

CHAPTER II

BACKGROUND

2.1 Deactivation of catalyst

Heterogeneous catalytic processes, especially in hydrocarbon conversion reactions, generally show a decrease in activity overtime. The time when a catalyst delivers unacceptable performance depends on process conditions and also the types of reactions. It varies from a few seconds contact time for a catalytic cracking catalyst to more than a year for catalyst in the reforming of naphtha.

The causes of losing catalyst activity can be associated with (i) Sintering, (ii) Loss of active species, (iii) Poisoning and (iv) Fouling.

Sintering happens when a catalyst loses its specific surface sites. The loss of active species is connected to the loss of dispersion of the metal crystallites. These occur when the catalyst is operated above the normal range of temperature. Poisoning is often caused by an impurity in the feed stream or products that induce the side reactions. Physical grinding in an agitated vessel is also reported as causing poison-like behaviour. In some cases, selective poisoning is used to increase one reaction on a multifunctional catalyst by inhibiting undesired functions. Causes of catalyst fouling may be divided into 2 groups (i) Carbonaceous deposits-Coke and (ii) Impurity fouling. Coke is associated with main chemical reactions (activate organic substance) and cannot be reduced by purification of the feed. This is the distinction between the two types. Fouling is dealt with relatively large amount of deposit that

cover the catalyst active sites. Pore blocking can occur and consequently cause the temporary loss in the activity.

In catalysis deactivation, poisoning and fouling processes can all occur at the same time with some sintering of the catalyst.

2.2 Catalyst fouling by Coke

This deactivation species is associated with main reaction. The way to decrease coke is by modifying catalyst function and reaction conditions. Various types of hydrocarbon reactions can produce coke under appropriate conditions. Generally the larger numbers of carbon atoms in molecules, such as aromatic and naphthenic rings, have higher potential to form coke. Reactions in which coking is important are catalytic reforming, isomerization and various hydrogenation/dehydrogenation. In most cases the catalyst may be regenerated by burning off the coke in a diluted oxidizing gas stream. Then the catalyst activity goes to the initial value again. The Coke burning is an exothermic reaction and careful operation must always be adapted to avoid catalyst damage. (Thermal deactivation by hot spot)

2.2.1 Coking path and mechanism

Hughes (1984) reviewed Froment and Bischoff (1961) work on a fixed bed reactor. The profile of coke deposits suggests both parallel and series fouling paths. When the reactants have a high concentration, they act as coke precursor and follows the parallel path. When the products concentrations are high, a series fouling path becomes significant. For Propane dehydrogenation

over Pt catalyst, multiple Pt atom sites were required (Dautzenberg et al., 1977) for coke formation.

The thermograms of the Temperature Programmed Oxidation(TPO) of coke on naphtha reforming catalysts (Pt/SiO₂ and Pt/Al₂O₃-Cl) were studied by Parera et al. (1983) . Each type of catalyst shows only one peak, 123 to 369 °C for Pt/SiO₂ and 369 to 555 °C for Al₂O₃-Cl. This result corresponds to the results of Barbier et al. (1985). The first combustion zone (lower temperature) belongs to the burning of the coke deposit on the metallic function (Pt).The second zone(higher temperature) belongs to the coke deposited on the acidic sites (Al₂O₃-Cl). The hydrogen to carbon ratio of different coked catalysts and the coking time suggests that the carbon deposits on the metal are less dehydrogenated than coke deposited on the support, and reaching a constant amount in the first minutes of the reaction and then remaining constant while the overall coke is still accumulating.

Caruso et al. (1989) found a continuous decrease in coking rate for reforming catalyst (Pt-Re/Al₂O₃) with increasing time on stream. The desired reaction and coking are also inhibited by the significant amount of coke on the catalyst surface.

Barbier et al. (1989) found an unidentifiable type of coke deposit on the catalyst that correspond to TPO profiles at 380-440 °C in the same conditions as already described. Because this peak appears between the two identified peaks (Coke on metal and supports), two different hypotheses were established to explain this phenomenon. One hypothesis states that it is coke deposited on a different type of acid center on alumina, based on the rapid appearance of the 3rd peak and also due to different hydroxyl groups found by

IR. Another compares the TPO profile with coke deposited on alumina that gave only the 3rd peak. This new type of coke may be deposited on the support near the metal particles with carbon filaments that can migrate from metal sites.

2.2.2 Effect of reaction conditions

Trimm (1983) has reviewed some methods to control coke deposits by modifying both physical and chemical reaction conditions. Dilution and Gasifying agents were introduced to the system. This decreased coke precursors and increased carbon gasification pathway.

Barbier et al. (1985) studied the coke deposited on the Pt/Al₂O₃-Cl during cyclopentane conversion. Both classical fixed bed and simple hydrogen/carbon analysis method were used. Smaller metal crystallites showed a resistance to higher coke deposits. This can be explained either by geometric or electronic transfer theories.

The effect of operating condition on Pt/Al₂O₃ over cyclopentane conversion was investigated by Barbier et al. (1988, 1989). An increase in active metal dispersion can delay the coking reaction at high reaction temperature. Low temperature gives the opposite result. Increased pressure promotes the degree of graphitization of coke on the support and inhibits the catalyst activity of Pt metallic phase. Steam can inhibit coking on the support also. The higher Pt in Pt/Al₂O₃ catalyst for reforming, the higher in percentage conversion and coke formation. Increases in intermediate hydrocarbons (coke-precursors) were discussed by Parera et al. (1989).

2.3 Effect of promoters loading

Addition of nonmetallic state Tin to nonacidic alumina to form a dual-function catalyst noticeably reduces the deactivation of the dehydrocyclization activity for benzene production (Dautzenberg et al., 1980). Not only the stability but also the selectivity of the Pt function is modified by addition of Sn. The formation of coke on the metal function is reduced by changing the adsorption properties of Pt by Sn, the ensemble effect explanation. Pt-Sn over Reforming catalyst give the corresponding adsorption improvement but explained as an Electronic effect (Burch,1980).

Lieske et al. (1987) compared the adsorption and coke formation from C_1 and C_6 between Pt/ Al_2O_3 with Pt-Sn/ Al_2O_3 catalyst. The ensemble effect was selected to explain the result. Coke precursors transferred from Pt sites, where they formed, to the support. The reduction in the strength of chemisorption of ethylene on the Pt surface was reported by Lin et al. (1990). With the same amount of coke, Pt catalyst has less proportion of carbon deposited on the support than Pt-Sn catalyst. Afonso et al. (1994) studied the coke deposits from Pt-Sn catalysts during dehydrogenation by solvent extraction. They also found more than one structure of carbonaceous material occurring. These help explain the previous results on the components of coke deposits from TPO studies of Pt-Ir/ Al_2O_3 and Pt-Re/ Al_2O_3 (Barbier et al., 1990). All types of coke are different in Hydrogen content.

2.4 Catalyst regeneration

From the previous section it has been shown that coking cause deactivation on the catalyst. The catalyst may be replaced or regenerated, depending on economical factors, to achieve acceptable performance.

For the catalyst deactivated by carbonaceous material, burning off the coke with an oxidative mixture can return the catalyst to its initial activity. Regeneration also acts to remove the moisture and redisperse the metal crystallites. The regeneration procedure can remove both carbonaceous supported coke and metal deposited coke (Thaddeus et al., 1983). The main problem in regeneration is to burn off the coke without creating irreversible damage to the catalyst, since a catalyst may be expected to be regenerated more than one hundred times in its life time.

2.4.1 Metal redispersion

Lieske et al.(1983) discussed the physical process to redisperse the Pt atom on the support by oxygen. The effects of Cl⁻ are summarized below.

(i) There is no redispersion without oxidation of crystalline Pt and no oxidation without redispersion. Because redispersion is associated with a proportional increase of the Pt oxidation state. (Redispersion and oxidation of crystalline Pt are inseparably connected)

(ii) The redispersion is unachievable with chloride free catalyst. The almost unchanged chlorine percentage in the spent catalyst has been reported by Parera et al.(1989)

(iii) The oxidized Pt must be movable and emigrated on the surface of the alumina.

(iv) A redispersion mechanism in 3 steps was established.

First step Special localized surface atom of Pt crystallites can be oxidized.

Second step These oxidized sites are attached by chloride ions from alumina surface.

Third step Oxidized sites migrate from Pt crystallites and trap on appropriate centers of the alumina.

2.4.2 Coke burning conditions and mechanism

There are some major variables that influence regeneration rate such as temperature, O₂ content in feed gas, amount of carbon on catalyst and Type of catalyst (Emmett, 1960). The analyses of carbon combustion products (Walker et al., 1959) were reviewed by Hughes(1984) as following.

(i) The combustion products give carbon dioxide and carbon monoxide as major products. Equilibrium limitations are not a concern.

(ii) The CO/CO₂ ratio is predicted by various workers and gives a value among 0.3-0.9. Types of carbon used are insignificant to this ratio.

(iii) The CO/CO₂ ratio increases with burning temperature.

(iv) Lowering the oxidative gas space velocity increases the secondary oxidation of CO to CO₂, addition of water vapor also gives the same result.

However oxidizing-reducing catalysts (that is Cr_2O_3 , Pd, Pt) can change the nature of the burning rate because of its catalytic properties, reducing the CO/CO₂ ratio to close to zero (Weisz et al., 1966) as reviewed by Charles (1970) and Bond et al., (1995).

The well known “ Shell progressive “ model provides a kinetic study of coke burning (Huges, 1984). The two significant rates determining steps are (i) intrinsic carbon burning kinetics and (ii) Oxygen diffusion through the catalyst pores. Either each step or both steps were mentioned to be the overall rate determining step (r.d.s.) depending on regeneration conditions. High burning temperatures make the regeneration diffusion limited.

Parera et al. (1985, 1989) investigated the coke burning function on bifunction metal-acid catalyst (Pt/Al₂O₃-Cl). According to the coke formation step on the previous section, the Pt function acts as a catalyst for combustion and coke deposits on Pt are richer in hydrogen. It causes the burning of coke to start from coke deposits on metal. An increase in burning temperature causes more O₂ spillover from Pt that can continue burning the coke near the metal through the coke on the support. Treating the catalyst with H₂ before burning the coke is easier for removing of coke. On Chromia-Alumina catalysts (Rayo et al., 1994). These procedures can avoid the high-temperature excursions in regeneration step. The aging of a coked catalyst before coke burning can change the less volatile hydrocarbon group to more aromatic and dehydrogenated structures.

2.4.3 Effect of promoters loading

The (Pt-Re-S/Al₂O₃-Cl) catalyst gives the same burning result (Parera et al., 1992). At low temperature, the coke burning is selective, surface C=O and C-OH groups are formed as intermediates. At high temperatures, the burning is nonselective, these groups rapidly complete the 2nd oxidation to CO₂.