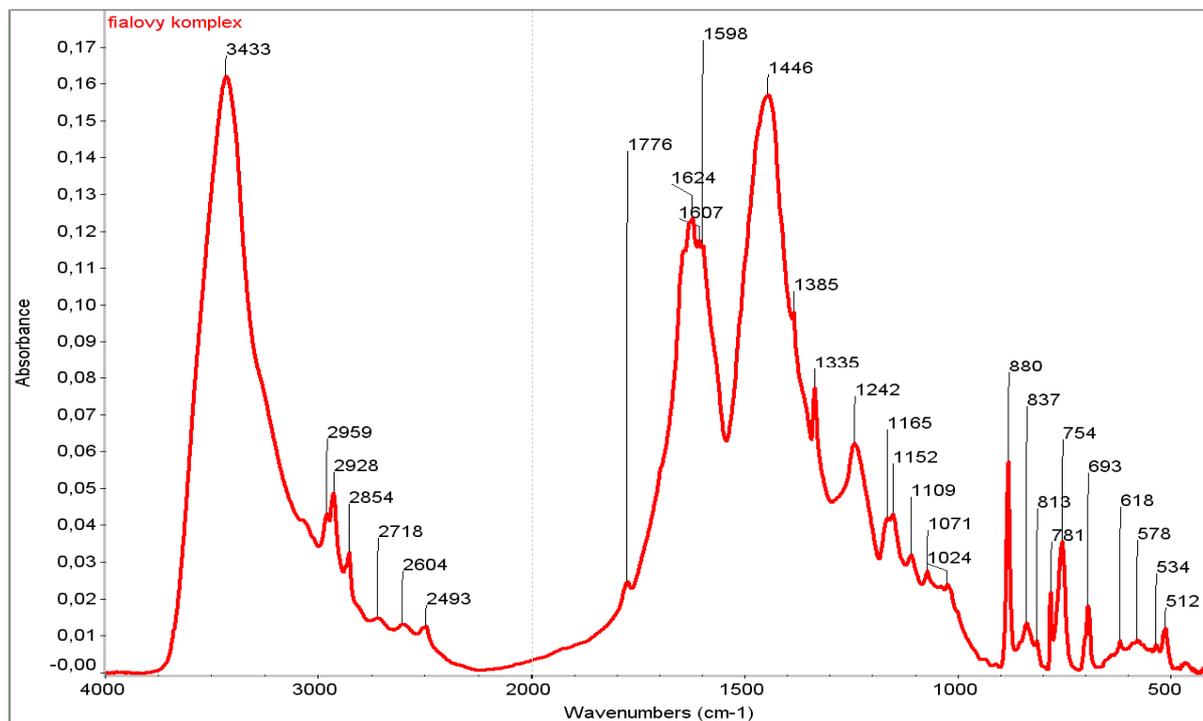


Fig. 3 FTIR spectrum of triaquo-hydroxo-diphenoxido-aluminum(III) complex (THDA).

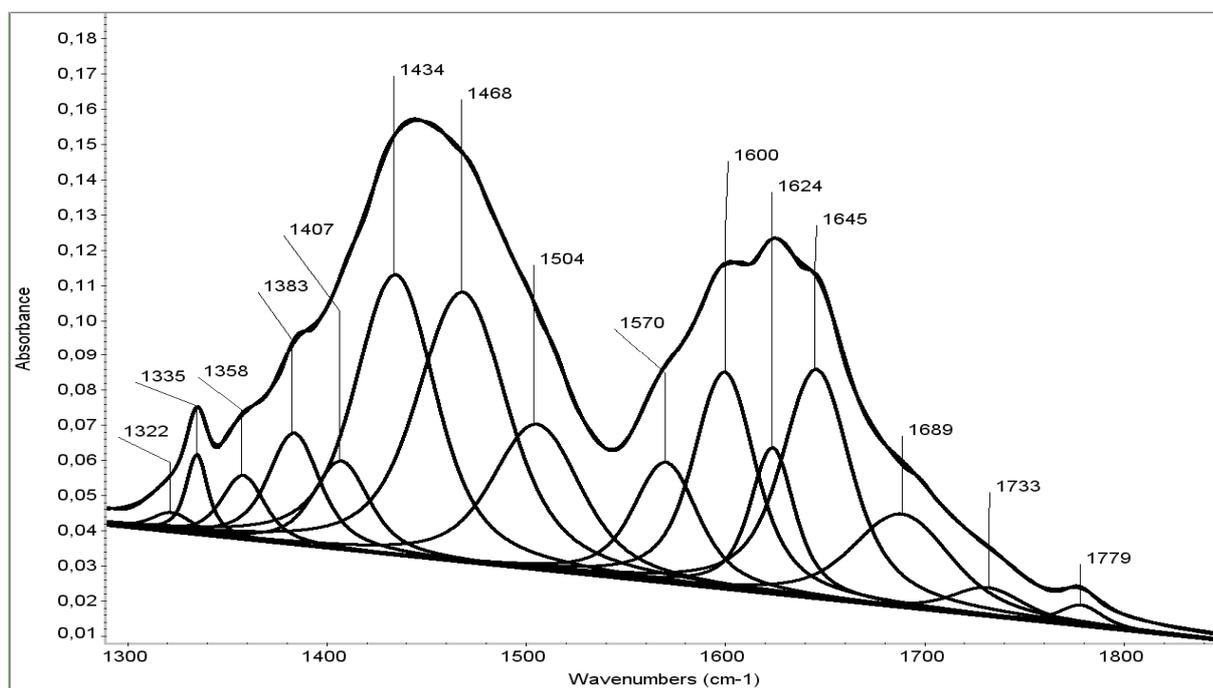


Fig. 4 Deconvolutions of the bands at 1624/1607/1598 cm⁻¹ and 1446 cm⁻¹ (see FTIR spectrum in Figure 3).

1570, 1600, 1624 and 1645 cm^{-1} . These peaks are assigned to Al–O–C covalent linkages (1434 cm^{-1}), in-ring CC stretches (1468, 1504, 1570 and 1600 cm^{-1}), and HOH bends (1624 and 1645 cm^{-1}). On the whole, FTIR spectrum is consistent with the formula of THDA.

From these data it can be deduced that THDA will not be too thermally stable. Therefore, the behavior of this complex during heating in an inert atmosphere was followed by TG and DSC methods (Straka and Náhunková, 2010). It was found that THDA is thermally stable up to 150 °C, rather less. Activation energy was very low: 3.12 kJ/mole. This means that the decomposition takes place quite easily and formation of structure {4Al} is thus easier than through usual thermal treatment of kaolinite at e.g. 600 °C. Therefore, during low temperature coal ashing, THDA or its part is transformed to {4Al} only at 350 °C. The decomposition temperature of THDA is comparable to that of aluminium phenoxide (below 155 °C, as found by TG/DSC). The reason is that the structure of both complexes is similar as Al phenoxide is in fact the triaquo-triphenoxido-aluminum(III) complex. This finding support the mentioned structure found by FTIR.

CONCLUSION

Probably, aluminum in coal originates from kaolinite, as this mineral is very frequent in coals. In the coal substance the triaquo-hydroxo-diphenoxido-aluminum(III) complex was formed through the long-term reactions of kaolinitic hexa-coordinated Al with phenols/polyphenols. During this process the octahedral structure of hexa-coordinated Al was retained, but ligands coordinated around the central Al atom changed. At first, delamination of a kaolinitic structure through the effect of coal organics proceeded and separation of the Al gibbsite octahedral and silica tetrahedral layers occurred. Then, two oxygens in the Al octahedron were substituted with two phenoxide $\text{C}_6\text{H}_5\text{O}$ groups while four OH groups were preserved. As result, Al-tetrahydroxo-diphenoxide ion was formed, further stabilized in a water environment as $\text{Al}(\text{H}_2\text{O})_3(\text{OH})(\text{C}_6\text{H}_5\text{O})_2$. During low temperature ashing this complex is transformed to Al tetra-coordinated with oxygen only at 350 °C. A similar process occurred in the case of oxidation of coal substance under low temperature conditions in the nature at temperatures below 150 °C.

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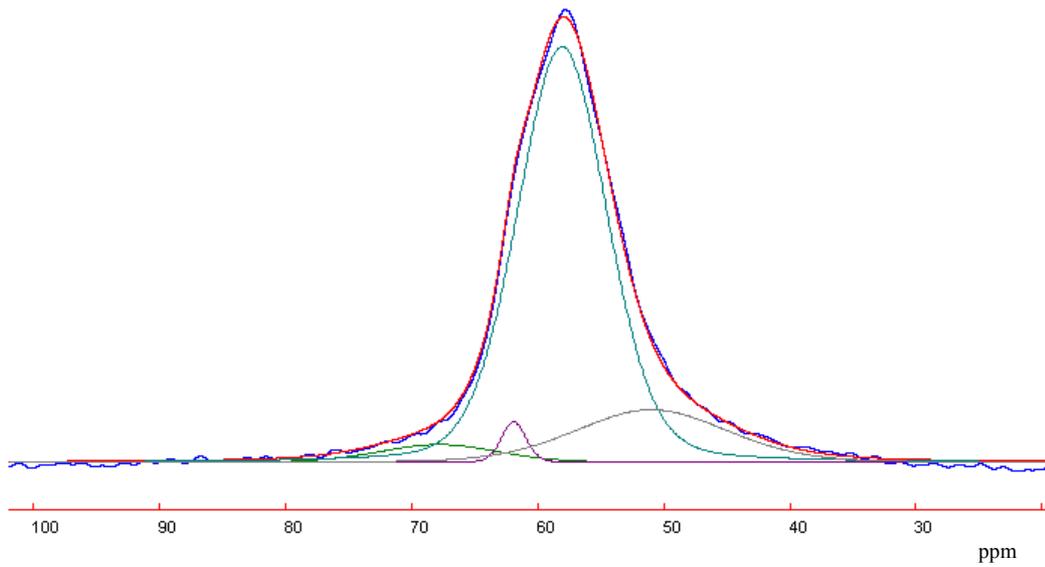


Fig. 1 ^{27}Al MAS NMR spectrum of the reference wood ash. Positions [ppm]: 67.85 (peak area 4.42 %); 61.89 (2.07 %); 58.05 (76.94 %); 50.98 (16.58 %).

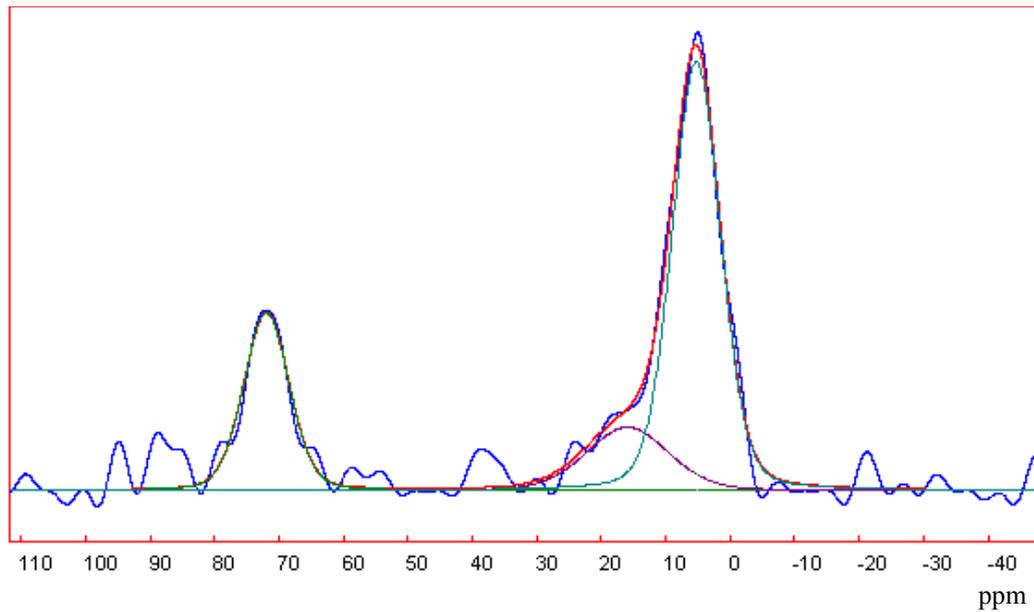


Fig. 2 ^{27}Al MAS NMR spectrum of bituminous coal altered through natural oxidation at temperature below 150 °C. Positions [ppm]: 71.93 (peak area 23.65 %); 15.94 (15.32 %); 5.22 (61.03 %).