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Coke deposition mechanism on the pores of a commercial Pt–Re/γ-Al_2O_3 naphtha reforming catalyst

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ABSTRACT

Coke deposition mechanism on a commercial Pt–Re/γ-Al_2O_3 naphtha reforming catalyst was studied. A used catalyst that was in industrial reforming operation for 28 months, as well as the fresh catalyst of the unit were characterized using XRD, XRF, and nitrogen adsorption/desorption analyses. Carbon and sulfur contents of the fresh and the used catalysts were determined using Leco combustion analyzer. The pore size distributions (PSD) of the fresh and the used reforming catalysts were determined using BJH and Comparison Plot methods. The Comparison Plot method produced the most reasonable PSDs for the catalysts. Through comparison of the PSDs of the fresh and the used catalysts, it was revealed that coke deposited on both micropores and mesopores of the catalyst at a constant thickness of 1.0 nm. The constant coke thickness on the catalyst pore walls in the naphtha reforming process (temp. ~500 °C) implies that coke deposition reaction is the slow controlling step in comparison to the fast mass transfer rate of coke ingredients into the pores. The bulk density of the deposited coke on the used catalyst was calculated as 0.966 g/cm^3.

1. Introduction

Platinum–rhenium catalysts supported on chlorinated alumina are widely used in industry for the catalytic reforming of naphtha. The catalytic function of platinum is dehydrogenation. The chlorine-promoted alumina support of these catalysts provides the required acidic sites. The addition of Re to Pt/Al_2O_3 significantly reduces the catalyst deactivation rate [1]. Before sulfidation, the Re promoter of the catalyst may be found: (a) in the reduced form alloyed with platinum, (b) in an oxidized form stabilized by the support, or (c) as a combination of both of the above [1]. Due to the high hydrogenolysis activity of metallic rhenium, catalysts containing this metal are treated with sulfur prior to use in order to passivate this high activity. If an inactive metal such as Sn is added instead of Re, no such pre-treatment with sulfur is required. For this reason Re–S compound is often considered to be an inert dilutant which modifies the reforming catalyst in a similar manner to Sn [1]. Fast deactivation of the reforming catalysts may be caused by the segregation of platinum and rhenium [2]. This segregation may occur due to either poisoning of the Pt–Re matrix or dehydroxylation of the alumina surface during pre-treatment or regeneration. Anderson et al. [3] further confirmed the stability effect of Re in the reforming catalyst by measuring the infrared spectra of CO adsorbed on Pt, Re and Pt–Re alumina-supported catalysts. The measurements were made before and after coking by exposure to heptane at 683°K. The coking severity was in the order of Pt greater than Pt–Re greater than Re [3].

According to the mechanism of coke formation, aromatic compounds are produced by the cyclic condensation of relatively reactive aliphatic compounds that have been formed on the catalyst, and eventually polymerized to asphaltenes to become precursors of the refractory hard coke. Consequently, the structure of the refractory coke is believed to be highly poly-aromatic [4]. The asphaltene aromaticity in the feed is, therefore, an important factor that is highly correlated with the coke deactivation mechanism of a catalyst [5]. It is believed that the strong acid sites of the catalyst support are involved in the coke formation mechanism [6]. Due to their highly aromatic character, coke species strongly adsorb on the acid sites, which leads to the reduction of the catalyst activity.

To regenerate the spent reforming catalysts, hydrogen is first circulated through the reformer, causing sulfur desorption. Chlorine is normally added during this hydrogen treatment step to enhance S desorption and to increase the chlorine content of Al_2O_3 to avoid the formation of excessive SO_4^{2-} poison during the subsequent coke-burning procedure. During this regeneration step, sulfur deposited on the metals is removed as SO_2 that is partially oxidized to SO_3. This, in turn, readily reacts with Al_2O_3 and forms $Al_2(SO_4)_3$, causing permanent deactivation of the alumina support. Treacy [7] has shown that the active metals in the catalyst pores agglomerate during operation or regeneration. Hence, in the subsequent step of regeneration, namely

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oxychloration, the metals must be re-dispersed using circulating gases. During this step, the presence of Cl and H_2O in the circulating gases can also displace some of the previously formed SO_4^{2-}. Before reformer start-up, the oxidized metals must be reduced with H_2 [8].

Liu et al. [9] performed laboratory reforming tests with different sizes of catalyst particles under otherwise constant conditions to check for pore diffusion limitations. They found minimal effect of particle size on reforming and coking reaction rates. This was consistent with their estimated effectiveness factor of about 0.9 for 1.6-mm extrudates at 772°K. They assumed that the coking kinetics model is based on the premise that site coverage is the sole cause of reforming catalyst deactivation. In their other works, Liu et al. [10,11] found that the coking rate is linear in C5N (five-membered naphthenes). C5N is the major coke precursors in *n*-heptane reforming over an unsulfided Pt–Re/Al_2O_3 catalyst under conditions close to those of a commercial reformer [10,11]. They found that there is a distinction between coke depositing on clean sites (monolayer coke) and coke depositing on already coked sites (multilayer coke). As a result, the total coke concentration would be the sum of the monolayer and multilayer coke concentrations. This model would predict that the actual monolayer coke coverage is never complete in a finite time. At the same time, multilayer coke formation would accelerate. Liu and co-workers calculated that after a significant portion of the active sites are coked, the rate of multilayer coke build-up would slow down.

Obviously, Liu et al. [9] have used one of the most comprehensive modeling approaches to predict the mechanism and kinetics of coke deposition on the naphtha reforming catalysts. Even for this detailed modeling approach, their calculations is only based on the measurements of coke ingredient concentration in the naphtha stream passing through the reactor, as well as the bulk coke concentration accumulated on the catalyst. Some of the most detailed information about coke on the catalyst may be obtained through pore size analyses of the catalyst before and after coke deposition. In the present work, we used the PSD analyses of a fresh and its used naphtha reforming catalysts to predict the coke deposition mechanism by analysing the coke thickness on the pore walls as a function of the pore sizes.

2. Pore size distribution theories

The PSD is an important characteristic for porous media such as the heterogeneous solid catalysts. Varieties of methods have been reported by researchers to identify the pore size distribution of porous materials. One of the experimental analysis that supply raw data for PSD analysis is the nitrogen physical adsorption at 77°K [12]. These methods include: MP [13], Jaroniec-Choma [14], Horvath-Kawazoe [15], DFT [16], BJH [17], and Comparison Plots [18]. Among these methods, BJH and Comparison Plots are the methods that are suitable for the range of mesopores. Each method determines the pore size distribution based on a unique approach. These two methods were implemented to determine the PSD of our fresh and its corresponding used naphtha reforming catalysts. These are briefly described in the following subsections.

2.1. BJH method

In this method, the pore size distribution is determined by means of analysis of nitrogen desorption data [17]. The applied computational algorithm is the procedure of Barret et al. [17]. Nitrogen molecules adsorb on pore walls through a multilayer film at lower pressures. At higher pressures, nitrogen molecules fill the pores through capillary condensation mechanism. The relative pressure that pore filling takes place by capillary condensation can be calculated from Kelvin's equation, Eq. (1).

$$RT \quad \ln\ (P/P_0) = -\frac{2\gamma V_L}{r_k} \tag{1}$$

Where r_k is the mean radius of curvature for any given liquid–vapor interface shape. In the case of adsorbing Nitrogen with the assumed contact angle = 0 (complete wetting), and assuming a hemispherical shape for the liquid–vapor interface that forms in a cylindrical pore, r_k(the mean radius of curvature) will be the pore radius. Also in Eq. (1), R, T, γ, and V_L are gas constant, temperature, surface tension, and liquid molar volume, respectively. By using Eq. (1), the pore radius (r_k) in which the capillary condensation is actively occurring can be determined as a function of the relative pressure(P/P_0). Eq. (1) can be simplified into the following form:

$$r_k(^\circ\mathrm{A}) = -\frac{9.574}{\ln(P/P_0)} \tag{2}$$

Eq. (2) can be obtained from Eq. (1), assuming: $T = 77.35$°K, $\gamma = 8.88$ mN/m, and $V_L = 34.76\ \mathrm{cm^3/mol}$. At each relative pressure, the average nitrogen multilayer film thickness (the film adsorbed on pore walls), t, is calculated from Eq. (3).

$$t\ (^\circ\mathrm{A}) = \left[\frac{13.99}{0.034 - \log(P/P_0)}\right]^{\frac{1}{2}} \tag{3}$$

The amount of nitrogen desorbed can be expressed as the sum of the amount resulting from pore evacuation and of the amount corresponding to the decrease of t in the pores which already lost their capillary condensate. In this method, a cylindrical pore model is assumed. Pores are treated as non-intersecting, open-ended capillaries that function independent of each other during adsorption or desorption of nitrogen. The method is useful for determining the pore size distribution in porous samples containing pore sizes in the range of 1.5 to 100 nm in radius. When applying this procedure for solids containing pores larger than 100 nm in radius, the accuracy is reduced considerably.

2.2. Comparison Plot method

The Comparison Plot method [18] is an important achievement in characterizing porous structures using adsorption data since the theory of Brunauer–Emmett–Teller (BET) [19]. Comparison Plots can provide pore structure information in a clear and reliable manner without introducing any major assumption.

The Comparison Plot method is based on comparing the adsorption data of the porous sample with that of a nonporous reference substance. From the N_2 isotherm on a nonporous reference solid, a relationship between the statistical thickness of the adsorbed film (t) and the relative pressure P/P_0 is obtained. The adsorption by the sample at various relative pressures is then plotted against the thickness of the adsorbed film on the nonporous reference at the same relative pressure. In the present work, we used an empirical equation that correlates the t values on the nonporous surfaces as a function of nitrogen relative pressure. For instance, Eq. (4) shows the relation for activated alumina [18].

$$\begin{aligned} t = 3.51 - 0.20/\ \log\ x + 1.49/\left[1000(\log x)^2\right] - 0.04\ \log x \\ - 0.32\ (\log\ x)^2 + 2.44\,x + 2.24\,x^2 \end{aligned} \tag{4}$$

where x is the relative pressure of nitrogen.

By only considering the tangent curve of a Comparison Plot, the PSD of a mesoporous or microporous solid can be qualitatively obtained. However, to drive the quantitative pore size distribution, the adsorption data is “calibrated” using an established relationship between the statistical thickness of the adsorbed film and the pore size of samples with uniform pore structure and known pore sizes (as measured by such techniques as XRD and TEM), such as alumina