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Deactivation of the Metal and Acidic Functions for Pt, Pt-Sn and Pt-Sn-K Using Physically Mixed Catalysts

Sunee Srihiranpullop†, Piyasan Praserthdam and Tharathon Mongkhonsi

Department of Chemical Engineering, Chulalongkorn University, 10330, Thailand

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Abstract−The effect of K addition on the amount and dispersion of carbon deposition on metal sites and support sites was investigated on a physical mixture for hexane dehydrogenation. TPO, BET and ESR experiments were used for characterization. The K addition significantly decreases catalyst deactivation involving the amount of coke deposits and the density of carbon radicals on the metal and support sites because of ensemble and electronic effects, especially on the metal sites. Coke on the metal sites associated with carbonaceous species rich in hydrogen is less polymerized than coke on the support sites, corresponding to a more graphitic-like carbon.

Key words: Deactivation, Pt-based Catalyst, Pt-based Catalyst Modified with Sn and/or K, Physically Mixed Catalyst

INTRODUCTION

Catalytic processing of many industrial feedstocks is frequently accompanied by the deposition of carbonaceous deposits. For metal catalysts, supported mono- and multi-metal Pt containing catalysts are widely used for dehydrogenation in the petroleum and other industries. The addition of modifiers such as K and/or Sn into Pt-containing catalysts may change the selectivity of catalysts and can increase the resistance of carbon deposition [Rotrup-Nielsen, 1997; Trimm, 1983, 1999]. Coking on the catalyst surface has been reported to be a dynamic process [Lietz and Volter, 1984; Biswas et al., 1988; Liwu et al., 1990; Bond, 1987]. Carbon deposition takes place on both the active metal sites and the support surface for supported metal catalysts. Numerous species of carbon are observed to be deposited or formed on the surface of coked catalysts, ranging from carbides or microcrystalline and amorphous species to highly aromatic/graphitic carbons apparently through polymerization reactions and rearrangement for the polymer formed to be stabilized [Trimm, 1999; Biswas et al., 1988; Afonso et al., 1994]. Additionally, 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 metal phase and the second type burns at high temperatures (amorphous/graphitized carbon), associated with the support [Barbier, 1987; Biswas et al., 1987]. Although catalyst deactivation has been studied for many years, coke growth completely separated between coke on the metal and coke on the support sites has not been investigated sufficiently so far. In order to shed some light on this matter, physically mixed Pt/SiO_2 and Al_2O_3 was used in this work as a representative catalyst of Pt/Al_2O_3. Since the SiO_2 support in Pt/SiO_2 has a very low acidity, its contribution to the acidic function is, therefore, negligible. The mesh sizes of Al_2O_3 and SiO_2 selected for the physically mixed catalyst are based on ones that give approximately the conversion of hexane similar to that obtained from the conventional Pt/Al_2O_3 catalyst [Bond, 1987; Shum et al., 1984; Inaba et al., 1996]. With this simulated catalyst associated with the presence of K and/or Sn, much debate about how the additive metal brings about the enhancement in catalytic properties should be better conceived.

Thus, this work involved a detailed study of coke deposition on Pt, Pt-Sn and Pt-Sn-K catalysts employed in a physically mixed system where silica-supported platinum, Pt/SiO_2, represents the metal sites and acidic alumina, Al_2O_3, represents the support sites. The dehydrogenation of n-hexane was adopted to cause coked catalysts with carefully selected reaction conditions so that thermal cracking effects may be negligible. The main goal was to determine the effect of K and/or Sn on coke distribution over the metal sites and support sites in order to better understand the deactivation process of the catalysts.

EXPERIMENTAL

1. Catalyst Preparation

The alumina used in this study was obtained from Sumitomo Alumina Smelting (type NKH-3) and the silica was manufactured by Merck. They were ground and then sieved to retain particles with sizes between 60-80 mesh and 100-120 mesh, respectively. Three types of catalyst, namely, 0.3 wt% Pt/SiO_2, 0.3 wt%Pt-0.3 wt%Sn/SiO_2 and 0.3 wt%Pt-0.3 wt%Sn-0.6 wt%K/SiO_2, were employed in this work. The catalysts were prepared by impregnation method using H_2PtCl_6, $SnCl_2$ and KNO_3 as salt precursors. All chemicals used were normally analytical grade. After drying at 110 °C overnight, the catalysts were calcined in an air flow at 500 °C for 3 h.

2. Coking Reaction

Coked catalysts were prepared from the dehydrogenation reaction of n-hexane (10% hexane in N_2). The reaction was carried out by using an ordinary flow microreactor under atmospheric pressure. The ratio of physically mixed catalyst between Pt/SiO_2 and Al_2O_3 was 1 : 1. About 0.2 g of catalyst was used in each run. The experiments began after a reduction of catalyst under hydrogen at 500 °C for 1 h. Then, the temperature was adjusted to the reaction temperature of 475 °C and allowed to stabilize at that tem-

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†To whom correspondence should be addressed.
E-mail: sunee11@hotmail.com

perature for 30 min before hydrocarbon was introduced. The reaction was run for 120 min on stream in absence of hydrogen. The gas composition was analyzed by GC-14A (Shimadzu) equipped with a capillary column and a flame ionization detector. Finally, the coked catalyst comprised of coked Pt/SiO_2 and coked Al_2O_3 in different mesh size was sieved and separated for the characterization of coke on metal and coke on support, respectively.

3. Characterization

Many techniques were used to analyze both the fresh catalysts and coked catalysts. The oxygen consumed and carbon dioxide of coke were determined by temperature-programmed oxidation (TPO) using oxygen (1%O_2 in He). After heating at 500 °C for 1 hr to remove the adsorbed species, CO_2 produced was measured with a gas chromatograph equipped with a TCD and an on-line gas sampling valve. The heating rate was 10 °C/min up to 700 °C. BET surface area was measured by a surface area analyzer (Micromeritics, Model ASAP 2000). Additionally, to determine the density of carbon radicals of coke computed from the area under the curve, electron spin resonance spectra were analyzed with an X-band Jeol JES-RE2X spectrometer at room temperature.

RESULTS AND DISCUSSION

1. Carbon Deposition on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

Carbon depositions on Pt-based catalysts were investigated by temperature-programmed oxidation (TPO). On the active metal sites of various catalysts, Fig. 1A shows TPO profiles of Pt, Pt-Sn and Pt-Sn-K catalysts, respectively. It is observed that two peaks appear at 300 °C and 425 °C in every TPO profile. This indicates that carbon depositions 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 correspond to other reports [Lietz and Jovanovic, 1984; Jovanovic and Putanov, 1997]. In addition, it is obvious that coke is depositing on different sites on the different catalysts and affecting deactivation to diferring extents. From Fig. 1a, the difference of the modified catalysts is that, for Pt and Pt-Sn catalysts, the area of the first peak at lower temperature is less than that of the second peak at higher temperature. For the Pt-Sn-K catalyst, the situation is just opposite. Interestingly, the peak of the K-doped catalyst decreased more than any other catalysts, especially in the position at 425 °C. Previous studies [Lietz and Volter, 1984; Biswas et al., 1988; Liwu et al., 1990; Bond, 1987; Afonso et al., 1994; Barbier, 1987; Biswas et al., 1987] speculated that the active metal site was linked with the originally generated coke precursors. Consequently, K addition dramatically inhibits the production of coke intermediates, resulting in the lower area of carbonaceous compounds. It is seen that the order of their TPO areas is as follows: Pt>Pt-Sn>Pt-Sn-K. Furthermore, the total carbon accumulate on the metal sites of different catalysts listed in Table 1 was determined from the areas under the TPO profiles. The order of decreasing amount of carbon per gram is Pt>Pt-Sn>Pt-Sn-K. The areas of the TPO peaks were found to increase with the amount of carbon deposition for the Pt-based catalysts.

On the other hand, Fig. 1b exhibits spectra of TPO on the acidic sites of Pt, Pt-Sn and Pt-Sn-K catalysts. It is observed that a single peak appears on the spectra of TPO for the modified catalysts. Coke burns off at higher temperature, about 525 °C, compared with coke on the metal sites. This implies that the peak shifts to a higher temperature because of a larger degree of polymerization of coke [Padro et al., 1997]. Moreover, the TPO area of the Pt catalyst is diminished by the addition of Sn and especially in combination with K. As presented above, it is relevant to note that the surface coverage has different compositions, which are summarized in Table 1. The amount of coke on both the metal sites and support sites decreased significantly by the addition of Sn and/or K.

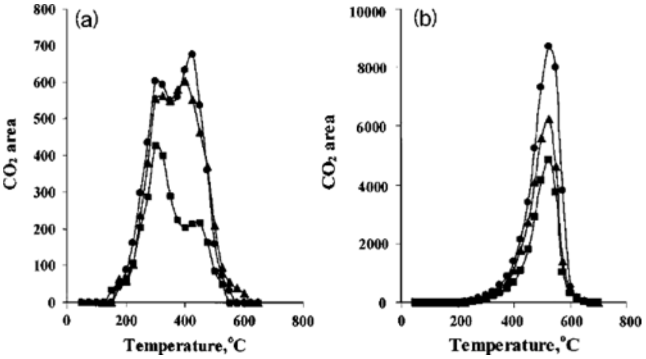

Fig. 1. (a) Temperature Programmed Oxidation of carbonaceous deposits produced on the metal sites with different catalysts. (b) Temperature Programmed Oxidation of carbonaceous deposits produced on the support sites with different catalysts.

Symbols: ● the Pt catalyst, ▲ the Pt-Sn catalyst and ■ the Pt-Sn-K catalyst.

Table 1. The amount of carbon deposited on the catalysts

Catalysts	Coke on the metal sites %C	Coke on the support sites %C
Pt catalyst	0.36	2.50
Pt-Sn catalyst	0.32	1.73
Pt-Sn-K catalyst	0.21	1.26

As mentioned above, carbonaceous materials deposit either on the active metal sites or on the acidic alumina support surface. The migration of coke precursor from one type of sites to another may possibly occur. Hence, a model of coking is proposed in Fig. 2. Hydrocarbons first undergo dehydrogenation and cracking on the active metal surface to form precursors of coke deposits. In general, unsaturated reaction intermediates such as monocyclic diolefins are formed and then reversibly adsorbed to form coke on the metal and in its direct vicinity. However, they can migrate to acid

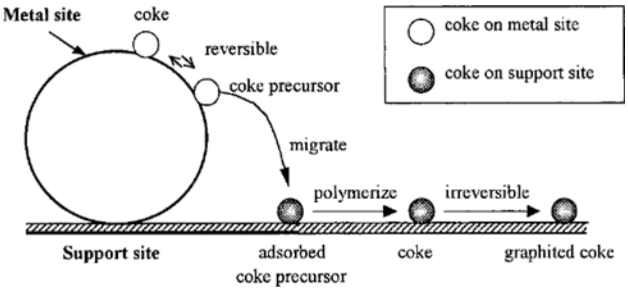

Fig. 2. Coking mechanism on both sites of catalyst.

sites and become polymerized to the more graphite-like material. Additionally, when comparing the amount of coke on the metal sites and the support sites as shown in Table 1, it is obvious that a small part of coke is located on the metal sites, whereas the major fraction is accumulated on the acidic sites. These results imply that coke deposits on the metal sites are less dehydrogenated and correspond to species rich in hydrogen in accordance with the literature reviews [Tao et al., 1991; Beltramini and Trimm, 1987]. Accordingly, the H/C ratio of coke deposits on metal sites is higher than that of the coke deposits on acidic support sites. This displays the different nature of coke between the metal sites and alumina. Finally, the modifications of Pt catalyst by addition of Sn and K are able to reduce the amount of coke on both sites.

2. Carbon Radicals of Coke on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

In order to examine the effect of Sn and K addition on coke formation with both sites in more detail, Electron Spin Resonance (ESR) has long been an effective technique to estimate the radical density of coke. ESR spectra are obtained by measuring the intensity vs. wavelength (or frequency) of a beam of electromagnetic radiation as it passes through a sample of matter, which is presented in a derivative trace of absorption curve. Then, the radical density can be computed from the integrated area of the spectra obtained [Werlz and Bolton, 1972; Lunsford, 1972]. Further coke radicals are representative of the overall coke, for both its nature and its amount because the amount of olefin or allylic radicals is characteristic of carbonaceous matter as introduced elsewhere [Butt and Peterson, 1988; Guisnet and Magnoux, 1989; Lange and Gutsze, 1988; Lange et al., 1988a, b]. In an earlier study, Karge et al. [Butt and Peterson, 1988; Guisnet and Magnoux; 1989] investigated low temperature coke (below about 500 K) and high temperature coke radicals (above about 500 K). They found that olefinic or allylic oligomeric species were low-temperature coke radicals while highly unsaturated species were high-temperature coke radicals. Consequently, the formation of radicals enables us to discriminate between individual coke of various catalysts including coke on the metal sites and the support surface. In this study, Fig. 3(A) shows the ESR spectra of coke radicals for various catalysts on the metal sites. The carbon radical's density computed form the total peak area is given in Table 2. The g value of coke radicals is estimated to be 2.003 in agreement with earlier literature [Lange et al., 1988; Gutsze et al., 1997]. It is found that the modification of catalysts displays a dominant role in reducing the intensity of carbonaceous radicals as well as reducing the amount of coke precursors. Interestingly, the K-doped sample has a sharply lower amount of radicals of coke, by 27 times, compared with the Pt catalyst, resulting in the lowest amount of coke shown in Table 1. Another modification of the Pt catalyst diminishes carbonaceous radicals about 1.7 times. A comparison between ESR results and TPO results, which are described above, exhibits a good correlation between the number of radicals and the amount of coke.

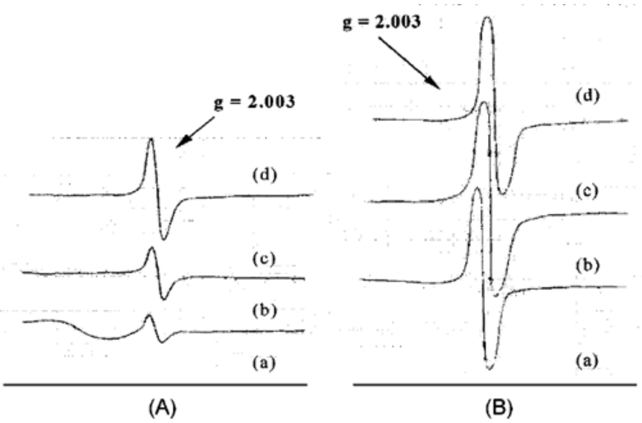

Fig. 3. (A) ESR spectra of coke on the metal sites; (a) reference spectrum before coking reaction (b) coke on Pt-Sn-K catalyst (c) coke on Pt-Sn catalyst and (d) coke on Pt catalyst. (B) ESR spectra of coke on the support sites; (a) reference spectrum before coking reaction (b) coke on Pt-Sn-K catalyst (c) coke on Pt-Sn catalyst and (d) coke on Pt catalyst.

Table 2. The density of carbon radicals of coke per gram catalyst

Catalysts	The metal sites	The support sites
Pt catalyst	8.55×10^5	3.02×10^6
Pt-Sn catalyst	5.18×10^5	2.07×10^6
Pt-Sn-K catalyst	3.17×10^4	1.83×10^6

For the acidic alumina, the ESR spectra of radicals are illustrated in Fig. 3(B) with the Pt-based catalysts. Table 2 also lists their intensity on these sites. This characteristic of carbon radicals is similar to that already reported above. However, the density of coke radicals is greater on the alumina sites than on the active metal sites. It is clear that the amount of radicals compared with the carbonaceous radicals intensity of Pt catalyst is reduced by 1.45 times for Sn modification and 1.65 times for K addition. As mentioned above, this indicates that the metal sites are relevant for generating coke intermediates, which are adsorbed to form coke on this site and can migrate to the acidic support sites. Thus, if the modification of catalysts inhibits the production of coke precursors on the metal sites, then the amount of carbonaceous compounds is consequently decreased. From the result shown in Table 2, it is obvious that the K-doped sample dramatically reduces coke radicals concerned with coke species on the active metal sites. Accordingly, a lower amount of coke deposits is produced as shown by the TPO results.

3. The Changes of Textural Properties and the Dispersion Factors of Coke on the Metal Sites and the Acidic Sites of the Pt, Pt-Sn and Pt-Sn-K Catalysts

Coking is claimed to be responsible for a decrease in the specific surface, pore surface and pore volume depending on a limitation of diffusion (dispersion) and nature of coke deposits. As a result, we investigated texture changes in surface area before and after coke deposition of Pt-based catalysts. Jovanovic and Putanov [Jovanovic and Putanov, 1997] introduced the dispersion factor to consider catalyst degradation of Pt/Al_2O_3 and Pt-Re/Al_2O_3. The dispersion factor is the ratio of change of surface area to the quantity of carbon deposits. Higher values of dispersion factor proved that carbon deposited on this catalyst is better dispersed with the fine small grain structure. In this work, the dispersion factor of carbonaceous deposit defined as the ratio of change of surface area to the amount of coke was investigated on Pt, Pt-Sn and Pt-Sn-K catalysts. Table 3 summarizes the textural properties of catalyst

Table 3. The textural properties of catalysts samples before and after testing and dispersion factor

Catalysts	The metal sites			The support sites		
	SA (m^2/g)		Dispersion factor	SA (m^2/g)		Dispersion factor
	Fresh	Used		Fresh	Used	
Pt catalyst	447	386	171	390	343	19
Pt-Sn catalyst	417	325	291	390	330	35
Pt-Sn-K catalyst	380	283	462	390	283	85

samples before and after coking and the dispersion factor, which is separated into the metal sites and the acidic alumina in each catalyst. The change of surface area may be attributed to the blockage of catalysts by coke, though thermal sintering and the other factor except coking should not be ruled out. It has been found that the modified catalyst lost their surface area after the reaction more than the unmodified one containing only platinum. This might be due to the fine structure of coke readily occurring in the case of Pt catalysts with the presence of Sn and/or K, which easily block the existing porous area of the catalyst. The results obtained were consistent with the report of fine small grain structure of coke deposits for the modification catalysts suggested in literature reviews [Lange and Gutze, 1988; Kirszensztejn et al., 1991; Mann, 1997]. Moreover, noticeably higher values of dispersion factors are obtained from the Pt-Sn and particularly Pt-Sn-K catalysts as illustrated in Table 3. Compared with the Pt catalyst, the dispersion factor of the Pt-Sn catalyst is about 1.7 times on the metal sites and about 1.8 times on the acidic sites. In the case of K addition, dispersion factors on the metal sites and on the support sites are about 2.4 times and 4.5 times compared with Pt catalyst, respectively.

3. The Influence of Sn and K Addition on Coke Formation

The main theories put forward to account for the improved properties of multi-metallic catalysts tend to involve either geometric or electronic effects. Coke formation is known to require relatively large clusters or ensembles of adjacent metal atoms. For the Sn addition, the presence of Sn improves the diluting of the active metal surface into smaller ensembles, which enhances the catalysts' resistance to deactivation. The addition of Sn to Pt catalyst forms substitutional surface alloys, and it has been shown that Sn interacts with platinum on silica to form a Pt/Sn alloy [Rostrup-Nielsen, 1997; Trimm, 1983, 1999; Hill et al., 1998; Macleod et al., 1998]. Thus, carbon intermediates cannot readily form multiple carbon-metal bonds. Furthermore, this inhibits the formation of highly dehydrogenated surface species that are intermediates for coking. According to Padro et al. and Larsson et al. [Padro et al., 1997; Larsson et al., 1996], one reason is that coke deposits bind more strongly to the Pt catalyst than to the Pt-Sn catalyst.

From TPO profiles and ESR spectra of the metal sites, the less strong attachment of the adsorbed species to the metal surface would be explained by the significant minimizing of these sites and promotion of the migration of coke precursors to the carrier. These effects are evident by the change in the heights of peaks in the TPO profiles and ESR spectra.

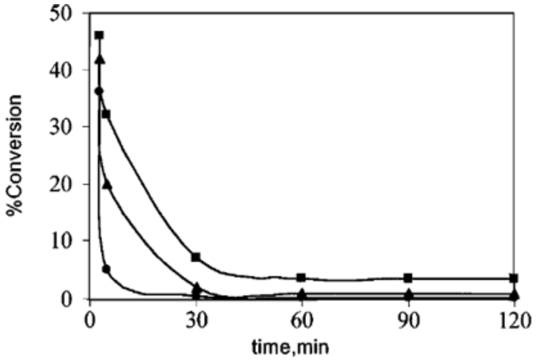

Fig. 4. %conversion of hexane dehydrogenation for physically mixed catalysts.
Symbols: ● the Pt catalyst, ▲ the Pt-Sn catalyst and ■ the Pt-Sn-K catalyst.

The addition of K into bimetallic Pt-Sn catalyst produces a significant decrease in the catalyst deactivation as shown in Fig. 4, illustrating the conversion of hexane as a function of time. The decline in conversion is slower for catalysts containing tin and potassium than for catalysts containing platinum only because less coke was formed on the modified catalysts. In Fig. 4 and Table 1, it is obvious that Pt catalyst deactivates quickly and a considerable amount of coke was formed. This may be related to the incorporation of tin into the surface of platinum through the formation of a substituted alloy, while potassium may be present on top of the platinum surface. As described elsewhere [Padro et al., 1997; Hill et al., 1998], it was found that K- doped catalyst significantly decreases the activation energy of CH dehydrogenation, which would suggest that K effect diminishes the interaction between Pt and Sn. This modification in the interaction between both metal components could be due either to a direct addition of K on the metal phase or to an indirect effect of the alkali metal addition to support, which could change the metal-support and the metal-metal interactions, as suggested in the literature [Hill et al., 1998; Larsson et al., 1996; Cortright and Dumesic, 1995]. This results 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 Fig. 1, Table 1, Fig. 3 and Table 2. This is known as an electronic effect [Rostrup-Nielsen, 1997; Trimm, 1983, 1999; Cortright and Dumesic, 1995].

CONCLUSION

The addition of Sn and K resists coke formation both on the metal sites and on the support sites. It seems due to the ensemble and electronic effects. They also reduce the density of carbon radicals and affect the nature of coke. For textural properties, noticeably higher values of dispersion factor were obtained on Pt-Sn and Pt-Sn-K catalysts than on Pt catalysts. This can indicate that coke on the Pt-Sn and Pt-Sn-K catalysts has a softer coke nature. Specifically, K addition significantly inhibits coking. Comparing coke on the metal sites and on the support sites, it can be concluded that coke on the metal is soft in nature, rich in hydrogen and has a lower degree of polymerization.

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