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## The Role of Hydrogen-Carbon Ratio of Coke in Cracking of Aromatic Hydrocarbons on Silica-Alumina Catalyst

Takehige TAKAHASHI\* and Ken-ichi WATANABE\*

The kinetics of coke formation in the cracking of some aromatic hydrocarbons over a silica-alumina catalyst and the effects of process time, or reaction period, and reaction temperature on the H/C ratio of coke were studied at various temperatures ranging from 470 to 500°C.

For the kinetics of coke formation, a simple semiempirical equation involving the relationship between coke yield and reaction period was proposed by Voorhies.

Although the rate of coke formation differed from one feedstock to another, the H/C ratio of coke did not, but rather it decreased with increasing reaction temperature and reaction period. Furthermore, the ratio of benzene extract to total coke content decreased with reaction period.

These results suggested that coke was formed by dehydrogenation of the substance deposited on the catalyst surface.

### 1. Introduction

Catalytic reactions such as isomerization, cracking, and hydrogenation are important processes in the petroleum refining industry. Catalytic activity is fouled by the deposition of carbonaceous materials, so called coke, on the surface of the catalyst. Many investigators have studied the kinetics of catalytic reactions in which the catalyst is subjected to fouling and suggested several decay models as a function of coke concentration<sup>1)~5)</sup>.

It is important to characterize the chemical properties of the coke deposited on the catalyst because of their effects on catalyst regeneration, but no papers have yet been reported on this subject.

In this paper, the effective chemical property of such coke will be characterized by its H/C ratio. Effects of reaction period and temperature on the rate of coke formation and its H/C ratio have been studied using some aromatic hydrocarbon feedstocks.

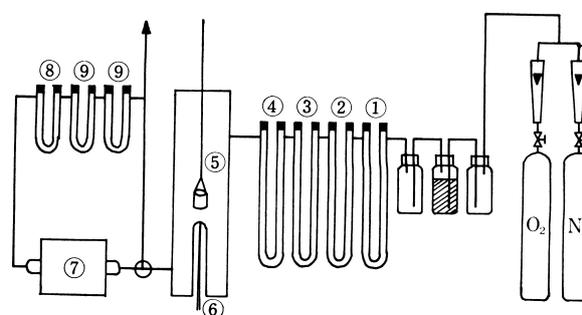
### 2. Experimental Apparatus and Procedure

Coke formation was carried out in a fixed bed reactor<sup>6)</sup>. The reactor was made of a pyrex tube with 600 mm effective length and 25 mm I.D. The reactor was provided with a porous glass disk to contain the catalyst in the reactor and heated with an electric furnace controlling within  $\pm 2^\circ\text{C}$ . The silica-alumina catalyst used was Silbead-W obtained from Mizusawa Chemical Co. The catalyst was

crushed and particles of 10-20 mesh were used after calcination at 500°C for 5 hrs.

Aromatic hydrocarbons (benzene, toluene, xylenes, and ethylbenzene) of commercially guaranteed grade were used without further purification. Feedstocks were passed through the silica-alumina catalyst column under following conditions; reaction temperature, from 470 to 500°C; time factor(W/F), 85(g-catalyst-hr/g-mol hydrocarbon); process time, from 30 to 300 min; hydrocarbon/N<sub>2</sub> ratio, 1/9.

Although hydrogen is usually used to dilute the feed in cracking or isomerization, we used nitrogen as a diluent in order to maintain a constant H/C ratio of the feed. A schematic diagram of the coke burning apparatus is shown in Fig. 1. Weight and H/C ratio of coke produced were measured with a thermogravimetric balance, one type of null beam balance, whose weighing sensitivity was 0.1 mg. 1.5 g of a fouled catalyst was weighed and placed



1. CaCl<sub>2</sub>, 2. Silica gel, 3. CO<sub>2</sub> absorbent  
4. H<sub>2</sub>O absorbent, 5. Thermogravimetric balance  
6. Thermocouple 7. Electric Furnace  
8. H<sub>2</sub>O absorber 9. CO<sub>2</sub> absorber

Fig. 1 Schematic Diagram of Coke Burning Apparatus

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in a platinum gauge basket. It was heated in a stream of nitrogen at the reaction temperature in order to desorb physically adsorbed water. After desorption of adsorbed water, dried and carbon dioxide free mixture of oxygen and nitrogen was introduced into the burning system. The total amount of coke deposited on the fouled catalyst was represented by the weight loss of the catalyst after calcinating at 500°C for 5,000 sec.

The H/C ratio of the coke was determined by the elemental analysis. Carbon monoxide contained in the stream that passed through the bed of fouled catalyst was oxidized to carbon dioxide over a CuO catalyst. The water and carbon dioxide in the effluent were absorbed onto magnesium perchlorate and soda-asbestos, respectively. The ratio of carbon to hydrogen was calculated from the gain in the weights of carbon dioxide and water absorber. The amounts of carbon and hydrogen agreed with the weight loss of the coke measured gravimetrically within less than 2% error.

### 3. Results and Discussion

#### 3.1 Rate of Coke Formation

A series of experiments using *m*-xylene was carried out at different reaction temperatures, and coke yields at different reaction periods were measured. Plots of coke yield against reaction period on a log-log scale are shown in **Fig. 2**. The experimental points obtained at the same temperature can be

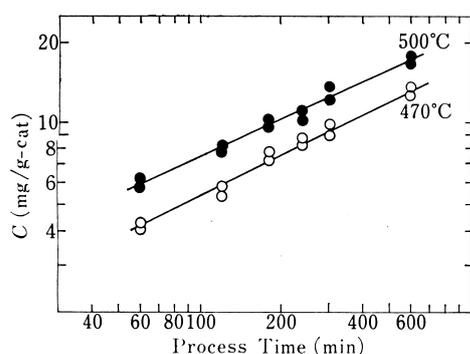


Fig. 2 Relationship between Coke Yield and Process Time in the Reaction of *m*-Xylene

represented by a straight line as predicted by Voorhies<sup>7</sup>.

According to Voorhies, coke yield,  $C$ , was given by the Eq. (1).

$$C = A\theta^n \quad (1)$$

where  $\theta$  is the process time, and  $A$  and  $n$  are constants. **Table 1** shows the values of  $A$  and  $n$  that varied with reaction temperature and kinds of feedstocks. The values of  $n$  for benzene, toluene, and ethylbenzene were close to 0.35, but the values for xylenes were nearly 0.5 as suggested by Voorhies.

Table 1 Variation of  $A$  and  $n$  with Reaction Temperature and Feedstocks

Hydrocarbon	Temperature (°C)	$A$	$n$
Benzene	470	0.087	0.36
Toluene	470	0.16	0.33
Ethylbenzene	470	0.16	0.34
<i>o</i> -Xylene	470	0.045	0.54
	485	0.055	0.53
	500	0.067	0.54
<i>m</i> -Xylene	470	0.071	0.46
	485	0.096	0.47
	500	0.11	0.48
<i>p</i> -Xylene	470	0.041	0.57
	485	0.051	0.54
	500	0.055	0.52

Catalytic reactions of aromatic hydrocarbons were carried out in a differential reactor at 500°C for 5 hrs. The composition of products changed with process time due to the fouling of the catalyst, and **Table 2** illustrates the composition after 50 min of reaction. For benzene, toluene, or ethylbenzene, cracking proceeded at low levels of conversion. On the other hand, isomerization and disproportionation of xylenes occurred simultaneously at high levels. In spite of lower levels of conversion of toluene or ethylbenzene, the rates of coke formation of these feedstocks were greater than those of xylenes.

These results suggested that coke formation in aromatic hydrocarbons occurred simultaneously with cracking of the feedstock.

#### 3.2 H/C Ratio of Coke

**Table 3** shows the relationship between the kind

Table 2 Product Composition in Reaction of Aromatic Hydrocarbons

Feedstock	Product Yield (%)						
	Benzene	Toluene	Ethylbenzene	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	Trimethylbenzenes
Benzene	100	—	—	—	—	—	—
Toluene	3.7	96.3	—	—	—	—	—
Ethylbenzene	2.8	0.2	97.0	—	—	—	—
<i>o</i> -Xylene	—	1.9	—	8.2	37.3	51.4	1.2
<i>m</i> -Xylene	—	1.8	—	18.8	59.2	18.3	1.9
<i>p</i> -Xylene	—	2.5	—	38.3	44.6	10.4	3.7

Reaction temperature; 500°C, Process time; 50 min.

Table 3 Relationship between Feedstocks and H/C Ratio of Coke at 500°C

Hydrocarbon	H/C Ratio
Benzene	0.30
Toluene	0.35
Ethylbenzene	0.37
<i>o</i> -Xylene	0.36
<i>m</i> -Xylene	0.31
<i>p</i> -Xylene	0.40
<i>o</i> -Xylene*	0.37
<i>m</i> -Xylene*	0.38
<i>p</i> -Xylene*	0.33

\* Hydrogen was used as diluent.

of feedstock and the H/C ratio of coke at 500°C. The value of H/C ratio was between 0.3 and 0.4 for all feedstocks. It does not seem to be effected greatly by the kind of feedstocks involved. **Table 3** also shows the H/C ratio of coke for isomerization of xylenes with hydrogen. As the values of H/C ratio were found to be from 0.3 to 0.4, it was considered that the H/C ratio was not affected by the kind of diluent used. **Fig. 3** shows the relationship between the H/C ratio of coke and temperature in the reactions of xylenes. The H/C ratio decreased with temperature. On the other hand, **Fig. 4** shows the relationship between the H/C ratio of coke and process time in the reaction of *p*-xylene. The H/C ratio at 60 min was about 1.0, but it decreased with reaction period.

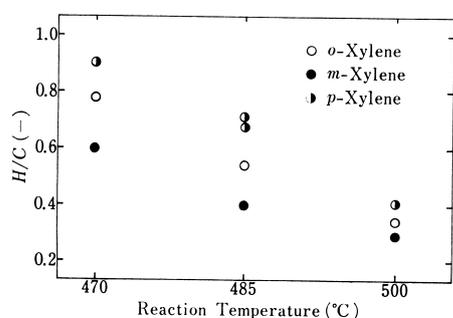


Fig. 3 Relationship between H/C Ratio and Temperature in the Reaction of Xylenes

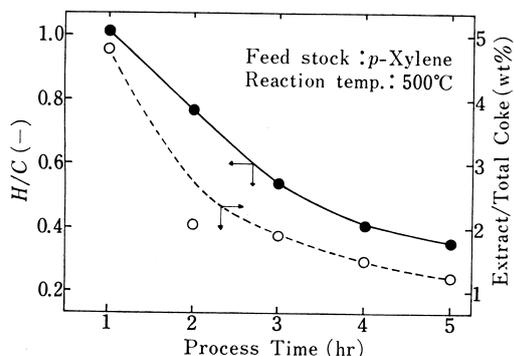


Fig. 4 Effect of Process Time on H/C Ratio and Extract/Total Coke Ratio

It has been reported that the H/C ratio of coke on zeolite catalyst was from 0.37 to 0.46 for toluene disproportionation<sup>9</sup>). Also the values of 0.05—0.15 have been observed for the dehydrogenation of isopentane on chromia-alumina catalyst<sup>9</sup>), and 0.4 for the cracking of furnace oil on silica-alumina catalyst<sup>10</sup>). Values of H/C of coke varied with experimental conditions, catalyst, and feedstocks.

To study the reaction path of this coke formation, the following experiments were performed. The catalyst that was used for various reaction period at 500°C was dried in nitrogen atmosphere at 500°C for 1 hr, and the coke deposited onto the catalyst was extracted with pure benzene for 5 hrs. The extract was a brown viscous oil whose infrared spectrum showed weak band at about 3,000  $\text{cm}^{-1}$  and 1,450  $\text{cm}^{-1}$  that were due to the CH stretching and CH bending, respectively. The effects of reaction period on the ratio of extract to total coke and H/C ratio of coke are shown by a dashed line and a solid line, respectively, in **Fig. 4**. Similar relationships were obtained in both lines in **Fig. 4**. In the extract, a small amount of *p*-xylene was detected by gas chromatographic analysis, although the fouled catalyst was dried at 500°C. Therefore, the higher H/C ratio of coke at early reaction period seems to be that of the feedstock adsorbed strongly on the catalyst surface.

From these results, a most likely reaction path for coke formation from the feedstocks used seemed to be the following: (1) the feedstock adsorbed on the active site of catalyst changed to a substance with its H/C ratio about 1.0, (2) the substance was then dehydrogenated gradually on the catalyst surface.

#### Acknowledgement

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## 要 旨

### 芳香族系炭化水素の分解時にシリカ-アルミナ触媒上に析出するコークの H/C 比について

高橋 武重\*, 渡辺 憲一\*

シリカ-アルミナ触媒を用いて種々の芳香族炭化水素の接触分解反応を行い、コーク生成速度およびコークの H/C 比に対する反応時間および反応温度の影響を検討した。10~20 mesh に破碎した触媒および原料炭化水素として *m*-キシレンを使用した時の反応時間とコーク収量の関係を Fig. 2 に示す。Fig. 2 からわかるように、コーク収量  $C$  [mg/g-catalyst] と反応時間  $\theta$  [min] は Voorhies<sup>7)</sup> によって示された Eq. (1) により相関された。

$$C = A\theta^n \quad (1)$$

ここで、 $A$  と  $n$  は定数である。この  $n$  と  $A$  を他の炭化水素について測定すると Table 1 のようになった。キシレン類において、コーク生成量は温度の上昇と共に増加するが  $n$  はほぼ一定になった。他の炭化水素の  $n$  はキシレン類に比較して小さな値を示したが、トルエンおよびエチルベンゼンのコーク生成量はキシレン類より大きくなった。また、Table 2 に各炭化水素を 500°C で反応させた時の生成物分布を示した。トルエンおよびエチルベンゼンでは、原料炭化水素の転化率は低い値を示したが、反応は脱メチルまたは脱エチル反応のような分解反応であった。一方、キシレン類では、主反応は異性化および不均化反応で脱メチル化反応は見いだされなかった。以上の結果から、コーク生成反応は主として分解反応と共に進行すること

が推測された。

コーク生成速度は原料炭化水素によって異なったが、コークの H/C 比は Table 3 に示すように原料炭化水素によらず 0.3~0.5 の値を示した。また、希釈ガスを窒素から水素に変えてもその影響は見られなかった。キシレン類のコークの H/C に対する反応温度の影響は、Fig. 3 に示すように温度の上昇と共に 0.6~0.9 より 0.3~0.4 に徐々に減少した。

500°C で *p*-キシレンを原料炭化水素として反応させた時のコークの H/C 比と反応時間の関係を Fig. 4 に示した。コークの H/C 比は反応時間と共に徐々に減少して行くことがわかった。また、各時間毎に生成したコークを 500°C, 1時間窒素気流中で乾燥後、ベンゼンで5時間抽出した。抽出物は粘性のあるかっ色の液体で赤外線吸収スペクトルでは 3,000  $\text{cm}^{-1}$  および 1,650  $\text{cm}^{-1}$  に吸収が観測された。全コーク量に対する抽出物量の割合を Fig. 4 に破線で示した。この曲線はコークの H/C 比の曲線と同様に、反応時間と共に徐々に減少して行くことがわかった。

さらに、この抽出物をガスクロにより分析すると、反応時間の短い抽出物から微量の *p*-キシレンが検出された。

以上の結果から、シリカ-アルミナ触媒上において、コークは次の経路により生成することが推定される。(1) 触媒表面上に吸着された原料炭化水素の分解反応と同時に H/C 比が約 1.0 のコークが触媒表面上に生成する。(2) このコークが反応時間の経過と共に脱水素して H/C 比が 0.3~0.5 のコークに変化する。また、コークの脱水素は反応温度により影響されるが原料炭化水素および希釈ガスの種類には影響されないことがわかった。

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## Keyword

Aromatics, Coke formation, Cracking, Hydrogen-carbon ratio