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THE TRIPLET DIMER OF M-DINITROBENZENE ANION RADICALS ADSORBED ON MAGNESIUM OXIDE

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The formation of the triplet state m-dinitrobenzene anion radical dimer adsorbed on magnesium oxide was observed at room temperature by means of visible and electron spin resonance spectroscopies. The amount of formed dimers could be controlled by pre-heat-treatment time of the oxide and remarkably decreased on adsorption after the calcination in air.

The formation and stabilization of negative radical ions from aromatic nitro compounds on the surface of MgO by electron transfer process are well known, but the dimerization of nitro-radical ions on the surface was not noticed.^{1,2)} In this communication, the author wishes to report about the dimerization of m-dinitrobenzene anion radicals adsorbed on the surface of MgO with a variety of pre-heat-treatment time.

For visible spectral measurement, $Mg(OH)_2$ powder was pressed into thin wafer, and evacuated at 900°C for 1 hr. Visible spectra of m-dinitrobenzene adsorbed on MgO from benzene solution are shown in Fig.1. The observed spectrum has two absorption maxima at 570 and 690 nm. The peak at 570 nm corresponds to the absorption band of anion radical of nitro aromatic compound,3) but the 690 nm band has not been reported. When dinitrobenzene was adsorbed on MgO calcined in vacuum at 900°C for 1 hr, the main peak was observed at 690 nm. This evacuated MgO was further ignited in air at 900°C, and dinitrobenzene adsorbed on it at room temperature. Then, the 690 nm band decreased and the 570 nm band appeared distinctly. In the case of MgO ignited in air at 900°C for 3 hr and over, the 690 nm band disappeared completely and only the 570 nm band was observed.

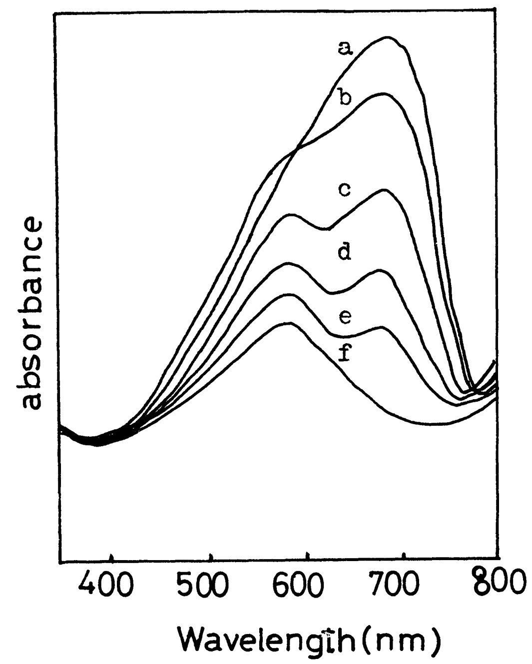

Fig.1.
Visible absorption spectra of m-dinitrobenzene adsorbed on MgO prepared from decomposition of $Mg(OH)_2$ in vacuum at 900°C and further ignited in air at 900°C. The time of ignition in air was (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1, (f) 3 hr

On the other hand, m-dinitrobenzene adsorbed on MgO gives the intense ESR signal at g=2.003 which has been attributed to the dinitrobenzene radical anion.1) But in addition to this signal, a weak signal at the half field stren th of g=2 region signal was observed. This g=4 region signal is the triplet state signal characteristic of a two spin system. This triplet signal was observed correspondingly along with the 690 nm visible absorption band. Those facts indicate that the pair of nearest neighboring radical anions on the surface of MgO dimerized to form biradical in triplet state at room temperature.

The site of anion radical formation was supposed to be the weakly coordinated O^{2-} ion which is thought to be formed during the dehydration of $Mg(OH)_2$ at high temperature ignition by Che et al.2) When MgO was ignited in air, the unstable surface formed by dehydration process became stable and the weakly coordinated O^{2-} ions were stabilized to normal lattice O^{2-} ions. It is therefore supposed that the nearest neighboring pairs of radical forming sites diminished and only isolated monomer radicals were observed.

References

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