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Characterization of Catalyst for Coal Liquefaction. Exchange of Hydrogen Attached to Condensed Aromatics with Deuterium in Heavy Water over Catalyst

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Synopsis. The H–D exchange reaction of hydrogen atoms attached to condensed aromatics with deuterium atoms in D_2O over catalyst for coal liquefaction was studied by means of D-NMR. MoO_3/ZrO_2, MoO_3/SiO_2, Fe_2O_3-SO_4^{2-}, $SbCl_3$ and $ZnCl_2$ showed a significant catalytic activity for the exchange reaction. The H–D exchange ability was discussed in terms of the acidic properties and concentration of Mo^{5+} over supports for coal liquefaction catalysts.

There is a continuing interest in the surface properties of catalyst, particularly in their acid strength, the number and nature of the active sites, and the question of how the activity at these sites can be controled by chemical or physical treatment.

Little detailed information is available about catalytic activity of catalysts at high temperatures. The effect of the surface properties of catalysts on their role in coal liquefaction remains unclear. Our previous ESR study in the anthracene/$ZnCl_2$/H_2O system[1,2] suggested that an exchange reaction takes place between the hydrogen atoms in H_2O which is adsorbed on $ZnCl_2$ and the hydrogen atoms in anthracene (which is a model compound of coal). Furthermore, the hydrogen transfer reaction is known to play an important role in coal liquefaction and hydrogen exchange is one of these hydrogen transfer reactions. Thus the object of this study, as a model reaction for coal liquefaction, is to examine the H–D exchange reaction between the hydrogen atoms attached to condensed aromatics and the deuterium atoms in D_2O over metal oxide and metal chloride catalysts at high temperature by means of D-NMR.

Experimental

The metal oxide catalysts selected were as follows: MoO_3-SiO_2, MoO_3-ZrO_2, MoO_3-MgO, Fe_2O_3 and Fe_2O_3-SO_4^{2-}. These catalysts were prepared and supplied by Drs. K. Tanabe and H. Hattori, the Faculty of Science, Hokkaido University.[3] $ZnCl_2$ and $SbCl_3$ of guaranteed grade, as Lewis acid catalysts, were used for the experiments without further purification. Anthracene of G. R. grade was used as a model compound of coal.

Anthracene, catalyst and D_2O (molar ratio; 1:1:10) were mixed and sealed in a Pyrex tube reactor (10 mm diam× 500 mm) and heated in a vertical i.r. image furnace at a given temperature for a given time and then rapidly quenched. The heating rate was 10 K/min. The product was extracted with $CHCl_3$ in a ultrasonic vibrater. D-NMR spectra of the $CHCl_3$ soluble materials were obtained at room temperature using a Varian XL-200 spectrometer.

The ESR spectra of Mo^{5+} ions in the Mo-containing catalysts were obtained using a Varian E109 spectrometer employing 100 kHz modulation and a nominal operating frequency of 9 GHz.

Results and Discussion

Molybdenum Containing Catalyst Systems. Several metal oxide catalysts with different acidities were tested with respect to the H–D exchange reaction. The D-NMR spectrum of the product from the anthracene/MoO_3-ZrO_2/D_2O system which was allowed to react at 573 K for 15 min is shown in Fig. 1a. It is apparent that the H–D exchange reaction takes place over an acidic catalyst, MoO_3-ZrO_2. Assignment of deuterium atoms attached to anthracene is made by comparison with the proton chemical shifts of anthracene.[4] A similar spectrum was observed when MoO_3-SiO_2 was used. On the other hand, no significant exchange reaction was observed for the basic catalyst MoO_3-MgO, as shown in Fig. 1b.

The fact that MoO_3-ZrO_2 and MoO_3-SiO_2 are more active than MoO_3-MgO for the H–D exchange reaction might be explained by a great ability of ZrO_2 and SiO_2 to reduce MoO_3 to form lower bonding stages of Mo, such active species as Mo^{5+}, Mo^{4+} and so on.[5] Since Mo^{5+} is a paramagnetic

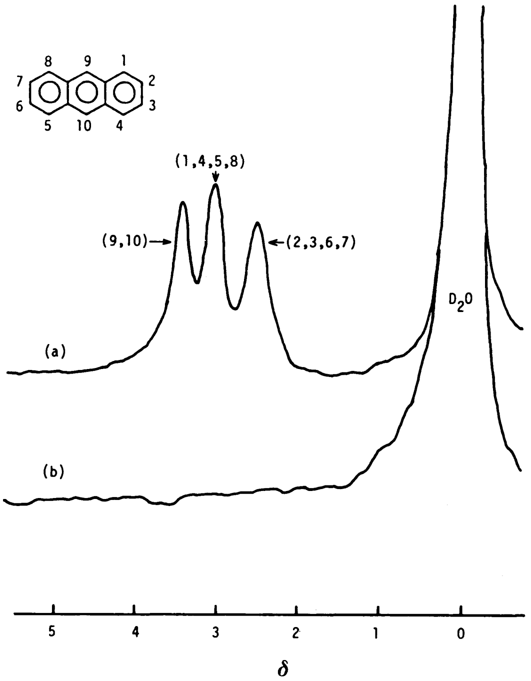

Fig. 1. D-NMR spectra of products from Anthracene/Catalyst/D_2O system.
(a): Anthracene/MoO_3-ZrO_2/D_2O 573 K, 15 min,
(b): Anthracene/MoO_3-MgO/D_2O 573 K, 15 min.

Table 1. Catalytic activity of MoO_3 over metal oxides for H-D exchange reaction on anthracene and their Mo^{5+} concentration

Catalyst	Exchanged product (%)	Mo^{5+} spin concentration (spins/g)
MoO_3/ZrO_2	8.3	2.52×10^{19}
MoO_3/SiO_2	8.2	1.42×10^{19}
MoO_3/MgO	0.0	0.77×10^{19}

species, it is detectable by ESR spectroscopy.[2] Table 1 shows the correlation between the propotion of the deuterium atoms incorporated in anthracene by the H-D exchange reaction and the Mo^{5+} spin concentrations in Mo-containing catalysts. The presence of reduced form of Mo species may be responsible for the H-D exchange reaction.

Iron Oxide Catalyst Systems. Fe_2O_3 is one of the most promising catalysts for the coal liquefaction process, because iron oxides and iron ore are disposable catalysts. One modification of Fe_2O_3 catalyst was attempted by including SO_4^{2-} ions.[3,6] The Fe_2O_3-SO_4^{2-} catalyst showed higher activity and selectivity for the liquefaction of both Akabira coal and Taiheiyo coal than those of pure Fe_2O_3 catalyst.[6]

The effect of SO_4^{2-} ion in Fe_2O_3 catalyst on coal liquefaction may be partly due to the increase in acid strength of catalyst. Therefore, it can be expected that SO_4^{2-} ion in Fe_2O_3 catalyst has an influence on the H-D exchange reaction of the anthracene/Fe_2O_3/D_2O system. In fact, evidence of such influence on the exchange reaction was obtained from the D-NMR spectrum of the product from the Fe_2O_3-SO_4^{2-}/anthracene/D_2O system which was allowed to react at 573 K for 15 min. On the other hand, any evidence of the H-D exchange reaction could not be obtained for pure Fe_2O_3 catalyst system.

Lewis Acid Catalyst Systems. Available evidence about metal chloride catalysts[7] suggests that Lewis acids first convert to Brönsted acids in the presence of water. Therefore, one can easily invoke a direct adduct of Lewis acid and anthracene as the intermediate allowing the H-D exchange. This consideration was confirmed directly by means of D-NMR for Lewis acid catalysts ($SbCl_3$, $ZnCl_2$) with anthracene.

The D-NMR spectrum of the product from the anthracene/$ZnCl_2$/D_2O system which was allowed to react at 483 K for 15 min is shown in Fig. 2a. It can be seen that the deuterium atoms are especially concentrated at the (9, 10) positions of anthracene. Fig. 2b indicates that a significant H-D exchange reaction also takes place over $SbCl_3$ catalyst, mainly at the (9, 10) and (1, 4, 5, 8) positions of the nuclei of anthracene. The deuterium distribution differs clearly from the case of the $ZnCl_2$ catalyst.

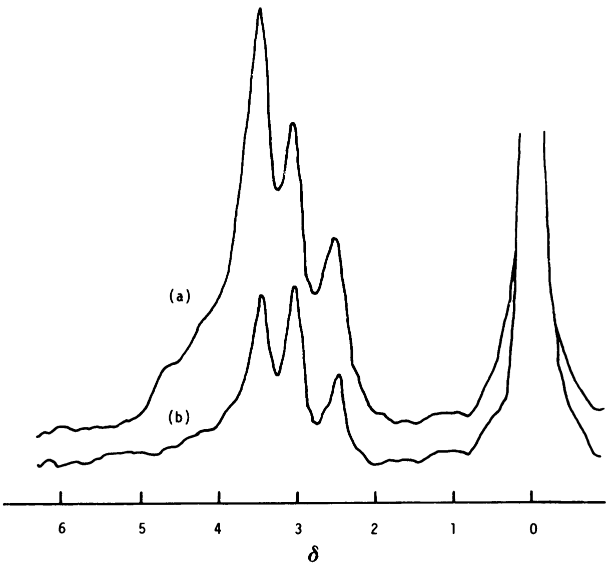

Fig. 2. D-NMR spectra of products from Anthracene/Lewis acid catalyst/D_2O system.
(a): Anthracene/$ZnCl_2$/D_2O 483 K, 15 min, (b): Anthracene/$SbCl_3$/D_2O 418 K, 15 min.

The D-NMR investigation of the H-D exchange reaction was extended to various polynuclear aromatics such as perylene, pyrene, phenathrene, benz[*a*]anthracene and naphthacene. Among the hydrocarbons so far tested, phenanthrene had the highest degree of H-D exchange reaction with respect to $ZnCl_2$ catalyst.

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