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Short communication

Coke formation over Pt–Sn–K/Al_2O_3 in C_3, C_5–C_8 alkane dehydrogenation

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Abstract

The effect of reactants on coke formation during dehydrogenation (DH) over 0.3 wt.%Pt–0.3 wt.%Sn–0.6 wt.%K/Al_2O_3 was investigated. The reactions were carried out in the temperature range 200–600°C at 1 atm with pairs of alkanes and alkenes (C_3, C_5–C_8). The carbonaceous deposits formed during the process were analyzed using the temperature-programmed oxidation (TPO) technique. With the same amount of coke, the TPO profiles of the short alkane and alkene (C_3) did not match completely, while those of the larger chain alkanes and alkenes (C_5–C_8) were virtually identical. From these results, a simple model of coke formation has been proposed. Short alkane DH provides coke in series and larger alkane DH generates coke in series and consecutive modes. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkane dehydrogenation; TPO; Coking

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1. Introduction

Deactivation of catalysts by carbonaceous deposits is a phenomenon frequently encountered in the petrochemical industry which has far-reaching applications and consequences. In recent years, it has received increasing attention, as evidenced by the rapidly growing number of publications dealing with this topic.

Dehydrogenation (DH) of alkanes is one of the most important reactions in increasing chemical feedstocks. However, the conditions needed for this process, high temperature and low pressure, result in the formation of coke over the catalyst, which leads to a short catalyst lifetime.

Many studies have been conducted to improve the catalyst in this reaction. Lin et al. [1] showed that Pt–Sn/Al_2O_3 can reduce the strength of chemisorption of the hydrocarbon on the metal site, and the carbon precursor can then migrate to the support easily. This process reduced coke accumulation over active sites. Recent work reported that the addition of potassium to Pt–Sn/$A1_2O_3$ for propane DH can extend the catalyst lifetime by decreasing the amount of coke on the metal site [2].

Several research groups have published mechanisms and kinetic models of coke formation [3–5]. A recent mechanism was proposed by Hughes [6], which explained the formation of coke by using a series and parallel model. However, the model did not explain the effect of different reactants with respect to coke formation. Since feedstocks contain mixtures of a variety of paraffins, it is important to know the effects of different paraffin components upon the activity, selectivity and stability of the catalyst. The outcomes could help to decide possible uses of a cut with a certain hydrocarbon composition.

Several techniques have been used to study carbonaceous residues, e.g. Fourier transform infrared (FTIR) [7], transmission electron microscopy (TEM) [8], nuclear magnetic resonance (NMR) [9], Auger electron spectroscopy (AES) [10], temperature-programmed oxidation (TPO) [11–13] etc. All of these techniques give different types of information on coke deposition. A technique widely used to characterize coke deposits is the temperature-programmed technique. This technique supplies information about the location and general structure of coke accumulation over the catalyst surface.

This paper presents the results obtained when a Pt–Sn–K/$A1_2O_3$ catalyst was used to dehydrogenate pure paraffins. This includes the analysis of the coke and a proposed coke formation model.

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2. Experimental details

2.1. Materials

High-purity alumina type NKH-3 (Sumitomo Aluminium Smelting, Japan) was used as the support. Chloroplatinic acid (Wako Pure Chemical I, Japan), stannous chloride dihydrate (Fluka Chemie AG, Switzerland) and potassium nitrate (KNO_3) (E. Merck, USA) were used to prepare the 0.3%Pt–0.3%Sn–0.6%K/Al_2O_3 catalyst. A gas mixture (TIG, Thailand) containing propane, pentane, hexane or octane was used as reaction feed. Diluted oxygen (1 vol%) in helium (TIG, Thailand) was used as an oxidant in the TPO process.

2.2. Catalyst

Alumina support was ground to a mesh size of 60/80, followed by washing with distilled water and then dried at 100°C overnight. The support was then calcined in air at 300°C for 3 h. The impregnation method was used to prepare a catalyst with a calcination step for each addition of the three active chemicals, Pt, Sn and K. Our full report describes this in more detail [14].

2.3. Apparatus and methodology

The apparatus used was an ordinary atmospheric flow system consisting of a quartz reactor. The reactor temperature was controlled by an electric furnace. A schematic diagram of the apparatus is shown in Fig. 1. A variety of gases, shown in Table 1, were used as feed. C_3 was fed directly into the reactor, while C_5–C_8 were vaporized in a saturator at a particular temperature. Nitrogen gas was carried along with the vapour in order to maintain the same concentration of carbon before being introduced into the reactor.

Table 1
Concentration and control temperature of reactants

Reactant	vol% in N_2	Control temperature in the saturator (°C)
Propane	20	–
Propene	20	–
n-Pentane	12	−14.2
1-Pentene	12	−19.5
n-Hexane	10	10.2
1-Hexene	10	5.6
n-Heptane	8.6	32.4
1-Heptene	8.6	28.1
n-Octane	7.5	52.9
1-Octene	7.5	48.8

In each run, 0.1 g of fresh catalyst was placed in the isothermal zone inside the reactor. It was then reduced by hydrogen for 1 h at a flow rate of $30\,cm^3\,min^{-1}$ at 500°C, and then cooled to the required temperature before the reaction. Afterwards, reactant gas was fed into the reactor with a GHSV of $20\,000\,h^{-1}$. The reaction products were analyzed between 5 min and 2 h during the process with a Shimadzu GC-14B flame ionization detector (FID) gas chromatograph (GC). Two kinds of GC columns were used for analysis. The first type was a capillary column. The temperature was initially programmed at 35°C and then followed by a $10°C\,min^{-1}$ ramp up to 140°C. The second GC column was a VZ-10 column with an initial temperature set at 65°C followed by an increase of $10°C\,min^{-1}$ to 80°C.

The coke formation over each spent catalyst was characterized by a TPO process. The carrier gas containing oxygen in helium was fed into the sample cell at a constant flow rate of $30\,cm^3\,min^{-1}$ under ambient conditions. The temperature was increased linearly from 50 to 700°C at a heating rate of $5°C\,min^{-1}$. At the end of the TPO process, the coke deposits were completely removed. The reaction products were analyzed by an on-line TCD GC with a packed column (Porapack QS). The column temperature was maintained isothermal at 90°C for the entire analysis.

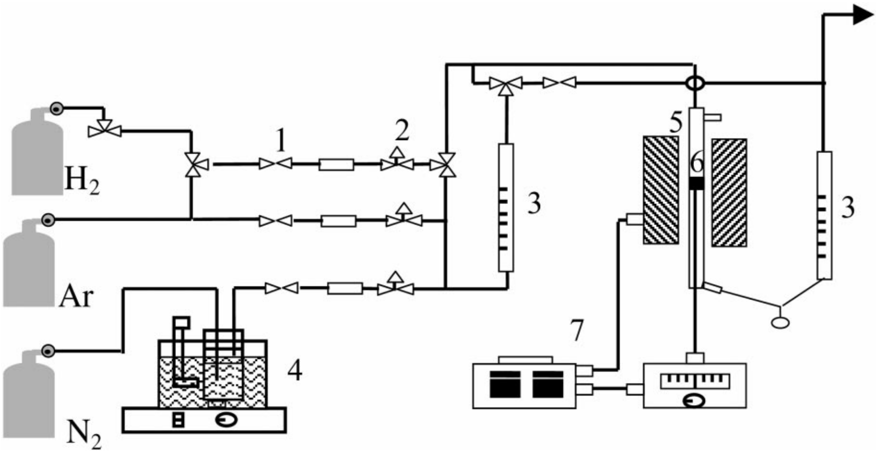

Fig. 1. Schematic diagram of the flow reactor: (1) on–off valve; (2) needle valve; (3) flow meter; (4) saturator; (5) reactor; (6) catalyst bed; (7) temperature control set.

The reaction selectivity of coke formation was defined as follows:

$$\%\ \text{Selectivity of coke formation} = \frac{\text{Atoms of carbon deposited on catalyst} \times 100}{\text{Atoms of carbon feed converted averaged with time}}$$

3. Results and discussion

It was apparent that the products of straight chain alkane DH would be the parent alkane, the corresponding alkene and hydrogen. To better understand the mechanism of coke formation, the corresponding alkenes needed to be investigated for DH as well. Therefore, normal paraffins and olefins from C_3 and C_5–C_8 were used as feeds.

The process for each feed in the absence of a catalyst was carried out to evaluate whether thermal cracking affected DH. It was found that thermal cracking occurred at 500°C; this side-reaction was quite significant, especially for high molecular weight hydrocarbons, accounting for 5–30% conversion for C_5–C_8 and almost none for C_3.

To reduce the effect of thermal cracking for higher molecular weight hydrocarbons, it was necessary to decrease the operating temperature. The experiments using C_5, C_6, C_7 and C_8 alkanes and alkenes showed insignificant thermal cracking at 350, 300, 250 and 200°C, respectively, and so the experiments were performed at these temperatures. The activity and the selectivity are presented below.

3.1. Activity and coke selectivity

In propane and propene DH, as shown in Fig. 2, the activity of propane DH is higher than that of propene DH. The results corresponded with those of the thermodynamic calculations. However, the activity declined markedly for propane DH. The major products from propane DH were propene, hydrogen and a moderate amount of propadiene. When using propene as a feed, more propadiene was produced. Considering the percentage of coke produced in the same reaction period, it was found that propene DH produced more coke than did propane DH. Therefore, coke selectivity via propene DH was higher than via propane DH, as shown in Table 2. Since propadiene by nature is extremely reactive towards other chemicals, it was reasonable to assume that propadiene would be one of the important precursors for coke formation in low molecular weight alkane DH.

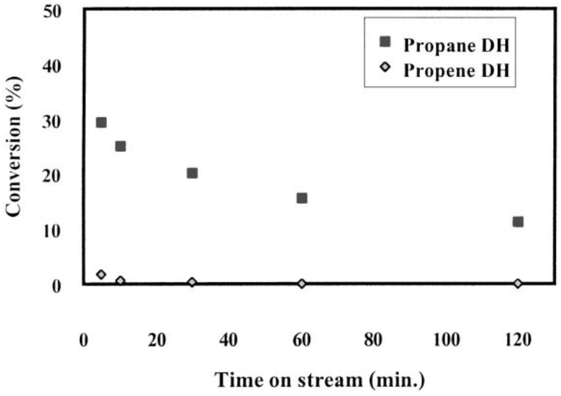

Fig. 2. Conversion as a function of time for C_3 DH at 500°C.

Table 2
Coke content and coke selectivity for 2 h time on stream over 0.3 wt.%Pt–0.3 wt.%Sn–0.6 wt.%K/Al_2O_3 operated with a variety of reactants

Reactant	Reaction temperature (°C)	Coke (%)	Selectivity of coke formation (%)
Propane	500	0.80	0.002
Propene	500	2.30	0.185
n-Pentane	350	2.35	0.922
1-Pentene	350	1.93	0.006
n-Hexane	300	1.61	0.393
1-Hexene	300	1.64	0.010
n-Heptane	250	0.22	0.080
1-Heptene	250	0.31	0.016
n-Octane	200	0.16	0.020
1-Octene	200	0.12	0.002

For higher molecular weight hydrocarbons, the activity results are reversed from those of C_3 DH. As shown in Figs. 3–6, the activities of alkene DH are higher than those

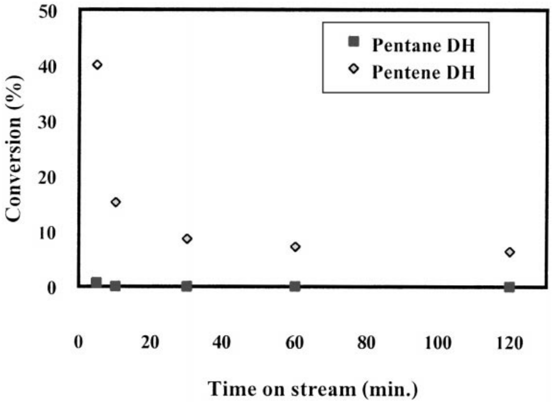

Fig. 3. Conversion as a function of time for C_5 DH at 350°C.

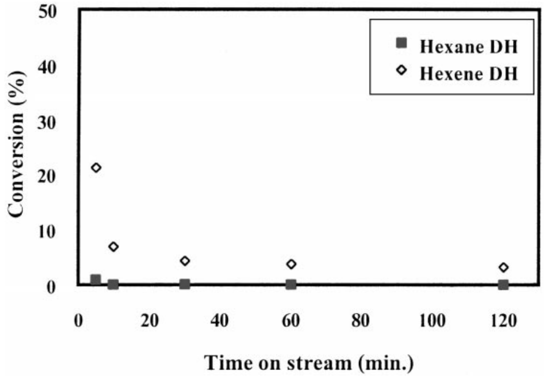

Fig. 4. Conversion as a function of time for C_6 DH at 300°C.

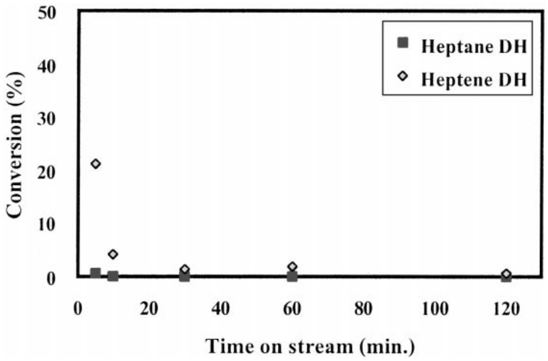

Fig. 5. Conversion as a function of time for C_7 DH at 250°C.

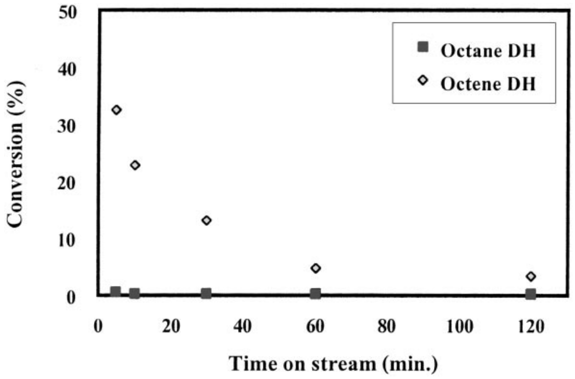

Fig. 6. Conversion as a function of time for C_8 DH at 200°C.

of the corresponding alkane DH. In the early stages, the chromatogram of alkene DH showed a variety of products, including dienes and cycloalkane, while these products were not observed from alkane DH. When the reaction time was increased, 120 min time on stream, both alkane and alkene DH provided similar products. This implied that higher alkane DH over Pt–Sn–K/Al_2O_3 would perform not only DH but also polymerization, cyclization and catalytic cracking. Coke analysis indicated that the percentage of coke was similar for each pair of alkane–alkene DH. The percentage of coke selectivity of the catalyst for alkane DH was higher than that for alkene DH as shown in Table 2. From a thermodynamic viewpoint, reaction through a cyclopentane pathway is one of the most favourable pathways. The experimental results also supported this, as the chromatograms for each feed (C_5–C_8) showed a peak for C_5. Moreover, this indicates that C_5 should be considered as an important coke precursor for high molecular weight hydrocarbons. This result is similar to the study of Beltramini et al. [15]. As shown in Table 2 for the results of pentane through octane, it was found that the higher molecular weight hydrocarbons provided a lower percentage of coke. This confirms that intermediate C_5 is the coke precursor.

Considering the percentage of coke for every reaction feed, it was found that propene DH gave a higher percentage of coke than propane DH, while in the case of large hydrocarbons, both alkane and alkene DH created an equal percentage of coke. The results suggest that coke formation from different kinds of alkanes occurs via different mechanisms. A schematic diagram of the coke formation mechanism is shown in Fig. 7. This shows that alkanes with a low molecular weight deposit coke via a series mode, while for high molecular weight hydrocarbons, coke formation over catalysts occurs via both consecutive and parallel modes. This also suggests that the coke amount and formation are not directly related to the molecular weight of the hydrocarbon, but related to the structure of the reactants and products, which is similar to the results of Beltramini's work [15].

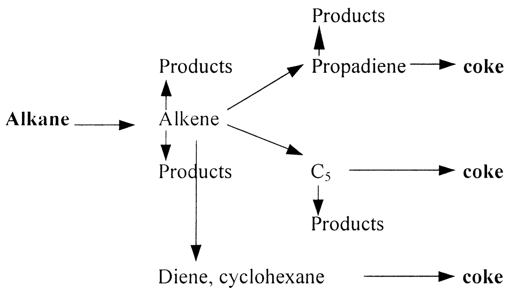

Fig. 7. Schematic representation of coke formation in C_3–C_8 alkane DH.

3.2. Coke analysis

It is accepted that the low temperature peak of the TPO spectrum (280–370°C) corresponds to coke deposited on or in contact with metal sites. The intermediate temperature peak at 445°C is associated with the coke on acid sites close to the metal. The 570°C peak is produced by coke on acid sites far away from any metal sites, called high temperature coke. The aim of this section is to understand the development of coke deposition [16,17].

Fig. 8 shows the TPO patterns of spent catalysts from propane and propene DH, which operated at 500°C after 2 h time on stream. The propene DH spectrum contains two peaks. In contrast, the propene TPO pattern has only one

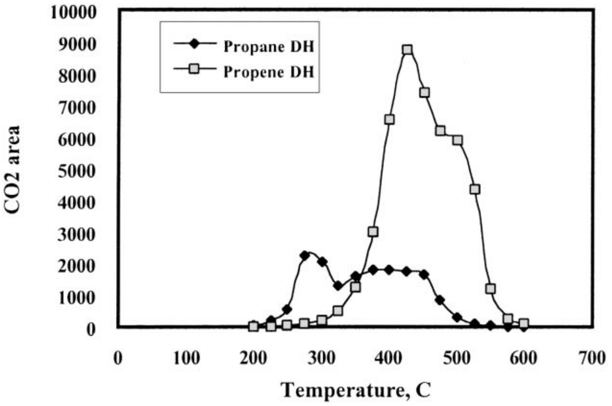

Fig. 8. TPO spectra for C_3 DH operated at 500°C and 2 h time on stream.

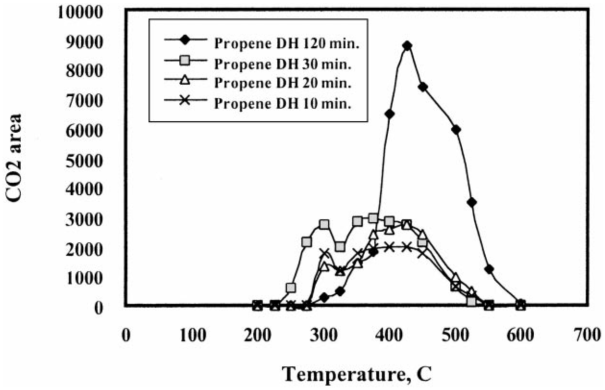

Fig. 9. TPO spectra for propene DH as a function of time on stream.

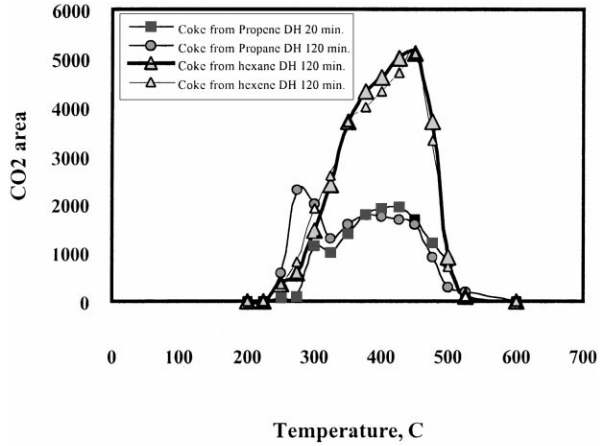

Fig. 10. TPO spectra for the same amount of coke from C_3 and C_6 DH.

peak. The coke deposited via propane DH is a low temperature coke and contains a simple structure, while the coke structure obtained from propene DH may be more complex. To understand the process of development of coke on catalysts and the content of the coke from propene DH, TPO spectra as a function of time were studied, as shown in Fig. 9. Two peaks are observed at the initial time interval (10–30 min). The first peak in the spectrum gradually shifts with time on stream and eventually becomes one peak. This shows that coke becomes more complex in structure with increased time on stream. It was therefore theorized that, after 120 min, coke was hard to deposit on a small site of metal. The structure also increased in molecular weight and moved to deposit over supports close to metal sites [18].

Fig. 10 presents the TPO patterns obtained from spent catalyst from propane–propene DH at 500°C. The results show that both propane and propene DH produce the same amount of coke at 120 min for propane DH and at 20 min for propene DH. It was found that both patterns did not completely match. In contrast, TPO patterns of coke by hexane–hexene DH at 300°C were perfectly matched. There was only one peak in the TPO pattern at 445°C and no peak was observed at 280°C. Comparing the amount of coke between C_3 and C_5 (area under the TPO pattern) at 120 min time on stream, C_5 DH had a higher coking rate than C_3 DH.

4. Conclusions

The effect of reactants on coke formation in hydrocarbon DH was investigated over 0.3 wt.%Pt–0.3 wt.%Sn–0.6 wt.% K/A1$_2$O$_3$ using the TPO technique. A reactant having three carbon atoms produced coke in a series pathway, while reactants with five to eight carbon atoms produced coke in series and parallel pathways. Propadiene is a coke precursor for C_3 DH and C_5 is a coke precursor for C_5 or higher hydrocarbon DH. Coke increases in molecular weight and prefers to cover the supports rather than the metal sites.

Acknowledgements

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