

## STRUCTURES AND CATALYTIC ACTIVITIES OF $C_{60}M_x$ AND $C_{70}M_x$ ( $M=Cs, K, Na$ ) for $H_2-D_2$ REACTION AND OLEFIN HYDROGENATION

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Summary: EDA (Electron Donor-Acceptor) complexes of fullerenes such as  $C_{60}$  and  $C_{70}$  with alkali metals ( $M=Cs, K$  and  $Na$ ) were studied on their structural and catalytic behaviors in dissociative activation of molecular hydrogen. It was found that  $C_{70}Cs_x$  ( $x=6$ ) exhibits higher activities for  $H_2-D_2$  reaction at 273K and ethene hydrogenation at 373K by factor of 5-50 times rather than  $C_{60}Cs_x$ . For the sorts of alkali metals as electron donors, catalytic activities of  $C_{60}M_x$  ( $M=Cs, K$  and  $Na$ ) in  $H_2-D_2$  reaction decrease in the following order:  $Cs \gg K \gg Na$ . IR studies has been conducted in chemisorption of CO and  $H_2$  on  $C_{60}Cs_x$ .

### 1. Introduction

Since the initial discovery and subsequent development of the large-scale synthesis of fullerenes such as  $C_{60}$  and  $C_{70}$ , they have been of fundamental interest[1] in chemically-modified fullerenes bound with metals in the interior and high-temperature superconductors[2]. On the other hand, they became a new type of  $\pi$ -conjugated carbon clusters, which could serve an electron acceptor molecule in forming charge-transfer complexes with metals such as alkali metals as an electron donor. We have explored various catalytic reactions known to activate molecules such as  $H_2$ , CO and  $CH_4$  on the stoichiometric EDA complexes of various aromatic hydrocarbons, e.g., anthracene and tetracene, including graphite as electron-acceptors with electron-donors such as alkali metals[3-5]. In this study, we have used fullerenes such as  $C_{60}$  and  $C_{70}$  in forming the EDA complexes with alkali metals and studied catalytic behaviors of alkali-metal fullerenes,  $C_{60}M_x$  and  $C_{70}M_x$  ( $M=Cs, K$  and  $Na$ ) in  $H_2-D_2$  reaction and olefin hydrogenation in conjunction with their structural and electronic properties.

### 2. Experimental

The fullerenes, high purity(99.7%)  $C_{60}$  and  $C_{70}$  powders(purchased from Scientific Lab.) were obtained by extraction from toluene/ $CS_2$  solution through a silica-column. The purity was checked by HP-liquid gc using  $\mu$ -Bondasphere C18 column(Waters Chromatography: 3.9X150 mm). The  $C_{60}$  or  $C_{70}$  powder(30-60 mg) was heated in vacuo at 673K for 7 days with  $Cs, K$  or  $Na$  which was distilled in a sealed tube, resulting in the greenish-black solids,  $C_{60}M_x$  and  $C_{70}M_x$  ( $M=Cs, K$  and  $Na$ , where  $x$  denotes the molar ratio of carbon cluster and alkali metal). The IR studies for  $C_{60}Cs_x$  films were performed with a specially designed

pyrex-glass cell, which allowed the treatment in vacuo and measurement in chemisorption of gas molecules. The IR spectra were recorded on a Shimadzu FTIR-8100 single beam spectrometer with 25-100 time scans at resolution of 2  $\text{cm}^{-1}$ . The  $\text{H}_2$ - $\text{D}_2$  exchange reaction and olefin hydrogenation were performed in a closed circulating pyrex-glass reactor (ca. 250 ml) and the products were analyzed by QP mass spectrometer (ANELVA QP-100) and TCD gc using columns of DMF/alumina and porapak Q.

### 3. Results and Discussion

#### 3.1. $\text{H}_2$ - $\text{D}_2$ Reaction and Ethene Hydrogenation on $\text{C}_{60}\text{M}_x$ and $\text{C}_{70}\text{M}_x$ ( $\text{M}=\text{Cs}, \text{K}$ and $\text{Na}$ )

The  $\text{C}_{60}\text{Cs}_x$  and  $\text{C}_{70}\text{Cs}_x$  ( $x=6$ ) powders (ca. 50 mg) were prepared by heating a mixture of  $\text{C}_{60}$  (or  $\text{C}_{70}$ ) and Cs metal in a sealed tube. The resulting EDA complex was transferred and charged in vacuo into a pyrex-glass reactor equipped to a closed circulating system. When a  $\text{H}_2$ + $\text{D}_2$  (1:1 v/v, total pressure 200 torr) mixture was admitted onto the  $\text{C}_{60}\text{Cs}_x$  (or  $\text{C}_{70}\text{Cs}_x$ ) it was found that the hydrogen exchange reaction proceeded rapidly to form HD even at lower temperatures of 173-273K, as shown in Fig.1. While, the exchange reaction occurred neither on  $\text{C}_{60}$  (or  $\text{C}_{70}$ ) film (60 mg) nor on Cs metal (200 mg) deposited in a pyrex-glass reactor under the similar reaction conditions up to above 373K. The specific activities (TOF=Turnover frequency on carbon cluster base) of  $\text{C}_{70}\text{Cs}_x$  in  $\text{H}_2$ - $\text{D}_2$  exchange reaction are comparable with those on noble metals such as Pt and Rh. The catalytic activities of  $\text{C}_{60}\text{Cs}_x$  and  $\text{C}_{70}\text{Cs}_x$  completely disappeared in exposure to  $\text{O}_2$  (100 torr) at 300K due to destruction of charge-transfer complexation.

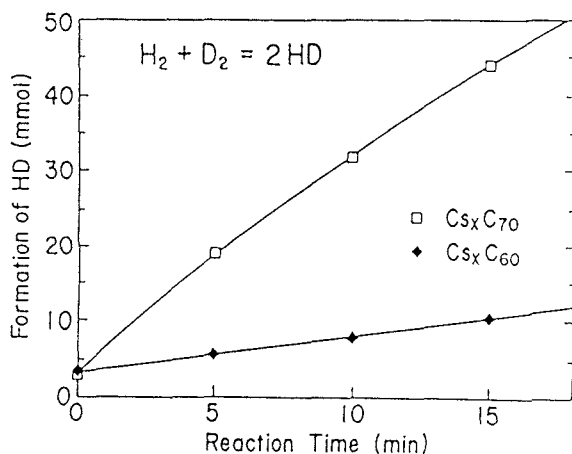


Fig. 1.  $\text{H}_2$ - $\text{D}_2$  Reaction on  $\text{C}_{60}\text{Cs}_x$  and  $\text{C}_{70}\text{Cs}_x$  ( $x=6$ ) at 273K,  $P(\text{H}_2)=P(\text{D}_2)=11\text{kPa}$ .

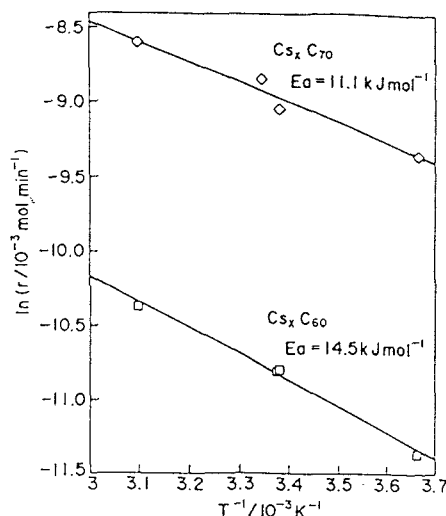


Fig. 2. Arrhenius Plots of Rates in  $\text{H}_2$ - $\text{D}_2$  reaction on  $\text{C}_{60}\text{Cs}_x$  and  $\text{C}_{70}\text{Cs}_x$ .

Thus, similarly as it has been reported on the EDA complexes of aromatic hydrocarbons and graphite with alkali metals [3-5], it is suggested that the

fullerenes, e.g., C<sub>60</sub> and C<sub>70</sub> become catalytically active for the H<sub>2</sub>-D<sub>2</sub> reaction in forming the charge-transfer complexation with alkali metals. The C<sub>70</sub>Cs<sub>x</sub> exhibits higher activities (E<sub>a</sub>=11.1 KJ/mole) for the catalytic reaction by 5 times at 273K rather than those of C<sub>60</sub>Cs<sub>x</sub> (E<sub>a</sub>=14.5 KJ/mole) under the similar reaction conditions (see Fig.2). The results imply that C<sub>70</sub> EDA complex provides higher active sites on cluster in charge-transfer complexation with alkali cation to dissociate molecular hydrogen, compared with C<sub>60</sub> core. For the sorts of alkali metals as electron donors, the catalytic activities of C<sub>60</sub>M<sub>x</sub> (m=Cs, K and Na) in H<sub>2</sub>-D<sub>2</sub> reaction drastically decrease in the following order: Cs>>> K >> Na (Table 1) in line with that of alkali cation size in fullerene-alkali metal adducts.

Table 1. Relative Activities of C<sub>60</sub>M<sub>x</sub> and C<sub>70</sub>M<sub>x</sub> (M=Cs, K, Na) in H<sub>2</sub>-D<sub>2</sub> Exchange and Ethene Hydrogenation Reactions.

Complex	HD Formation <sup>a)</sup> H <sub>2</sub> + D <sub>2</sub> = 2HD	Ethane Formation <sup>b)</sup> (C <sub>2</sub> H <sub>4</sub> +H <sub>2</sub> =C <sub>2</sub> H <sub>6</sub> )	Ion Radius <sup>c)</sup> M <sup>+</sup> (Å)
C <sub>70</sub> Cs <sub>x</sub>	10	0.45	1.70
C <sub>60</sub> Cs <sub>x</sub>	2	0.008	1.70
C <sub>60</sub> K <sub>x</sub>	0.08	-	1.33
C <sub>60</sub> Na <sub>x</sub>	0.001	-	0.97

a) Rate(TOF); P(H<sub>2</sub>)=P(D<sub>2</sub>)=50 torr, at 300K: mol/mol(cluster)/min b)Rate(TOF); P(C<sub>2</sub>H<sub>4</sub>)=P(H<sub>2</sub>)=100 torr, 373K c) Ion radius of alkali metal

The hydrogenation of ethene proceeded catalytically on the C<sub>70</sub>Cs<sub>x</sub> and C<sub>60</sub>Cs<sub>x</sub> (x=6) at 293-373K, as shown in Table 1. It is worthy to note that C<sub>70</sub>Cs<sub>x</sub> is much more active (ca 50 times) for ethylene hydrogenation rather than C<sub>60</sub>Cs<sub>x</sub>, possibly due to stronger interreaction of ethene on C<sub>70</sub>Cs<sub>x</sub>.

### 3.2. IR study in chemisorption of H<sub>2</sub> and CO on C<sub>60</sub>Cs<sub>x</sub> film.

The transmission FTIR studies have been conducted using a pyrex-glass cell as depicted in Fig.4, where C<sub>60</sub> is evaporated on KBr disc, followed with the exposure to Cs vapor in vacuum. The C<sub>60</sub> film gives four intense peaks at 1429, 1183, 577 and 526 cm<sup>-1</sup> (Fig.3a) due to the stretching and deformation modes of C=C and C-C in the cluster framework[6]. It is interesting to find that the IR bands at 1429 and 576 cm<sup>-1</sup> for C<sub>60</sub> are broaden and shifted to lower frequencies at 1340 and 566 cm<sup>-1</sup>, respectively. Furthermore, those at 1183 and 526 cm<sup>-1</sup> in C<sub>60</sub> are strongly suppressed due to charge-transfer complexation with Cs (see Fig.3b). When H<sub>2</sub> (or D<sub>2</sub>) (100 torr) was admitted onto the resulting

$C_{60}Cs_x$  film at 300K, no appreciable change of IR spectra(Fig.4a) was observed (with a negligible C-H or C-D bond), although  $H_2$ - $D_2$  reaction occurred to form HD in the gas phase which was monitored by Mass spectroscopy. This suggests that hydrogen is activated on  $C_{60}Cs_x$  without formation of a hydrogenated intermediate  $C_{60}H(D)_y$ . In contrast,  $C_{60}Cs_x$  reacts with CO at 300K(see Fig.4b) to give new bands at 1282(s), 1606(w) and 1433(w)  $cm^{-1}$ , possibly being related to subcarbonyls( $O=C=O$ )<sub>n</sub> attached with  $C_{60}$  framework and Cs.

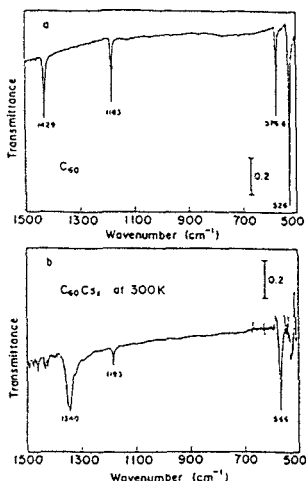


Fig. 3. FTIR Spectra of  $C_{60}$  and  $C_{60}Cs_x$  Films in vacuo at 300K.

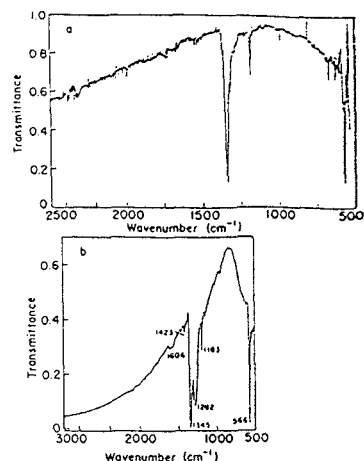


Fig. 4. IR Spectra of  $C_{60}Cs_x$  Film upon admission of  $H_2$  and CO at 300K.

#### 4. Conclusion

The  $C_{60}Cs_x$  and  $C_{70}Cs_x$  ( $x=6$ ) in charge-transfer complexation exhibit remarkable catalytic activities in  $H_2$ - $D_2$  reaction at 173-273K and ethene hydrogenation at 273-373K, whereas fullerenes and Cs metal are inactive alone.  $C_{70}Cs_x$  exhibits higher activities for both catalytic reactions by 5-50 times rather than  $C_{60}Cs_x$ . For the sorts of alkali metals, the catalytic activities of  $C_{60}M_x$  in  $H_2$ - $D_2$  reaction decrease in the following order:  $Cs \gg \gg K \gg Na$ .

#### References

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