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THERMOANALYTICAL STUDIES OF CARBON DEPOSITION ON Pt/Al_2O_3 AND Pt–Sn/Al_2O_3 CATALYSTS FOR DEHYDROGENATION OF BUTANE IN THE PRESENCE OF HYDROGEN

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ABSTRACT

The carbon deposition on Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts in the dehydrogenation of butane in the presence of H_2 was studied by thermogravimetry. It was found that the addition of Sn and alkali metals K and Li markedly improved the anti-coking ability of Pt/Al_2O_3. Coke deposited mainly on the metal surface of Pt/Al_2O_3 and predominantly on the internal surface of the carrier of Pt–Sn/Al_2O_3. After addition of alkali metal, the coke deposit was notably reduced on both the metal surface and the internal surface of the carrier. The amount of coke deposited from isobutane dehydrogenation was far lower than from *n*-butane dehydrogenation; this is because isobutane has a much higher dehydrogenation activity and is easily broken down into small molecules.

INTRODUCTION

The production of olefins by the dehydrogenation of lower alkanes is an important use of oil-field gas and refinery gas. At first, a Pt/Al_2O_3 catalyst was used as it has assured activity and selectivity, but carbon deposits form easily during reactions at high temperature and low H_2 pressure, so that its stability is not good. Later, a high stability Pt–Sn/Al_2O_3 catalyst was developed and gave rise to considerable interest [1,2].

In this work, the carbon deposition on highly dispersed Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts in the process of butane dehydrogenation in the presence of H_2 was studied by thermal analysis. The effects of the addition of a promoter, Sn, and of alkali metals, Li and K, on the carbon deposition were investigated. The location of the carbon deposit and the effect of the promoter on the amount of carbon deposited on different locations were predicted from the burn-off of coke from deactivated catalysts. Finally, the mechanism of coke deposition is discussed with reference to the coking behaviour of the possible olefins (butene-1, butene-2, butadiene, etc.) produced by the dehydrogenation of *n*-butane and isobutane.

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EXPERIMENTAL

Catalyst

The carrier used was γ-Al_2O_3 beads. Pt/Al_2O_3 was prepared by the conventional impregnation method; Pt–Sn/Al_2O_3 was prepared by a complex method. The alkali metals were introduced by impregnating Pt/Al_2O_3 and Pt–Sn/Al_2O_3 with solutions of the relevant nitrates. All the catalysts contained 0.375% Pt.

Reaction gases

The gases used were butane, including *n*-butane and isobutane, and butene, including butene-1, butene-2, butadiene and isobutene.

Carbon deposit measurement

The carbon deposit measurement was performed on a thermobalance of a Shimadzu DT-20B type thermoanalyser. The experimental conditions were as follows: measuring range, 2–5 mg; heating rate, 10 °C min^{-1}; paper speed, 1.25 mm min^{-1}; atmosphere, the above reaction gases together with H_2.

The catalyst was weighed in a quartz basket which was then hung on one end of the balance in the reactor and balanced with weights. The carrier gas was introduced along two routes: one entered the balance box as a gas seal; another brought the reaction gas through the reactor. The catalyst was reduced in H_2 by heating in a temperature-programmed mode up to 500 °C and this temperature was maintained for 1.5 h; then the sample was heated to 580 °C and this temperature was maintained for 30 min. After this, reaction gas was brought to the reactor by the carrier gas. The temperature and the amount of carbon deposit were recorded with a two-pen recorder.

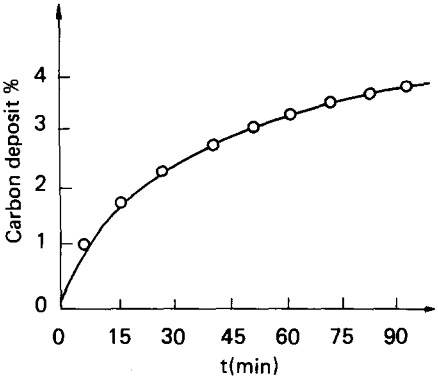
RESULTS AND DISCUSSION

Carbon deposition on Pt/Al_2O_3 catalyst

Figure 1 shows the carbon deposit at constant temperature on Pt/Al_2O_3 catalyst for the dehydrogenation of *n*-butane in H_2. It can be seen that the amount of carbon increases with the increase in reaction time; the increment decreases as the reaction time is prolonged.

The carbon deposit curve can be represented by Voorhies' empirical formula [3]

$$C = K_c t^n \qquad (1)$$



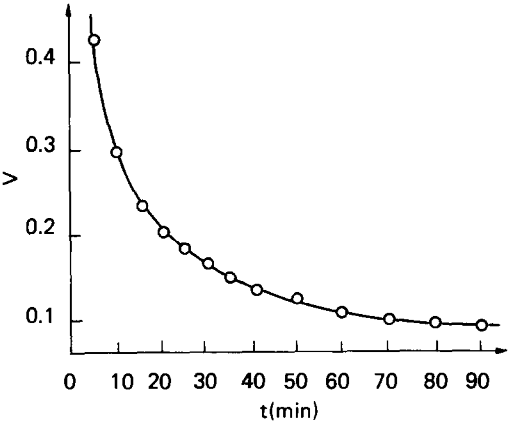


Fig. 1. Carbon deposit of *n*-butane dehydrogenation on Pt/Al_2O_3 vs. reaction time.

Fig. 2. Dependence of rate of carbon deposit on reaction time.

where C is the amount of carbon deposited, K_c is a constant, t is the time of carbon deposit and n is the exponent. The logarithmic form of eqn. (1) is

$$\log C = \log K_c + n \log t \qquad (2)$$

The plot of $\log C$ vs. $\log t$ should be a straight line; the value of n derived from the slope is 0.47, and K_c derived from the intercept is 0.28. Thus the relationship between the carbon deposit and reaction time is

$$C = 0.28 t^{0.47} \qquad (3)$$

Differentiating eqn. (3) gives the rate of carbon deposition

$$dC/dt = 0.13 t^{-0.53} \qquad (4)$$

Figure 2 presents the relationship between the rate of carbon deposition and reaction time. The rate of carbon deposition is very high in the initial reaction stage; then the active site of the metal and the acid centre of the carrier are gradually covered by coke as the reaction continues, and the effective surface of the catalyst decreases so that the rate of carbon deposition drops progressively.

Carbon deposit on $Pt-Sn/Al_2O_3$ catalyst

Figure 3 shows the carbon deposit at constant temperature on $Pt-Sn/Al_2O_3$ catalyst for the dehydrogenation of *n*-butane in H_2. For comparison, Fig. 3 also shows the curve for carbon deposit on Pt/Al_2O_3.

It is clear that the amount of coke on $Pt-Sn/Al_2O_3$ catalyst is lower than that on Pt/Al_2O_3. The effect of Sn on carbon deposition varies with the amount of Sn added. When $Sn/Pt = 2$, carbon deposition is slightly lower, at first, than that on Pt/Al_2O_3 and is more or less the same after 90 min;

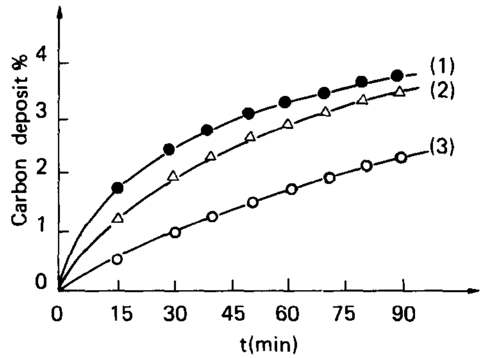


Fig. 3. Carbon deposit of *n*-butane dehydrogenation on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ vs. reaction time. (1) Pt/Al_2O_3; (2) $Pt-Sn/Al_2O_3$ ($Sn/Pt = 2$); (3) $Pt-Sn/Al_2O_3$ ($Sn/Pt = 10$).

when $Sn/Pt = 10$, either the initial carbon deposition tendency or the amount of carbon deposit itself decreases. Some suggest that this is due to the dilution of active metal by inactive metal, and thus the hydrogenolysis and carbon deposition are inhibited; some suggest that Pt and Sn may form a metal cluster, with an electron transfer taking place between Pt and Sn which, therefore, restricts the deep dehydrogenation function of the catalyst and inhibits the formation of carbon deposit. This question has yet to be resolved.

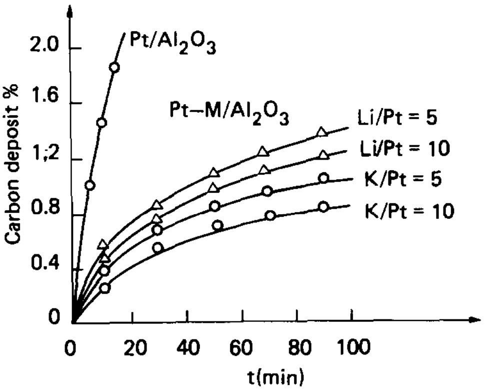
Effect of alkali metals, Li and K, on carbon deposition on Pt/Al_2O_3 catalyst

Polymerization on the acid centre of a carrier plays an important role in the formation of carbon deposit. Reducing the number of acid centres will decrease the carbon deposition. For this reason, addition of an appropriate amount of alkali metal, M, may reduce the number of acid centres of a catalyst, and thus decrease the formation of coke. Figures 4 and 5 show the coke deposit curves of $Pt-M/Al_2O_3$ and $Pt-Sn-M/Al_2O_3$ catalysts respectively for the dehydrogenation of *n*-butane at constant temperature.

It is clear that carbon deposition on the catalyst is greatly decreased by the addition of an alkali metal, the decrement increasing with the increase of the amount of alkali metal introduced. Furthermore, for both $Pt-M/Al_2O_3$ and $Pt-Sn-M/Al_2O_3$, in the case of the same M/Pt atomic ratio or the same amount of alkali metal, the decrease caused by K is more noticeable than that caused by Li. This is attributed to the fact that the alkalinity of K is stronger than that of Li; thus more acid centres of the carrier can be neutralized by K [4–6].

Location of carbon deposit and effect of promoter

The measurement of the carbon deposit shows that for butene-2 the amount of coke on Pt/Al_2O_3 far exceeds that for *n*-butane. In order to



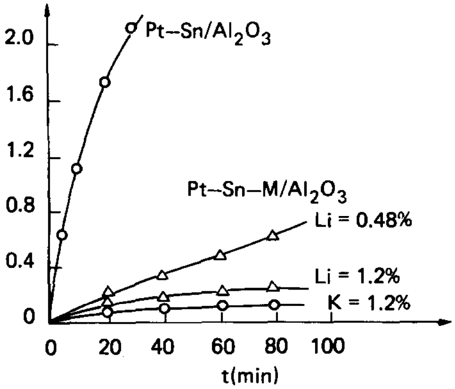


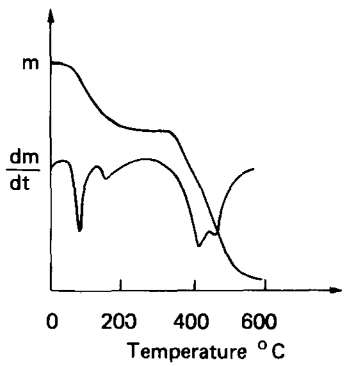
Fig. 4. Carbon deposit of *n*-butane dehydrogenation on Pt–M/Al_2O_3 vs. reaction time.

Fig. 5. Carbon deposit of *n*-butane dehydrogenation on Pt–Sn–M/Al_2O_3 vs. reaction time.

predict the location of carbon deposit, the burn-off behaviour of a coke sample from butene-2 was investigated. Figure 6 presents the TG–DTG curve for the burning off of a coke sample from butene-2 in air.

We can see that there are four peaks in the DTG curve with the corresponding weight loss in the TG curve. The first peak, in the range of 35–155 ° C, is the desorption of surface water; the second peak, in the range of 155–235 ° C, is probably the coke burning off from the external surface of the carrier; the third and fourth overlapping peaks, in the range 350–540 ° C with peak temperatures of 435 and 476 ° C, are the coke burning off from the metal surface and the internal surface of the carrier, respectively [7]. The boundary temperature is about 465 ° C as established by a gaussian distribution graph.

Figure 7 shows the DTG curves of the burning off of coke samples from



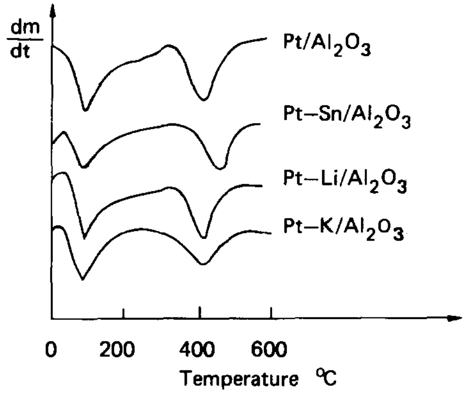


Fig. 6. TG–DTG curves of burning off of coke sample of butene-2 on Pt/Al_2O_3.

Fig. 7. DTG curves of burning off of coke sample of *n*-butane on Pt/Al_2O_3 and Pt–M/Al_2O_3.

TABLE 1

The calculated carbon deposition on the metal surface and the internal surface of carrier

Catalyst	M/Pt	Temperature range for coke burning (°C)	Carbon deposited on metal surface (%)	Carbon deposited on internal surface of carrier (%)
Pt/Al_2O_3	–	355–532	3.6	1.7
$Pt-Sn/Al_2O_3$	Sn/Pt = 2	350–548	1.1	4.0
$Pt-Li/Al_2O_3$	Li/Pt = 5	345–540	1.79	0.65
$Pt-K/Al_2O_3$	K/Pt = 5	355–512	1.51	0.47

n-butane on Pt/Al_2O_3 and $Pt-M/Al_2O_3$ catalysts. On Pt/Al_2O_3, the DTG curve of coke burning-off of *n*-butane is essentially the same as that of butene-2, except that the second peak, the burning-off peak of coke on the external surface of carrier, is no longer present. This may be because the carbon deposit on Pt/Al_2O_3 in the case of *n*-butane is far inferior to the carbon deposit in the case of butene-2. Moreover, in the presence of promoter, the DTG curve of coke burn-off of *n*-butane is essentially the same as that of Pt/Al_2O_3, the only difference being that the peak temperature of the overlapping third and fourth peaks is not clear. The amount of coke deposited on the surface of the metal and the internal surface of the carrier calculated by taking 465 °C on the TG curve as a boundary is given in Table 1.

The results in Table 1 show that for Pt/Al_2O_3 catalyst, the coke deposits mainly on the metal surface and internal surface of the carrier, the amount of coke deposited on the metal surface being twice that on the internal surface of the carrier. For $Pt-Sn/Al_2O_3$ catalyst, the amount of carbon deposited is markedly lower on the metal surface and clearly higher on the internal surface of the carrier; it is possible that introduction of Sn reduces the adsorption ability of the reactant on the Pt surface, and the reactant migrates to the internal surface of the carrier. For $Pt-Li/Al_2O_3$ and $Pt-K/Al_2O_3$ catalysts, the amount of carbon deposited on the metal surface and on the internal surface of the carrier are both lower; the stronger the basicity of the alkali metal, the greater the decrease in the amount. This implies that the neutralization of some acidic functional sites of the metal and acid centres of the carrier by alkali metals causes the simultaneous decrease in the coke deposit on both surfaces.

Carbon deposition mechanism of butane on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$

On the same catalyst and under the same reaction conditions, the initial activities for the dehydrogenation of *n*- and isobutane are about the same; however, the amount of carbon deposited differs greatly (about 3 : 1). The

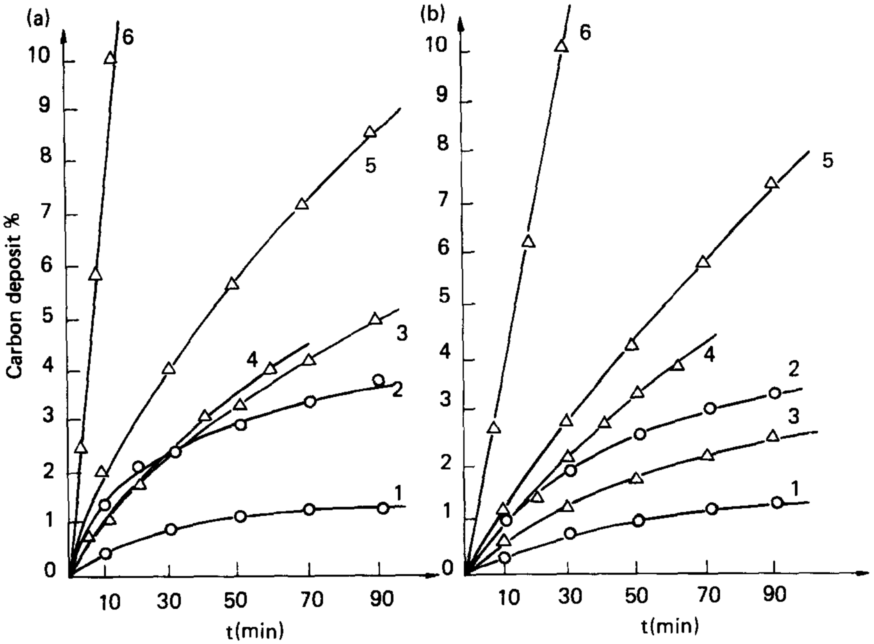


Fig. 8. Carbon deposit of C_4 hydrocarbons on (a) Pt/Al_2O_3 and (b) $Pt-Sn/Al_2O_3$ vs. reaction time. 1, Isobutane; 2, *n*-butane; 3, isobutene; 4, butene-2; 5, butene-1; 6, butadiene.

carbon deposition behaviour of *n*-butane and isobutane and the possible dehydrogenation products (including isobutene, butene-1, butene-2, butadiene and so on) on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalysts were studied in order to elucidate the mechanism of coke deposition. The curves of carbon deposit of the above-mentioned hydrocarbons at constant temperature on Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$ catalysts are given in Fig. 8 which shows that the carbon depositing abilities of Pt/Al_2O_3 catalyst decrease in the following sequence: butadiene > butene-1 > butene-2 > isobutene > *n*-butane > isobutane. Among the C_4 hydrocarbons, the coke depositing ability of olefins is higher than that of alkanes, and that of *n*-butane is higher than that of isobutane. Therefore, butadiene is the most likely precursor in the carbon deposition. Because the dehydrogenation of *n*-butane readily yields olefin, carbon is easily deposited. Because isobutane is dehydrogenated and cracked into small molecules more easily than *n*-butane, the possibility of olefin formation by isobutane dehydrogenation is relatively lower than by dehydrogenation of *n*-butane [8]. Thus, the deposition following isobutane dehydrogenation on the catalyst is far lower than after *n*-butane dehydrogenation.

The sequence of the coke depositing ability of the aforesaid C_4 hydrocarbons on $Pt-Sn/Al_2O_3$ catalyst is almost the same as that on Pt/Al_2O_3, except that the order of *n*-butane and isobutane is reversed, showing that the addition of Sn does not alter the mechanism of carbon deposition, but it clearly reduces the amount of coke deposited from precursors, especially butadiene and butene-1. These results illustrate that the deep dehydrogenation of olefin and the formation of carbon on the catalyst can be inhibited by the addition of Sn, and thus the stability of the catalyst is improved.

CONCLUSION

In the dehydrogenation of butane, similar carbon deposit curves are observed on highly dispersed Pt/Al_2O_3 and $Pt-Sn/Al_2O_3$. The anti-coking behaviour of Pt/Al_2O_3 catalyst can be distinctly improved by the addition of Sn and alkali metal, Li or K. The carbon deposits mainly on the metal surface of Pt/Al_2O_3 and deposits mainly on the internal surface of the carrier of $Pt-Sn/Al_2O_3$. The addition of Sn leads to the migration of coke deposit. The amount of carbon deposited on the metal surface and the internal surface of carrier is clearly decreased by the addition of Li or K, showing that there are acid sites on the metal, in addition to the acid centre of the carrier. The amount of coke deposited in the dehydrogenation of isobutane is lower than in that of *n*-butane; this is attributed to the fact that isobutane is readily dehydrogenated and cracked into small molecules.

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