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UNUSUALLY STRONG BASIC SITES AS ACTIVE SITES FOR CIS-TRANS INTERCONVERSION OF 2-BUTENE ON CaO

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A good correlation was found between the amount of NO_2^{2-} formed by adsorption of NO on CaO and the rate of cis-trans interconversion of 2-butene. The cis-trans isomerization which occurred very rapidly over CaO evacuated at 700-900°C was inhibited by adsorption of NO, whereas the double bond isomerization was not. Active sites for the cis-trans interconversion was ascribed to unusually strong basic sites.

Alkaline earth metal oxides are known to show a remarkable catalytic activity for the double bond isomerization of 1-butene and the active sites are considered to be basic.1-5) However, the active sites for the cis-trans isomerization of 2-butene is not fully understood on these oxides. In this communication, we wish to report that the cis-trans isomerization is very rapid over CaO evacuated at 700-900°C and the active sites are unusually strong basic sites on the basis of adsorption experiment of nitric oxide on CaO.

Calcium oxide was prepared by evacuation of calcium carbonate (Merck & Co. Inc., guaranteed reagent) at various temperatures for 2 hr. The reaction of cis-2-butene was carried out at 30°C in a circulation system having a volume of 1.4 l, the pressure of cis-2-butene being 40 mmHg. Butene gas was purified by passing through molecular sieves 4A maintained at -78°C. Esr spectra were recorded at room temperature with a JEOL JES-3X spectrometer.

The change of isomerization rate of cis-2-butene with evacuation temperature is shown in Fig. 1. The selectivity (the ratio of trans-2-butene to 1-butene) at the initial stage of the isomerization of cis-2-butene goes up to more than 5 on CaO evacuated at 700-900°C. The cis-trans interconversion which occurs rapidly is in marked contrast to the fact that the double bond migration occurs in preference to the cis-trans interconversion on CaO evacuated at 500-600°C.

When NO was adsorbed on CaO at room temperature, a triplet unsymmetrical esr signal was observed. The spectrum was shown in Fig. 2. The change in the signal intensity with evacuation temperature correlated very closely with that of the cis-trans isomerization rate (Fig. 1).

The esr signal of NO adsorbed on CaO was almost the same as that of NO adsorbed on MgO or ZnO which was assigned by Lunsford to NO_2^{2-} formed by adsorption of NO on the surface O^{2-} ion adjacent to cation vacancy.6) Since NO dose not produce NO_2^{2-} on the usual basic sites such as O^{2-} on CaO calcined in air at 900°C, the site formed by evacuation is thought to have a strong basic character.

The cis-trans interconversion was strongly poisoned by NO, whereas the double bond isomerization to 1-butene was almost unchanged. The former was also poisoned by diethylamine, but hardly poisoned by triethylamine. This indicates that trans isomer is formed on the strong basic O^{2-} which is poisoned by the dissociation of amino proton of diethylamine on it.

From these facts, it is concluded that the cis-trans interconversion occurs on unusually strong basic sites which appear on evacuation at 700-900°C and produce NO_2^{2-} when NO is adsorbed, while the double bond migration takes place on usual basic sites which appear on evacuation at 500-600°C and are not sufficiently strong to produce NO_2^{2-} from NO.

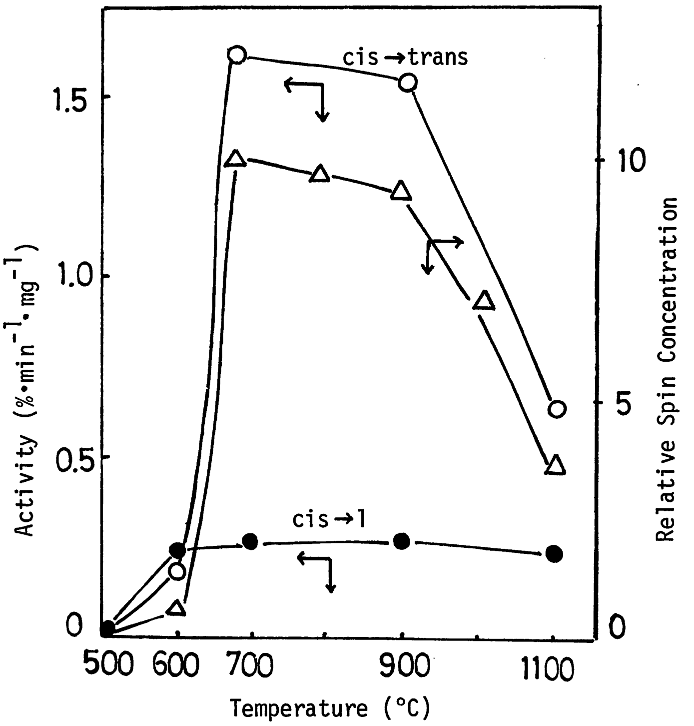

Fig. 1. Evacuation temperature dependences of the activity of cis-2-butene isomerization and the spin concentration of NO_2^{2-} on CaO.

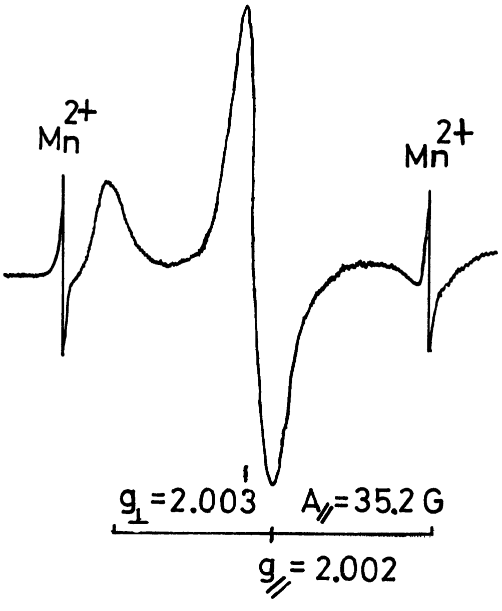

Fig. 2. ESR spectrum of NO adsorbed on CaO evacuated at 700°C.

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