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Probability of Chain Growth in Coke Formation on Metals and on Supports during Catalytic Reforming over Pt, Pt-Sn and Pt-Sn-K Catalysts Mixed Physically with Al_2O_3

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Abstract−The main goal of this contribution was to study the probability of chain growth of coke on metal sites and on support sites for hexane dehydrogenation. The coke structure of the catalysts examined by IR was found to have the aromatic structure. Soxhlet extraction coupled with GC-14B (DB1 column) analysis was mainly employed for coke composition analysis and determination of the probability of chain growth (alpha value). It was found that the soluble coke was mainly composed of C_8-C_{12} on both sites. Interestingly, the probabilities of chain growth on both sites were identical. However, the extracted coke on the metal site was more easily removable and had lower carbon numbers than that on the support site. Moreover, the addition of promoter, especially of K promoter, was sensitive to inhibit the probability of chain growth, resulting in the reduction of the amount of coke.

Key words: Probability of Chain Growth, Coke, Physically Mixed Catalyst, Promoter with Sn and K

INTRODUCTION

Catalytic reforming has become one of the most important industrial applications of catalysis. Operation conditions for the process reflect the balance between the thermodynamics of desired and undesired reactions. Desired reactions are favored by high temperature and low pressure conditions, which also favor coke formation [Biswas et al., 1988; Trimm, 1983]. The forms of deposited carbon (usually called "coke") may vary from high molecular weight hydrocarbon species (polymeric carbon) to graphitized carbon corresponding to the formula CH_x [Biswas et al., 1987; Barbier, 1987; Froment, 1991]. There is a general agreement that this envisions coke formation as more of a polymerization process than a degradation process [Biswas et al., 1988; Froment, 1997; Rostrup-Nielsen, 1997; Forzatti et al., 1999]. Generally, the standard catalysts are Pt-based catalysts (especially Pt/Al_2O_3) [Froment, 1991].

The kinetics of coke deposition, influence of bimetallics, effect on different active sites and structure of coke [Figoli et al., 1983; Lietz et al., 1984; Van Trimmpont et al., 1986] have been studied. Interestingly, the analysis by temperature-programmed oxidation (TPO) generally indicates two types of coke: the first one burns at low temperatures (polymeric carbon), which is associated with the metallic phase. The second type burns at high temperatures (amorphous phases/graphitized carbon), corresponding to the support [Rostrup-Nielsen, 1984]. However, complete segregation of the coke growth on the metal site from that on support site has not been investigated sufficiently yet. According to Bond [1987], Inaba et al. [1996] and Hamada [1997], we applied the physically mixed catalyst with the appropriate size which gave the same behavior of Pt/Al_2O_3 in order to study deactivation of the metal and acidic functions as previously proved [Sunee et al., 2001]. In the latter, the deactivation on both sites was examined for Pt, Pt-Sn and Pt-Sn-K [Sunee et al., 2000]. To understand the deactivation more completely, the probability of chain growth was newly investigated by employing the Schulz-Flory distribution theory (ASF plot) to calculate these values (usually called alpha value), which deal with the relationship between the carbon number and weight fraction or the distribution of the hydrocarbons [Flory, 1953; Lox et al., 1993]. The rate-determining step of coke formation is polymerization. The coked catalyst must be recovered by a Soxhlet extraction and then analyzed through GC.

Consequently, the subject of this work is a continuation of the study of coke formation on Pt, Pt-Sn, Pt-Sn-K catalysts by using a physically mixed system (Pt supported on SiO_2 represented the metallic site and Al_2O_3 represented the support site). The main goal was to determine the probability of chain growth of coke formation on both sites. Schulz-Flory distribution was applied to better understand the deactivation process of the catalyst.

EXPERIMENTAL

1. Catalyst and Coking Process

The experiments were performed by using the following reagents: $H_2PtCl_6 \cdot 6H_2O$ (Wako), $SnCl_2 \cdot 2H_2O$ (Fluka), KNO_3 (Merck), Al_2O_3 type NKH-3 (Sumitomo) and SiO_2 (Merck). The alumina and silica supports were ground to the required mesh sizes of 60/80 and 100/120 meshes, respectively. To prepare the Pt catalyst, 0.3% Pt was impregnated into the support. Then, it was dried at 110 °C overnight and subsequently calcined in air at 500 °C for 3 hours. For preparing the 0.3%Pt-0.3%Sn/SiO_2 and 0.3%Pt-0.3%Sn-0.6%K/SiO_2 catalysts, the same procedure was employed with co-impregnation.

The dehydrogenation was performed with 10% n-hexane in N_2.

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The ratio of physically mixed catalysts of the Pt-based catalyst and Al_2O_3 was 1 : 1. At the beginning, 0.2 g of the catalyst was packed in quartz tube (6 mm in diameter). Next, the catalyst was *in situ* reduced in hydrogen at 500 °C and 100 cm^3/min for 1 hour. The reaction temperature was adjusted to 475 °C and then 10% n-hexane in N_2 was flowed to the system with the flow rate of 60 cm^3/min. The mixed coke over catalyst was separated by sieving to Pt-based catalyst and Al_2O_3 for coke characterization.

2. Analytical Methods

IR was used to characterize the structural properties of carbonaceous deposit by the lattice vibration. The vibration bands between 400-4,000 cm^{-1} can indicate the structural framework of coke. The wafer was prepared by mixing KBr and the sample with the weight ratio of 100 : 1. The IR spectra were recorded by Nicolet mode Impact 400.

During the temperature-programmed oxidation, the amount of CO_2 formed from the coked catalyst was analyzed by GC-8AIT with a heating rate of 5 °C/min until the temperature reached 700 °C.

In order to characterize the coke composition, the soluble coke was extracted from the deactivated catalyst (50 mg) with toluene in a Soxhlet apparatus. The amount of toluene was 250 ml and the time of extraction was 24 h. The extracts were analyzed by GC14-B (a DB1 capillary column).

RESULTS AND DISCUSSION

1. Structural Analysis

The IR spectra of the coked Pt, Pt-Sn and Pt-Sn-K catalysts are illustrated in Fig. 1. In the region from 1,300 to 1,900 cm^{-1}, there was one band on the metal sites (Fig. 1A), whereas there were two main bands on the support (Fig. 1B). The most intense band was at

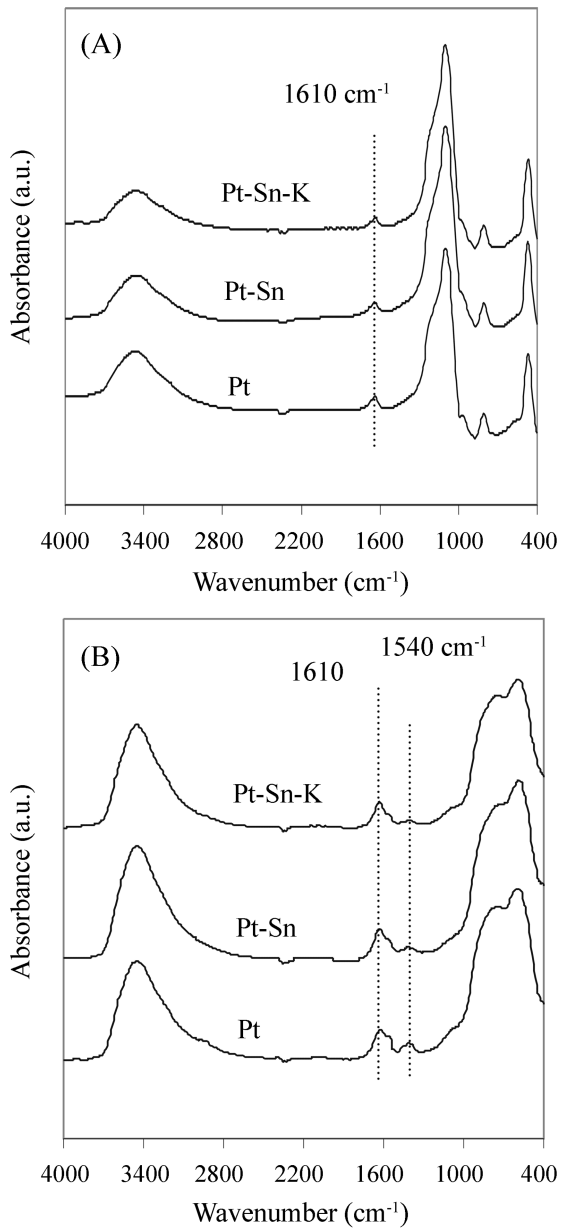

Fig. 1. IR spectra obtained after coking over (A) the metal sits and (B) the support site.

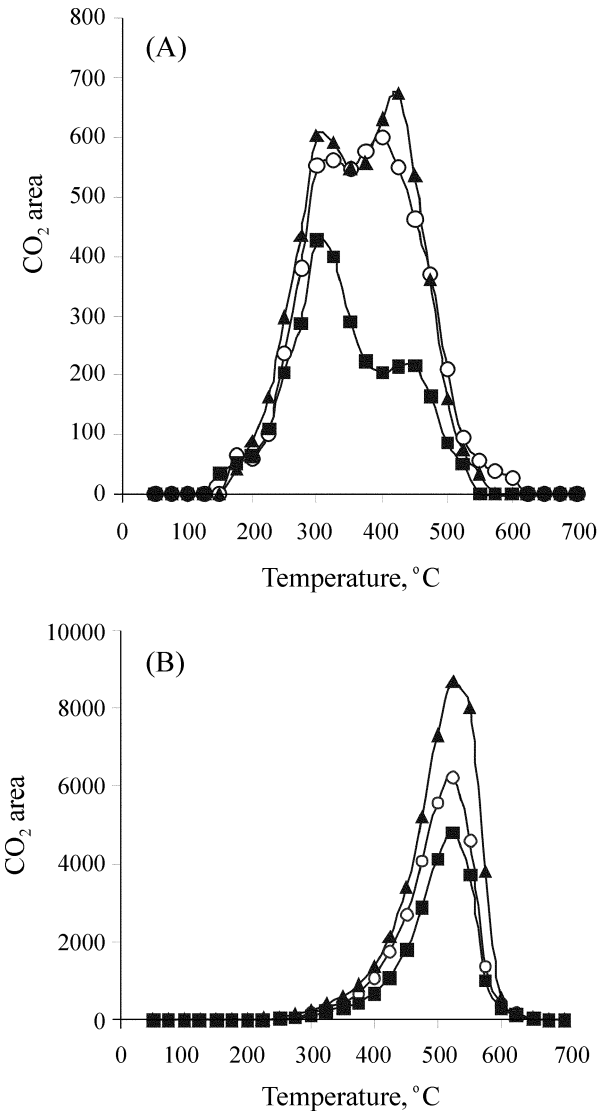

Fig. 2. TPO profiles for carbonaceous deposits produced at 475 °C for 120 min; (A) on the metal sites and (B) on the support sites. ▲: Pt catalyst, ○: Pt-Sn catalyst and ■: Pt-Sn-K catalyst.

1,610 cm^{-1}, which appeared both on the metal and support sites. This absorption band was assigned to the aromatic-ring bending vibration. Interestingly, the C=C stretching vibration around 1,540 cm^{-1} occurred only on the support sites. The difference between the IR spectra of coke on the metal and support sites reflected different rate of formation and H/C ratio of coke. Moreover, it is seen that the order of intensity was Pt>Pt-Sn>Pt-Sn-K on both sites. Although the Sn and K addition did not affect the overall patterns of these spectra in each site, a difference of intensity level was observed, indicating different rate of coke formation.

Fig. 2A shows the TPO profiles of Pt, Pt-Sn and Pt-Sn-K catalysts for the active metal sites of various catalysts. Two peaks appear at 300 °C and 425 °C in every TPO profile. This indicates that the carbon deposited on these catalysts can be divided into two types: (i) coke deposited directly on metal, and (ii) coke in the vicinity of metal centers, which corresponds to the report elsewhere [Lietz et al., 1984; Jovanoviæ and Putanov, 1997]. On the acidic sites, it is observed that a single peak appears on TPO spectra for all the three catalysts as seen in Fig. 2B. This peak presents the coke burnt off at a higher temperature, about 525 °C, compared with the coke on the metal. The amount of coke on both the metal and support decreased significantly by the addition of Sn and/or K.

2. Carbon Number Composition of the Coke Extracts

Fig. 3 presents typical chromatograms for the coke extracts from the metal sites and the acidic sites. The compositions of soluble coke are listed in Table 1. It was noticed that the soluble coke was mainly composed of C_8-C_{12}. On the metal (Fig. 3A), the amount of C_{12} components on the Pt-Sn and Pt-Sn-K catalysts almost vanished. On the support sites, the amount of the C_8 components on the Pt-Al_2O_3 catalyst was considerably smaller than that on the other modified catalysts while the C_{12} component was much larger. That is, the soluble coke on the Pt-Sn and Pt-Sn-K catalysts was mostly con-

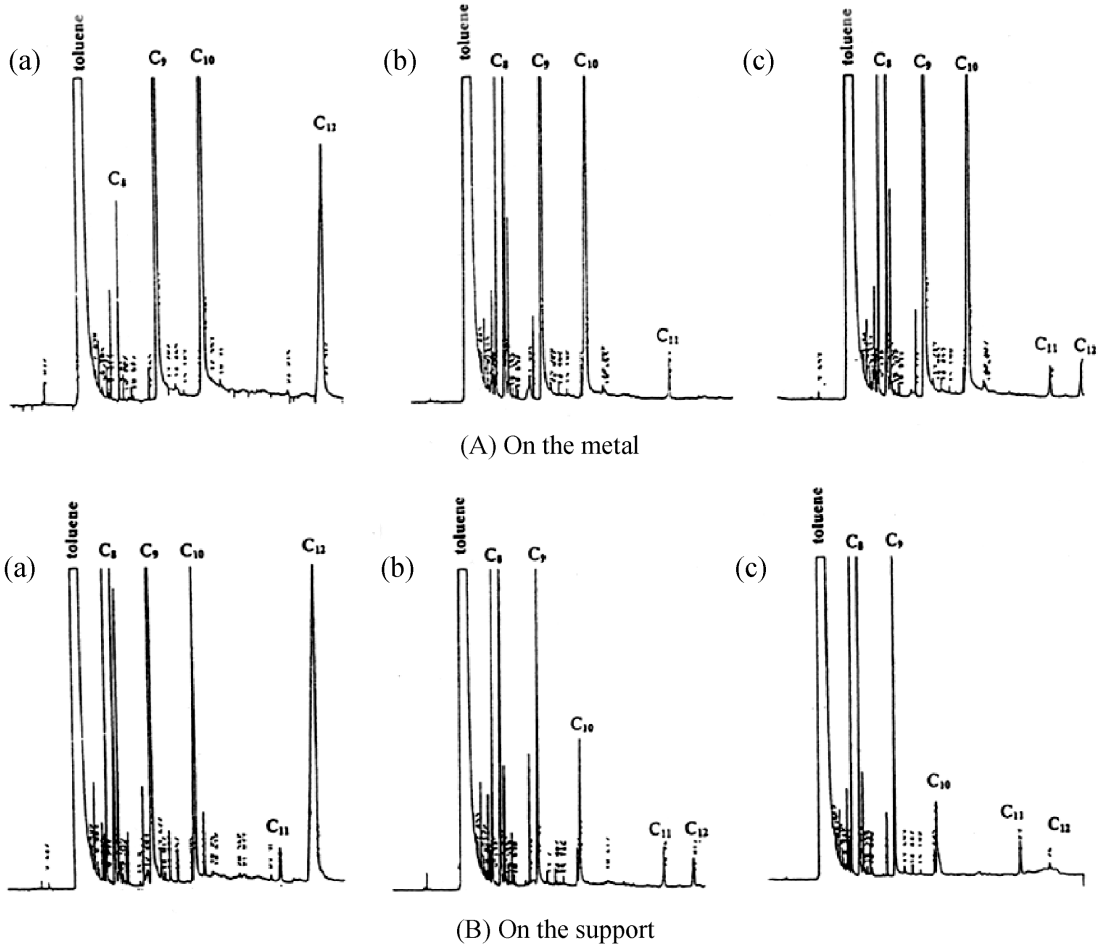

Fig. 3. Gas chromatograms for the coke extracts from a) the Pt-catalyst, b) the Pt-Sn catalyst and c) the Pt-Sn-K catalyst.

Table 1. Composition of soluble coke (mole)

Catalyst system	Metal					Support				
	C_8	C_9	C_{10}	C_{11}	C_{12}	C_8	C_9	C_{10}	C_{11}	C_{12}
Pt+Al_2O_3	284.77	335.36	107.36	12.18	199.08	47.26	431.80	235.78	1.01	115.16
Pt-Sn+Al_2O_3	250.49	123.88	32.61	7.65	6.03	338.17	361.74	156.05	6.95	0.00
Pt-Sn-K+Al_2O_3	183.76	70.12	21.53	6.41	1.33	378.77	452.21	198.01	5.54	6.64

stituted of lower carbon number fractions content (C_8-C_{10}), resulting in reduction density and mesoporosity of the cokes on both sites. The decrease in the acid site density was shown to hinder bi- and poly-molecular reactions involved in coking while the absence of a significant secondary-mesoporous system appeared to limit the room available for voluminous coke precursor molecules. The latter characteristic particularly resulted in significant reduction of insoluble coke content with decreasing mesoporosity.

3. Probability of Chain Growth of Coke

The hydrocarbon compositions in the cokes, which were analyzed as described previously, are presented in ASF plots in order to calculate a values, as shown in Figs. 4A and 4B. Fig. 4A demonstrates the Schulz-Flory diagrams for the soluble coke deposited on the metal sites in different catalysts. The modification of the catalyst influenced the probability of chain growth. Decreases in the a value were observed over the modified catalysts. The a values on both sites in each catalyst system were almost the same. This means that the chain continued to grow with a constant probability on both sites. The order of increasing a value was Pt>Pt-Sn>Pt-Sn-K. It implies that the addition of Sn and K considerably affected the change in the structure of carbon intermediates. The reasons for the difference in these results were not clear, but they may have to do largely with the relative adsorptivities of intermediates on these catalysts. As reviewed by Gerard and Beenackers [1999], the effect of stronger physisorption for larger olefins could predict the increase of the chain growth probability with chain length. Consequently, the intermediates obtained from the Pt were generally the heaviest in nature. The deviation of the Schulz-Flory diagram may be due to higher molecule formation of carbon, because Sn and K reduce the metal-carbon bond strength, leaving a larger metal surface, and promote the migration of coke precursors to the carrier. This is attributed to the greater transport of intermediates to the carrier, as associated with the literature reviews [Vértes et al., 1991; Lamy-Pitara et al., 1992].

4. Formation of Insoluble Coke on the Pt Supported Catalyst

The present study confirms that coke was built up on both the metal and support. Coke accumulation was found to take place predominantly on the support. Furthermore, it was found that coke had polyaromatic structure, while the aliphatic structure was not found. The extracted soluble coke had main components of C_8-C_{12}. The soluble coke on the metal was constituted of lower carbon atoms that could easily be removed. However, similar probabilities of the chain growth on both sites were found. This reason was attributed to the production of original coke precursor or coke intermediates

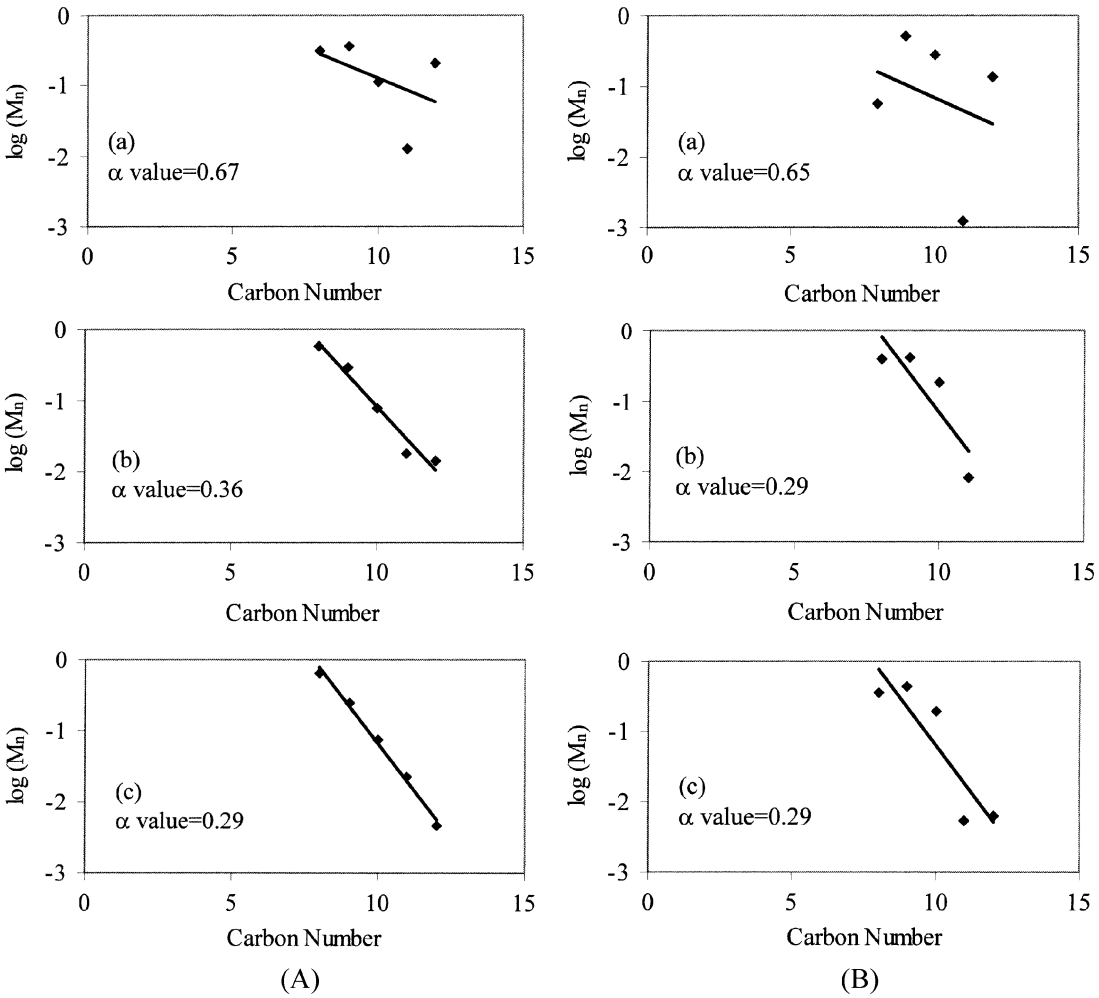

Fig. 4. (A) Schulz-Flory diagrams of soluble cokes from the metal sites: (a) Pt catalyst, (b) Pt-Sn catalyst and (c) Pt-Sn-K catalyst. (B) Schulz-Flory diagrams of soluble cokes from the supports: (a) Pt catalyst, (b) Pt-Sn catalyst and (c) Pt-Sn-K catalyst.

on the metal. It can reasonably be assumed that the soluble coke molecules are intermediates in the formation of the insoluble coke, which is composed of higher polynuclear aromatics [Reyniers and Froment, 1994; Radwan et al., 2000].

Moreover, the transport of the intermediates from the metal to support sites occurred, as discussed in the above analysis results. The more intermediate generated, the more carbonaceous deposits produced. The soluble coke molecules were therefore intermediates in the formation of insoluble coke, which was what allowed us to suppose that: (i) insoluble coke is not formed at low coke content, and (ii) the aromaticity of the soluble coke increases with the coke content (indeed insoluble soluble coke is composed of highly polyaromatic molecules). This discussion emphasizes the readsorption rate of coke intermediates on the metal that was the most importance on coke formation.

5. The Role of Sn and K Promoter on the Coke Formation

Coke formation is known to require relatively large clusters or ensembles of adjacent metal atoms. For the Sn addition, the presence of Sn improved the diluting of the active metal surface into smaller ensembles like surface alloy, which enhanced the catalysts resistance to deactivation. Carbon intermediates cannot readily form multiple carbon-metal bonds, which consequently inhibits the formation of highly dehydrogenated surface species that are intermediates for coking.

The addition of K into bimetallic Pt-Sn catalyst significantly decreased the catalyst deactivation. This may be related to the incorporation of tin into the platinum surface through the formation of a substituted alloy, while potassium may be present on the top of the platinum surface affected the changes of metal-support and the metal-metal interactions. On the other hand, K-doped catalyst significantly decreased the activation energy of HC dehydrogenation and the potassium diminished the interaction between Pt and Sn. This resulted in a weakening of Pt-C bond strength to make the catalyst less susceptible to deactivation by deposition of carbonaceous species on both sites as illustrated in these results. This is known as an electronic effect [Trimm, 1997].

CONCLUSION

A better understanding of coke formation on the metal and the support was obtained by employing the cooperative effect and SF techniques. Conclusions observed from the model system can be made as follows:

1. At the beginning of the reaction, a dominant reaction was found to be the polymerization which forms the soluble coke. The probabilities of the chain growth on metal and support revealed the same value.

2. Addition of promoter greatly reduced the coke formation, which is related with readsorption of the coke intermediates.

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