Effect of Calcium on the Catalysis of Nickel in the Production of Crystallized Carbon from Lignocresol for Electromagnetic Shielding

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Char with turbostratic structure of carbon (T-component) that could afford a practical electromagnetic shielding capacity at 50–800 MHz was produced from lignocresol added with nickel and calcium by its carbonization at 900 °C, although the addition of nickel alone gave amorphous carbon. This lignin char exceeded the corresponding char obtained from acid-demineralized alkali lignin in the shielding capacity. The formation of T-component can be accounted for by the promotion action of calcium to prevent nickel catalyst from agglomeration.

Wood and its components, such as cellulose and lignin, are believed to be unsuitable raw materials for crystallized carbon. This is because wood-derived carbon is a typical nongraphitizing or soft carbon. However, graphitic carbon was obtained by carbonizing wood at about 2000 °C[1] under 49 MPa.[2] Carbon fiber also can be made from rayon[3] and modified lignins[4,5] through heat treatment at above 2000 °C. These results disprove the evaluation of woody resources, but according to our opinion, a great problem lies in the operation conditions similar to those used for fossil carbonaceous materials. Another problem is that only graphite has been directed as the objective. In such ways, wood resources containing a large amount of oxygen will never be able to compete successfully with petroleum and coal with much less oxygen. Thus carbonization at lower temperature and/or pressure to produce other functional carbons having practical use than graphite is desired for wide utilization of woody materials as the precursors. Recently Suzuki, one of the authors, reported effective formation of carbon with turbostratic structure (T-component) from wood added with nickel by 900 °C-carbonization at ordinary pressure to afford the resulting char practical electromagnetic shielding (EMS) capacity (over 30 dB[6]) at 50–800 MHz.[7] The good capacity of EMS can be explained by adequate electro-conductivity of T-component with regular stack layers of carbon basal plane. It is also to be emphasized that the metal loading required for char was only 2 wt% (equivalent to about 0.5 wt% for raw wood). In this study, the nickel-catalyzed carbonization with the same purpose was applied to lignocresol (LC) that is a modified lignin recovered from wood by using sulfuric acid and *p*-cresol[8,9] and now gains much attention as a promising functional polymers material[10] because of the unique structure and properties. For comparision, acid-demineralized commercial alkali lignin (DAL) was used. Results obtained disclosed what was critical for producing char with T-component usable as EMS.

LC used as the raw material was that obtained from Hinoki cypress by two step process II.[8,10] DAL was prepared by soaking a commercial alkali lignin in 1 M HCl with stirring at room temperature for 24 h and then washing exhaustively with distilled water. The demineralization of alkali lignin was done for avoiding the influence of the coexistent mineral matter (about 15 wt%) on the catalysis of nickel as much as possible. Ash content (incombustible residue at 600 °C) for LC and DAL was <0.1 and 1.4 wt%, respectively. In DAL, calcium that is relevant to the later discussion was negligibly contained (the percentage in ash was <1 wt%). As the precursor of nickel catalyst, $(CH_3COO)_2Ni\cdot4H_2O$ was loaded alone or together with $(CH_3COO)_2Ca\cdot H_2O$ onto both lignins by mixing the solutions. The aim of coloading with calcium is described later. Each lignin dissolved in THF was mixed with an aqueous solution of either nickel or nickel and calcium in a rotary evaporator at 25–30 °C and 20–30 kPa. Calcium alone also was added. After vacuum drying at 50 °C, individual lignin sample (20–30 g) packed in a stainless steel vertical reactor was electrically heated in a flow of nitrogen at 900 °C for 1 h. For char obtained, X-ray diffraction (XRD) and EMS capacity measurements were made after weighing, in addition to the determination of nickel and calcium. Char yield was given in a dry, ash- and additives-free basis. In XRD, the crystal structure of carbon was evaluated in the usual manner from the profile obtained by Cu Kα radiation. For EMS capacity, shielding effectiveness (S.E.) was measured in the range of 50–800 MHz for a disk molded in a vessel after mixing char with epoxy resin. The detailed procedures are given elsewhere.[7] Both metals in char were determined by atomic absorption analysis for the HNO_3–HCl solution of ash, and they indicated loading amounts. In connection with the coloading of calcium, additional experiment using wood (larch) with and without acid-demineralization was made in the same manner as above. Ash in larch was 0.2 and <0.1 wt% before and after the demineralization, respectively, and calcium made up about 40% of ash for raw larch.

The addition of nickel alone to LC gave no T-component, even when it was increased up to 10% and more, although char yield greatly increased (24.9 and 35.6% for none and Ni 9.9%, respectively) in agreement with previous wood carbonization.[7] This was also the case with DAL, and yields of none- and Ni 11.2%-chars were 40.2 and 46.7%, respectively. It is evident from these situations that nickel favored the chemical process of charring, but could not facilitate rather physical steps to form crystallized carbon in such a generally accepted way that non-crystalline carbon dissolves into the metal followed by re-deposition on the surface. To our knowledge, no effective means have been proposed thus far as to how the crystallization of carbon can be realized by catalyst without losing the activity against chemical reactions. However, the size of catalyst particles is likely to have great influence on the growth of the stack layer of

carbon basal plane.[11] Suzuki described that as the method of nickel addition, wet mixing was more effective than dry mixing in the production of T-component.[7] It is thus presumed that high dispersion of nickel in the working state will be a key to development of the crystal structure of carbon. In low temperature (<700 °C) hydrogasification of nickel-loaded wood char, the presence of calcium compounds that are transformed into the oxide or carbonate by heating in nitrogen can prevent the catalyst from agglomeration so as to keep the high activity.[12] According to this finding, coloading with calcium acetate was tried in expectation of such effect on nickel catalyst, although the temperature is different. As shown by XRD profiles in Figure 1.A, it permitted LC char to produce a relatively sharp peak at 26° assigned to T-component. The formation of T-component was also observed for DAL char by a similar coloading (Figure 1.B). The promotion action of calcium was confirmed by the fact that its single loading, similarly to none-loading, gave amorphous carbon. The difference from wood for which foreign calcium was unnecessary[7] can be understood by the presence of this metal as a major inherent mineral component in the substrate. Actually, char prepared from acid-demineralized larch with impregnated nickel gave no crystallized carbon, whereas T-component was produced from nickel-impregnated raw larch, as can be seen from Figure 2. The crystallization of carbon in both lignin chars induced a considerable decrease of the yield (28.6 and 32.5% for LC and DAL chars containing nickel and calcium, respectively)
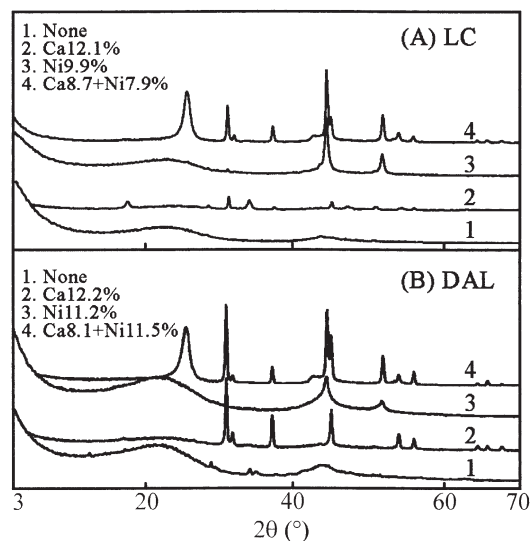

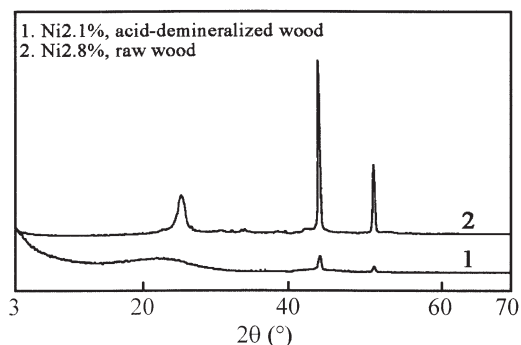**Figure 1.** XRD profiles of (A) LC chars and (B) DAL chars with various additives.

Figure 2. XRD profiles of nickel-loaded chars from raw and acid-demineralized woods.

Table 1. L_c, d_{002}, yield, and S.E. for various lignin chars

Lignin	Additives	L_c (Å)	d_{002} (Å)	Yield[a] (wt%)	S.E.[b] (dB)
LC	None	<10	3.81	24.9	18.9
	Ni9.9%	<10	3.78	35.6	24.0
	Ca12.1%	<10	3.86	35.4	16.2
	Ni8.7+Ca7.9%	167	3.37	28.6	37.8
DAL	None	<10	3.99	40.2	6.2
	Ni11.2%	<10	3.97	46.7	16.5
	Ca12.2%	<10	4.00	45.3	6.6
	Ni8.1+Ca10.5%	108	3.41	32.5	30.9

[a]Dry ash-free, additives-free basis. [b]Value at 800 MHz.

Ni species + Ca species $\longrightarrow$ (NiO)x · (CaO)y $\longrightarrow$ Fine Ni metal (active)
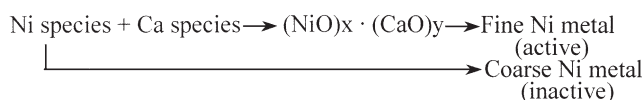$\longrightarrow$ Coarse Ni metal (inactive)

Figure 3. Proposed action of calcium species on nickel species.

that implies the facilitation of gasification. The coloading with calcium thus raised as well the activity of nickel against the co-current chemical reaction. EMS capacity for LC char with both nickel and calcium, as well as DAL char, could surpass 30 dB at any frequency. This demonstrated successful production of crystallized carbon usable for EMS from both lignins, although nickel loading was larger compared to wood. Less amount of nickel required for wood will suggest that better dispersion of the catalyst particles can be achieved in nonartificial wood than in isolated lignin denatured to some extent. A similar interpretation will hold for the difference between inherent calcium and foreign calcium: the former in wood that probably distributes more homogeneously can produce greater effect with a smaller quantity compared to the latter added to lignin. In Table 1, S.E. at 800 MHz that was the lowest in the whole frequency range for all of chars was listed together with L_c and d_{002}. Nickel alone gave larger S.E. than none and calcium alone, chiefly due to metallic nickel (recognized by XRD peaks at 44 and 51°) existing as electro-conductive component in char. Even if the contribution is significant, there is no doubt that a marked increase of L_c with diminution of d_{002} resulted from the formation of T-component was a dominant factor in bringing a practical level of EMS capacity to lignin char. The superiority of LC char to DAL char in the capacity, though the yield was reversed, will give evidence of relatively high suitability of LC as the raw material for converting into T-component. As for the promotion by calcium for nickel, the following mechanism involving the formation of a certain double oxide of nickel and calcium (Figure 3) can be proposed from Ref. 12 and its validity is now being examined.

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