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ROLES OF Pt AND ALUMINA DURING THE COMBUSTION OF COKE DEPOSITS ON PROPANE DEHYDROGENATION CATALYSTS

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Abstract – Temperature programmed oxidation of coke deposited on Pt based propane dehydrogenation catalysts reveals that the deposited coke can be categorised into three groups according to their burning temperatures. When coke was separated from the catalyst, however, only one TPO peak could be observed. Experimental results suggest that γ-Al_2O_3 enhances the coke burning process by increasing coke surface area contacts to oxygen. Pt may also act as a catalyst for the coke combustion reaction. Experiments also show that changing dehydrogenation reaction temperature, variation of H_2/HC ratios, addition of only Sn or Sn and an alkali metal (Li, Na and K) can significantly affect the amount of each coke formed. Sample weight used in the temperature programmed oxidation (TPO) experiment also affects the resolution of TPO spectrum.

Key words: Temperature Programmed Oxidation, Dehydrogenation, Pt/γ-Al_2O_3, Coke Combustion

INTRODUCTION

Deactivation by coking is a serious problem of the Pt/γ-Al_2O_3 catalyst used in propane dehydrogenation process. Since the deactivation occurs in a very short time, *i.e.*, a few minutes, the deposit coke must be removed continuously by burning with gas containing oxygen to maintain catalyst activity. The burning temperature, however, must be carefully controlled to avoid local hot spots, which leads to sintering of metal sites and/or phase transformation of catalyst support, and must not too low to remove coke. In addition, some promoters such as Sn and alkali metals are also added to increase catalyst life and reduce the deposition of coke.

Coke has several complex structures by nature. For this reason, the coke category normally uses combustion temperature. Coke which can be burnt at about the same temperature is suggested to have a similar structure. Usually, the more graphitic the structure is, the higher the combustion temperature is. Temperature programmed oxidation (TPO) technique is such a technique commonly used in characterization of coked catalysts to give information on location and total amount of carbon deposited by several research groups because of its simplicity [eg. Barbier et al., 1980, 1985; Carlos et al., 1989; Pieck et al., 1989; Liwu et al., 1990; Zhang et al., 1991; Querini and Fung, 1994, 1997; Bartholdy et al., 1995; Larsson et al., 1996; Marécot et al., 1996; Reyes et al., 1996]. This technique measures the amount of CO_2 formed during the burning of coked catalyst using a thermal conductivity detector (TCD). With careful experiment, H_2O formed from the coke combustion reaction can be measured and C : H ratio of coke can be calculated. Some researchers have suggested the use of methanator to convert CO_2 to CH_4 and used a flame ionization detector (FID) to enhance sensitivity of the technique [Querini and Fung, 1994, 1997]. The TPO experiments were normally carried out in the temperature range 0-900 °C with a heating rate between 5-10 °C/min. O_2 diluted in an inert gas was normally used as coke removal gas. However, in some specially designed experiments other gas mixtures such as H_2 and H_2O have been applied [Querini and Fung, 1997]. Two major CO_2 evolution peaks were commonly observed. The first peak appeared in the temperature range 350-450 °C. This peak was identified as the combustion of coke on a metallic site [Barbier et al., 1980]. The second peak normally appeared around 450-550 °C depending upon the total amount of coke on the catalyst samples. This peak is ascribed to coke deposited on the support.

The TPO profile, however, does not give any information on coke structure, but it is widely believed that the higher the burning temperature, the more graphitic like the structure. It is still a subject of discussion that the appearance of several CO_2 evolution peaks in the TPO spectra is due to the difference in coke structure and/or location.

In our research, we have tried to identify relationships between the burning character of coke deposited on metal site and catalyst support, and catalyst composition. Factors affecting TPO technique were also investigated.

EXPERIMENTAL

Pt/γ-Al_2O_3, Pt-Sn/γ-Al_2O_3, Pt-Sn-Li/γ-Al_2O_3, Pt-Sn-Na/γ-Al_2O_3 and Pt-Sn-K/γ-Al_2O_3 catalysts were prepared by conventional dry impregnation method using H_2PtCl_6, $SnCl_2$ and appropriate alkali nitrate salts. γ-Al_2O_3 was obtained commercially from Sumitomo Aluminium Smelting Co. Ltd. The specific surface areas were determined from nitrogen physisorption using a Micromeritics ASAP 2000 instrument. Pt active site was measured

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Table 1. Catalyst composition, surface area and Pt active site

Catalysts	wt% of metal loading					Surface area	Pt active site
	Pt	Sn	Li	Na	K	m^2/g cat	molecule CO/g cat
$Pt/\gamma\text{-}Al_2O_3$	0.3	-	-	-	-	330	5.55×10^{18}
$Pt\text{-}Sn/\gamma\text{-}Al_2O_3$	0.304	0.292	-	-	-	320	3.17×10^{18}
$Pt\text{-}Sn\text{-}Li/\gamma\text{-}Al_2O_3$	0.299	0.266	0.528	-	-	248	3.26×10^{18}
$Pt\text{-}Sn\text{-}Na/\gamma\text{-}Al_2O_3$	0.288	0.269	-	0.590	-	289	4.26×10^{18}
$Pt\text{-}Sn\text{-}K/\gamma\text{-}Al_2O_3$	0.283	0.311	-	-	0.577	304	4.17×10^{18}

by CO adsorption technique on the basis that one CO molecule is adsorbed per one Pt atom [Biswas et al., 1987]. The actual catalyst compositions, surface areas and number of Pt active sites of fresh samples are reported in Table 1. The catalysts were coked using the dehydrogenation reaction of propane to propene at different reaction temperatures and H_2/HC ratios. 20 % vol C_3H_8 balanced with N_2 was used as reactant gas. In order to change H_2/HC ratio, an appropriate amount of N_2 was replaced by H_2. All results reported here are based on the following reference conditions unless otherwise stated: reaction temperature 600 °C, time on stream 40 minutes, H_2/HC=0. The reactor was operated at atmospheric pressure and the gas hourly space velocity (GHSV) was 25,000 hr^{-1}. Coke deposited on the catalyst was studied by Temperature Programmed Oxidation (TPO). Thermogravimetric analysis (TGA), Shimadzu model TG-50, was also used to cross check some TPO results. In the TPO experiment, 1 % O_2 in He was used as the oxidizing gas. About 90 mg of coked catalyst sample was used in each experiment unless otherwise stated. The coked catalyst sample was packed in a quartz tube, supported by glass wool and burnt at a constant heating rate of 5 °C/min from 50 °C to 700 °C. The effluent gas was directed to a gas chromatograph Shimadzu model GC-8A equipped with a 1 ml gas sampling loop and a thermal conductivity detector. The gas sampling was performed every 5 minutes (or 25 °C). Our experience on TGA and results reported in some literatures [*e. g.* Barbier et al., 1980, 1985] have shown that the main TPO peaks usually distance from the adjacent peak(s) by about 100 °C. Therefore, this sample interval is considered appropriate. In addition, it can be seen later that there are other factors affecting locations of TPO peaks apart from C/H ratio of coke.

Separation of coke from the coked catalysts was achieved by dissolving the coked catalyst sample in a warm mixture of HCl and HNO_3. $\gamma\text{-}Al_2O_3$ and Pt can dissolve in this acid solution, but SiO_2 which is present as the major impurity (up to about 20 wt%) cannot dissolve in this manner. Several drops of HF have to be added to the solution to dissolve the remaining SiO_2 particle but coke. Separation of coke from the solution was performed by using a centrifuge. After each centrifuge, the clear solution was pipetted out and distilled water was added instead. This step was to wash any remaining acid and dissolve solid from the coke sample. The centrifugal and washing steps were repeated until most of the acids added were removed. The obtained coke sample then was dried in air at 110 °C overnight. Further details of experimental system and experimental procedures are described elsewhere [Atchara, 1995; Bualom, 1995; Nonglak, 1996].

RESULTS AND DISCUSSION

Effects of H_2/HC ratio and reaction temperature are shown in Figs. 1 and 2, respectively. From the TPO spectra, despite the differences in H_2/HC ratio and reaction temperature, we can categorise coke into three groups. The first group appears in a very small amount and burns around 110 °C (in the small boxed area). Since this coke appears in a very small amount, there will be no further discussion on this coke. The second coke is the one that can be removed at around 450 °C and the last one must use temperatures higher than 450 °C. Location of the second coke on the coked catalyst was determined by the CO adsorption technique. The CO adsorption results obtained from coked catalysts regenerated at different temperature show that burning the coked catalyst at 450 °C can recover all Pt active

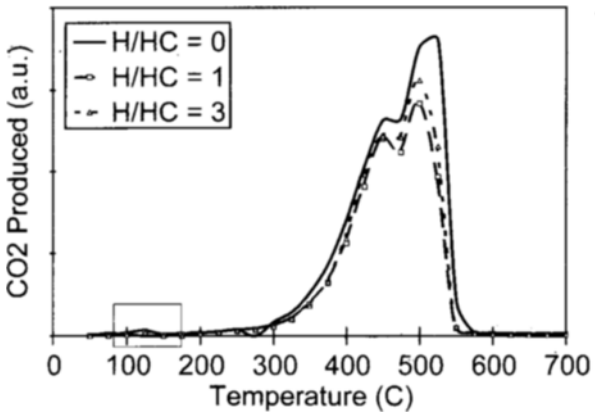

Fig. 1. TPO spectra of $Pt\text{-}Sn/\gamma\text{-}Al_2O_3$ at different H_2/HC ratios.

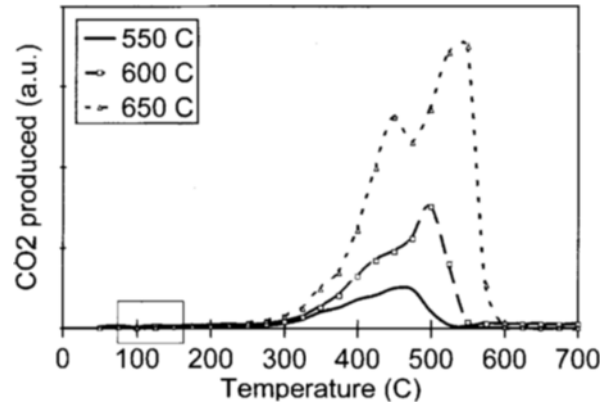

Fig. 2. TPO spectra of $Pt\text{-}Sn/\gamma\text{-}Al_2O_3$ at different reaction temperatures.

sites. The TPO spectra of the coked catalyst regenerated at 450 °C (not shown here) did not show the peak of the second coke while the peak of the third coke still remained. Therefore, it can be identified that the second coke is the coke on metal site and the last is the coke on alumina support. The TPO results clearly show that both H_2/HC ratio and reaction temperature can alter the amount of coke formed. The burning characteristic of the coke on the coked catalysts is still the same. Reaction temperature rather than H_2/HC ratio has a stronger effect on the amount of coke. The slight shift of TPO peaks in both figures is the effect of the amount of coke on each sample. The sample with a larger amount of coke exhibits a higher temperature of TPO peak for the same group of coke.

Fig. 3 shows TPO spectra of coked Pt-Sn/γ-Al_2O_3 after being used at different time on stream. The TPO peak of the coke on the metal site still appears around 450 °C and seems not to depend on the total amount of coke. The location of the peak of coke on the support shifts to a higher temperature as the total amount of coke increases. At a high coke content the peaks of the coke on the metal site and on the support lump together into one large peak.

The effect of promoters (Sn, Li, Na, K) on propene yield is demonstrated in Fig. 4. Fig. 4 shows that addition of Sn to the Pt catalyst significantly enhances propene yield. Addition of Li, Na and K further increases yield of propene. TPO spectra of the unpromoted and promoted catalysts are shown in Fig. 5. Despite the differences in catalyst compositions and

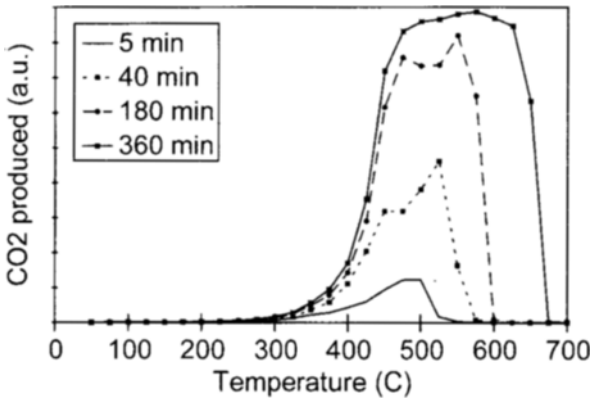

Fig. 3. TPO spectra of Pt-Sn/γ -Al_2O_3 at different time on stream.

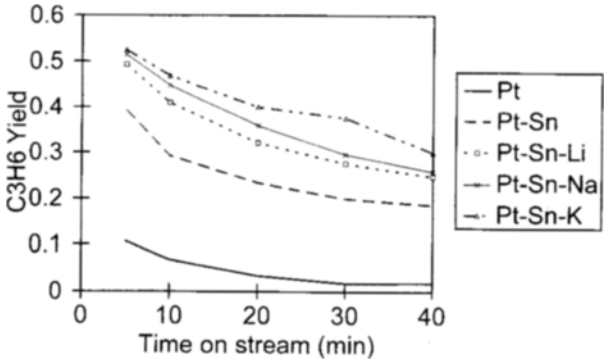

Fig. 4. Effect of promoters on propene yield.

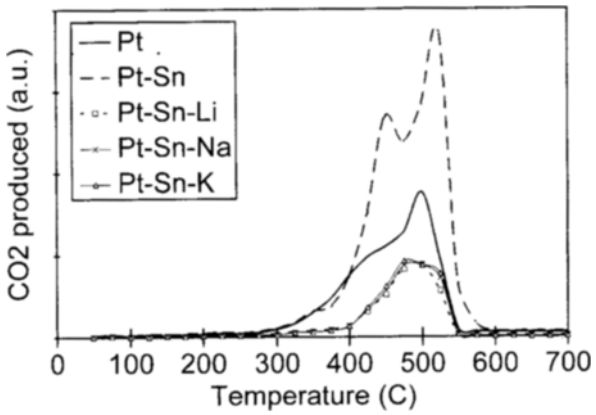

Fig. 5. Effect of promoters on TPO spectra of Pt based catalyst.

reaction conditions, all TPO spectra exhibit similar behaviour. It is found that Pt-Sn catalyst produced more coke per unit mass of catalyst more than the unpromoted one. This is because propane conversion is higher on Pt-Sn catalyst, and if propane conversion is taken into account it will be found that selectivity to coke on Pt-Sn catalyst is lower. Addition of alkali metals suppresses the formation and accumulation of coke on metal sites and catalyst support by reducing acidity of the catalyst surface. However, no significant effect on locations of TPO peaks is observed.

The roles of Pt and γ-Al_2O_3 during coke combustion were clarified by separating the coke from the coked catalyst and performing a TPO study on the carbonaceous compound obtained. Since the results shown previously indicate that the structure of coke formed does not likely to depend on reaction condition and catalyst composition, only the coke formed on Pt-Sn/γ-Al_2O_3 at the reference condition was studied. Fig. 6 demonstrates the comparison between TPO spectra of the coked catalyst and the coke sample. The figure shows that the absence of the metal and the support has an obvious effect on the characteristics of coke combustion. Only one CO_2 evolution peak was detected from the coke sample. This peak also appears at a higher combustion temperature than that of the coked catalyst. This result suggests that the appearance of two CO_2 evolution peaks of the coked catalyst relates to the

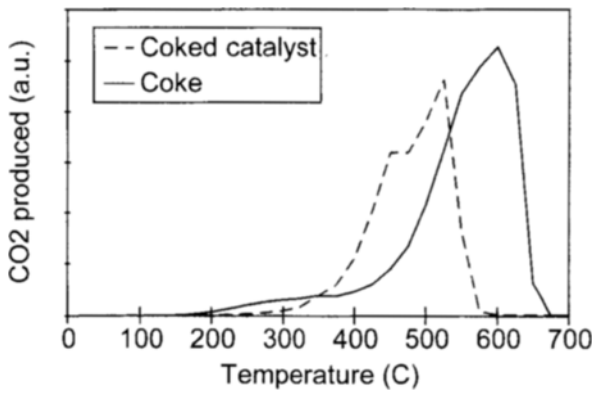

Fig. 6. Comparison between TPO spectra of coked Pt-Sn/γ-Al_2O_3 catalyst and coke separated from Pt-Sn/γ-Al_2O_3 catalyst.

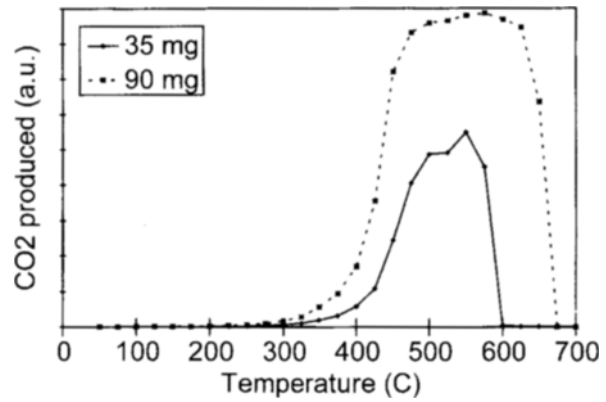

Fig. 7. Effect of weight of coked catalyst (Pt-Sn/γ-Al_2O_3) on TPO profiles.

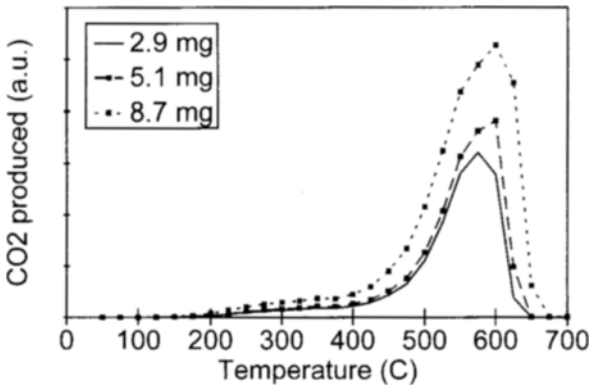

Fig. 8. Effect of weight of coke separated from coked Pt-Sn/γ-Al_2O_3 on TPO profiles.

presence of the metal and the support. The high surface area and porosity of the support promote the combustion of coke by increasing coke surface area contact to oxygen. In addition, Pt may also be involved in the combustion process by acting as a catalyst since CO_2 evolved from the coked catalyst at a lower temperature than the coke sample.

The effect of sample weight on the resolution of TPO spectra is shown in Fig. 7. TPO spectra of 90 mg coked catalyst sample show only one large peak but it cannot be determined whether it consists of only one large peak or several small peaks lumped together. Using a smaller sample amount shows a different result, *i.e.*, better resolution. Here, when the amount of coked catalyst sample was reduced to 35 mg a shoulder near 500 °C becomes distinct from the peak at 550 °C.

Fig. 8 shows TPO spectra of a coke sample by using different sample weights. The spectrum patterns do not show any obvious difference. Only one combustion peak can be observed independent from sample weight. When the TPO spectrum of the coke sample is superimposed on the TPO spectrum of coked catalyst (Fig. 6), one can see that the coke on the catalyst can be burned off at a lower temperature. This result provides further support for the hypothesis that both the metal site (in this case Pt) and the support should play some role in coke burning process.

CONCLUSIONS

At least three groups of coke can be present on the Pt based dehydrogenation catalyst. The first group, which appears in a very small amount, is the coke that can be removed at a temperature only around 110 °C. The second group, the amount of which increases with time on stream but up to a limit, can be burned using higher combustion temperatures, *i.e.*, >450 °C. These two groups are determined to be the coke that deposits on metal sites. The third coke, which keeps increasing with time on stream and can be removed by using further higher temperature, *i.e.*, 550 °C, is the coke that deposits on alumina support. Experiments also show that changing dehydrogenation reaction temperature, variation of H_2/HC ratios, addition of Sn or alkali metals (Li, Na and K) significantly affect mainly the amount of each coke formed.

TPO is a powerful technique widely used in coke characterization. However, one must be careful in interpreting the obtained spectra since the amount of sample used can lead to a different explanation. An optimal sample weight which is a compromise between sensitivity and resolution of the technique should be determined.

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