

OXIDATIVE REGENERATION OF HYDROTREATING CATALYSTS

by

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ABSTRACT

Oxidic and sulphided cobalt-molybdate catalysts used for hydrodeoxygenation of a phenol solution were regenerated by oxidative burnoff performed in a thermogravimetric analysis reactor and in a fixed bed reactor. For the sulphided catalyst, at 250°C the removal of sulphur and carbon reached about 80% and 20%, respectively. For both catalysts a complete removal of carbon requires a burnoff temperature of about 500°C.

Rate constants of burnoff of the sulphided catalyst estimated in the chemically controlled region were markedly higher than those for the oxidic catalyst indicating a higher reactivity of coke formed on the surface of the former. Activation energies for the oxidic catalyst were higher than those for the sulphided catalyst. Some experimental problems were identified when determining kinetic parameter of the sulphided catalyst.

INTRODUCTION

The catalyst inventory represents a significant portion of the overall cost of catalytic operations thus a careful maintenance of this inventory is necessary to decrease operational costs. The aim is to use the catalyst for as long as possible.

During catalytic reaction catalyst activity declines. In systems where the catalyst is continuously fed to and withdrawn from the reactor the activity may be maintained by periodically withdrawing a portion of the used catalyst which is replaced by fresh catalyst. In fixed bed reactors, which is the case for most hydrotreating units, the decline of activity may be offset by a change of processing parameters such as temperature, pressure and residence time. At certain point however the operation has to be shut down and the catalyst bed replaced. The spent catalyst is then regenerated and returned to the operation.

Molybdate catalysts supported on alumina and promoted by either cobalt or nickel are the most common hydrotreating catalysts. A great deal of attention has been given to the loss of activity of these catalysts. The scientific literature strongly suggests that the formation of carbonaceous deposits is perhaps the most common cause of the activity decline (1, 2, 3). It was generally established that the rate of deposit formation depends on the origin of feedstock. Thus, nitrogen bases and some aromatic structures are known precursors for deposit formation (4). Organometallic species containing transition metals deactivate the catalyst surface as well (5).

The removal of deposits from the catalyst surface is essential for the recovery of its original activity. This may be accomplished by an oxidative burnoff in the presence of a medium containing O_2 . In this respect air appears to be the most attractive option. However, the burnoff must be carefully controlled to avoid overheating which may lead to sintering of the catalyst. Therefore, in some cases diluted air may be more appropriate.

The rate of deposits removal during burnoff depends on their structure. Thus, as observed by Massoth and Menon, the part of deposits having a high H/C ratio is removed during the very first contact with oxygen (6,7). When measuring the yield of H_2O and carbon oxides they concluded that the removal of hydrogen from deposits is more rapid than that of carbon.

For example, at 50% level of hydrogen removal the carbon conversion was only about 10%. The rapid reaction of oxygen with hydrogen-containing groups may lead to an uncontrolled temperature increase. In some cases the reactive species may be removed by pretreatment at high temperatures either under vacuum or nitrogen. The dependence of burnoff kinetics on aging history was also confirmed by Nalitham et al. and Hertan et al. while studying the regeneration of nickel-molybdate catalysts (8, 9).

Burnoff is influenced by mass transfer as well. This may occur especially during the regeneration of the catalyst in the form of pellets or extrudates. It was established that the mass transfer limitations may be minimized by grinding the deactivated catalyst to a fine particle size (7, 10).

The cobalt-molybdate catalysts investigated were used during hydrodeoxygenation of a phenol solution. In the first case an oxidic catalyst was used and in the second a sulphided catalyst was used. The aim was to determine the difference between the chemistry of regeneration of these catalysts. For preliminary assessments thermogravimetric analysis was applied whereas a specially designed fixed bed reactor was used to follow the kinetics of the burnoff. The catalysts were ground to a fine particle size in order to minimize mass transfer effects.

EXPERIMENTAL

CATALYST

The cobalt-molybdate catalysts were obtained from Strem Chemicals Inc., and contained 14 wt % MoO_3 and 4 wt % CoO supported on γ -alumina. The extrusions of the catalyst (1.5 mm x 3.0 mm) had a pore volume of about 0.6 mL/g and a BET surface area of about 210 m^2/g . The sulphided catalyst was prepared by sulphiding at 400°C for 1 h using a $\text{H}_2 + \text{H}_2\text{S}$ mixture containing 20 vol % H_2S . The oxidic and the sulphided catalysts were used for hydrodeoxygenation of the solution containing 0.1 mol of O-ethyl phenol in hexadecane. The 3-h experiments were performed in a continuous benchscale unit at 350°C, H_2 pressure of 10.34 MPa and LHSV of about 1.0. At the end of each experiment the content of the fixed bed reactor was drained into a high pressure receiver and the catalyst bed was cooled under H_2 . For the

burnoff experiments the extrusions of spent catalyst were extracted by tetrahydrofuran in the Soxhlet apparatus. This was followed by vacuum treatment at 250°C for 4 h, then crushing and sieving to required particle size.

The elemental analysis performed on the spent and subsequently treated catalysts showed the carbon content for the oxidic and sulphided catalysts to be 4.4 wt % and 2.5 wt %, respectively. The sulphur content of the spent sulphided catalyst was 6.0 wt %.

APPARATUS

Thermogravimetric analysis (TGA) of the catalysts was performed using a Dupont 951TGA analyzer equipped with Dupont 1090 data system. Before each burnoff experiment about 100 mg of accurately weighed catalyst of 100 to 200 mesh was maintained at a corresponding temperature under N_2 until no further weight change occurred. Then the N_2 was replaced by a mixture of $N_2 + O_2$ containing 5 vol % O_2 flowing at a rate of 100 mL/min.

The fixed bed reactor, 15 mm ID and 0.5 m long, is constructed of 316 stainless steel. The bed was supported on a perforated plate of the same material. The reactor was heated externally using a Lindberg furnace controlled with digital temperature programmer. A chromel-alumel thermocouple was used to measure the temperature. The thermocouple well in the middle of the reactor permitted the positioning of the thermocouple in the catalyst bed.

PROCEDURE

The fixed bed consisted of a 30-mm layer of quartz particles (42 to 80 mesh) placed on the plate. About 1-mm layer of catalyst (100 to 200 mesh) was placed on top, then covered by a 60-mm layer of quartz particles of similar size to those of the bottom layer. This arrangement ensured a sufficient dissipation of the excess of heat. For example, the temperature increase after the introduction of the $N_2 + O_2$ mixture during the burnoff at 500°C was only 6°C and after less than 2 min the temperature stabilized at 500°C. During the burnoff performed at lower temperatures the temperature increase was even lower, e.g., at 350°C only about 3°C. This bed arrangement was based on several preliminary runs. Thus, with 2 g of sample a rapid tempera-

ture increase (about 30°C) was observed for both the extrudates and the crushed catalyst. Moreover, the centre part of the extrudates remained black after burnoff indicating the presence of mass transfer limitations. For the crushed catalyst such limitations were insignificant. This was confirmed by an experiment carried out to a partial burnoff. After this experiment the catalyst particles were all black indicating a continuous burnoff.

N₂ and O₂ were supplied from cylinders and passed the chromatographic specialties moisture trap before entering the reactor at the top. Gas flow was monitored by Matheson flow regulators.

ANALYSIS

Perkin Elmer CHN 240 and Leco analyzers were used for determination of carbon and sulphur, respectively.

An on-line Perkin Elmer 1200 multiple mass spectroscope analyzed and continuously monitored the concentration of products formed during regeneration, e.g. CO₂, CO and SO₂. No attempts were made to analyse H₂ and H₂O. For most experiments the gas exiting the reactor passed the tube filled with CuO and at about 450°C before entering the analysis system.

A data log system attached to the mass spectroscope provided printouts of results every 20 s. The concentrations determined by this procedure together with the volume of flowing gas were used to calculate the number of moles of individual components in the gas exiting the reactor. The number of moles of carbon containing components and SO₂ were used to calculate the amount of carbon and sulphur removed during burnoff.

RESULTS AND DISCUSSION

The TGA technique is a convenient means to obtain preliminary information on properties of carbonaceous deposits. Burnoff profile examples obtained by this technique for the spent oxidic and sulphided catalysts are shown in Fig. 1. Before the burnoff the catalyst was heated in N₂ at burnoff temperature until no weight change occurred in addition to the pretreatment described earlier. Then, the N₂ was replaced by a mixture of N₂ + O₂ (5 vol % O₂). For the oxidic catalyst the weight increase was recorded during the initial stages of burnoff contrary to that for the sulphided catalyst. A similar weight increase was observed by Massoth during regeneration

of a spent silica-alumina catalyst (7). The weight increase was evident in the whole temperature range applied, i.e., 350°C to 500°C and was more pronounced at lower temperatures. This observation is attributed to an oxidative association of O_2 with the deposits, e.g., via the formation of carbon centered hydrogen peroxides (11). Such reaction may be catalyzed by transition metals (12). Also, the adsorption of H_2O formed during the initial contact of O_2 with deposits cannot be ruled out completely. It is believed that these effects will be much less pronounced for the sulphided catalyst. These facts together with known conversion of MoS_2 to MoO_3 and Co_9S_8 to CoO explain more rapid weight decrease during burnoff of the sulphided catalyst compared with that of the oxidic catalyst. The significantly larger driving force for the conversion of MoS_2 and Co_9S_8 to their oxides and SO_2 compared with that for the conversion of carbon to CO_2 and CO may be another reason for the difference in the initial pattern of burnoff (13).

Typical trends in component concentrations in the exiting gas from the burnoff using the fixed bed reactor are shown in Fig. 2. These results were obtained at 400°C using 0.25 g of the spent sulphided catalyst in the $N_2 + O_2$ mixture (500 mL/min) containing 20 vol % of O_2 . In region A only N_2 flowed through the bed. During the initial stages of the burnoff all O_2 was consumed as indicated by its low concentration in the exiting gas (region B). This was complemented by a rapid buildup of CO_2 , CO and SO_2 .

Another series of experiments was carried out in this work and was based on an isothermal burnoff performed in steps at different temperatures using the same catalyst bed. The procedure included heating the catalyst bed in N_2 to 100°C. At this point N_2 was replaced by a $N_2 + O_2$ mixture and the CO_2 concentration in exiting gas, which passed through the tube filled with CuO , was maintained at about 500°C, and monitored continuously. The burnoff was carried out for about 1 h. As shown in Fig. 2, the concentration of combustion products increased rapidly during the initial contact of the $N_2 + O_2$ mixture with the catalyst. After reaching a maximum the concentrations declined and approached detection limits of the mass spectroscope. Then, the $N_2 + O_2$ mixture was replaced by N_2 and the temperature was increased by 50°C. At the increased temperature the burnoff was performed in the same way. These steps were repeated until 500°C. The CO_2 concentrations

together with the volume of gas exiting the reactor were used to calculate the yields of CO_2 produced during each burnoff step. Results for the spent oxidic and spent sulphided catalysts are shown in Fig. 3a and 3b, respectively. The broken line indicates the amount of CO_2 which was produced during heat up periods. It is believed that this carbon was removed in the reaction with O_2 which was originally adsorbed or remained adsorbed at the end of the burnoff steps. The total amount of carbon, obtained from the sum of CO_2 yields for each burnoff step accounted for more than 95% of carbon removed from the catalyst surface, as determined from the carbon content before and after burnoff.

The trends in sulphur removal during stepwise burnoff of the unspent and spent sulphided catalysts are shown in Fig. 4a and 4b, respectively. During these experiments the gas exiting the reactor did not pass the CuO tube. Therefore, the CO_2 yields do not include the carbon removed as CO. The SO_2 concentrations and the volume of gas exiting the reactor were used to calculate the CO_2 yields. It appears that a substantial portion of sulphur can be removed at temperatures where carbon removal is still relatively slow. This is in agreement with large driving forces for the conversion of Mo and Co sulphides to their oxides and SO_2 compared with that for the conversion of carbon to CO_2 (13). Further, the formation of SO_2 takes place in a narrower temperature range compared with that of CO_2 . The presence of carbonaceous deposits seems to have little effect on the conversion of Mo and Co sulphides to their oxides as indicated by similar trends in SO_2 formation for the unspent and spent sulphided catalyst. The broken line indicates the effect of adsorbed O_2 on SO_2 formation during the heat up period, as was observed for CO_2 .

Figures 3 and 4 suggest that the removal of carbon may not be complete unless the burnoff temperature of about 500°C is maintained. Cumulative percentages of carbon and sulphur (of total carbon and sulphur removed during all steps) removed at given temperatures are shown in Fig. 5. At 200°C , for the spent sulphided catalyst about 80% of sulphur and about 20% of carbon were removed. Above 250°C the carbon removal becomes more pronounced whereas that of sulphur attains a steady state. For the oxidic catalyst the carbon removal follows a trend similar to that for the sulphided catalyst. Higher carbon removal at low temperatures for the latter may be attributed to

the different amounts of catalyst used for the experiment, i.e., 0.59 g and 0.40 g for the sulphided and oxidic catalyst, respectively. It may be concluded from Fig. 5 that at temperatures lower than 500°C a certain amount of carbon (after burnoff carbon) remains on the surface in a non-reactive form. The amount of this carbon increases with decreasing temperature of oxidative burnoff. Thus, rather prolonged burnoff would be required to achieve a high level of carbon removal at temperatures lower than 500°C. These observations confirm a wide range of reactivities of carbonaceous deposits towards their oxidation. Also, some mass transfer factors may contribute to these effects. For example, increased lattice vibrations at higher temperatures may improve the access of O_2 to some inaccessible carbon inside the particles. At the same time the diffusion of CO_2 and CO from the particles may improve as well.

The amount of carbon converted as CO_2 was dependent on residence time of the gas mixture flowing through the fixed bed of catalyst, i.e., on the Fo/W ratio (Fo - flow of gas in cm^3/min , W - weight of catalysing in grams). The CO_2 yields from eight runs performed in steps from 100°C to 500°C are shown in Fig. 6, where numbers indicate the run number. Runs 1 to 4 used 0.4 g of the spent oxidic catalyst whereas run 5 used 1.0 g. The Fo/W ratio of runs 2 and 5 is the same. This is complemented by the same yields of CO_2 . Run 6 used 0.4 g of the spent sulphided catalyst. The lower CO_2 yield for run 6 and 7 compared with that for run 2 and 3 agrees with reported catalytic effects of Mo and Co oxides for oxidation of carbon (12). Runs 8 used spent oxidic catalyst. Here, the gas exiting the reactor was passed through the tube filled with CuO. With this arrangement almost complete conversion of CO to CO_2 was achieved as indicated by almost 100% material balance of carbon detected and carbon removed.

The content of carbon and sulphur in regenerated catalysts and conditions of regeneration are summarized in Table 1. It is emphasized that detection limits of the analyzer for carbon were about 0.2 wt %. It is therefore assumed that the catalysts containing 0.2 wt % carbon or less were completely regenerated with respect to carbon removal. Thus, conditions for complete carbon removal were attained for all experiments performed at 500°C or higher. The presence of carbon seems to decrease the removal of sulphur, the last portion of sulphur in particular. For example, after regeneration of the spent sulphided catalyst performed at 500°C, 10 to 20% sulphur still remains in the catalyst in spite of a complete removal of carbon. The form

of the sulphur remaining on the catalyst after burnoff is important. The sulphide sulphur is preferable to the sulphate sulphur. The latter may contribute to an irreversible deactivation of part of the catalyst surface. The overall sulphur removal increases with increasing temperature. The temperature increase may influence the ratio of sulphidic/sulphate sulphur in regenerated catalysts.

To obtain kinetic data the burnoff experiments were performed in a single stage at 300°C, 400°C and 500°C. Before the catalyst bed was brought to burnoff temperature it was heated at 500°C in N₂ for 1 h. For these runs the exiting gas passed through the CuO furnace before entering the analysis system. The production of CO₂ (in cumulative yields) for the oxidic and sulphided catalysts is shown in Fig. 7. For the former the material balance was almost 100% whereas that for the sulphided catalyst was only about 70%. The lower material balance for the latter is attributed to the interference of SO₂ during CO oxidation in the CuO furnace. The shape of correlations in Fig. 7 indicates the presence of two burnoff regions. It is believed that in the first region the burnoff is chemically controlled whereas in the second the presence of diffusion limitations may be important.

Rate constants were estimated in the chemically controlled region and are shown in Table 2 together with those estimated from the TGA data. The rate equation used for the estimate, i.e., $r = P_{O_2}C$, assumed the first order kinetics with respect to partial pressure of oxygen (P_{O_2}) and concentration of carbon (C) (10). At the same temperature the rate of burnoff in the fixed bed reactor for the sulphided catalyst was significantly higher than that for the oxidic catalyst. This indicates a higher reactivity of coke formed on the surface of the former. In view of a more efficient hydrogen transfer during hydrotreatment in the presence of sulphided catalyst compared with that in the presence of oxidic catalyst (14), the higher reactivity of coke formed on the surface of the former indicates a high concentration of reactive species which according to Massoth are those with high H/C ratios (7). Rate constants obtained in the fixed bed reactor were higher than those obtained from TGA data. A more efficient contact of oxygen with catalyst in the fixed bed, i.e., a turbulent flow of gases in the fixed bed compared with a laminar flow in the TGA reactor may be responsible for the difference.

Activation energies were estimated from the plots shown in Fig. 8. The values for the oxidic catalyst were higher than those for the sulphided catalyst for both the TGA and fixed bed burnoff data. For the TGA, the activation energy for the sulphided catalyst was affected by the weight loss contribution from the conversion of sulphides to oxides. This would suggest that the TGA technique is not suitable for determining kinetic parameters of burnoff of a sulphided catalyst unless this effect is considered. For the sulphided catalyst the plot obtained from the fixed bed data exhibited some curvature at lower temperatures resulting from a higher rate of burnoff than expected. This affected the accuracy of the activation energy estimate.

Present experimental results indicate that kinetics of burnoff of coke deposited on a catalyst surface depends on its chemical structure. This structure is influenced by many factors such as catalyst composition, catalyst pretreatment, type of treated feedstock and processing conditions. Experimental conditions applied during burnoff are of crucial importance as well. All these factors should be considered when analyzing the differences in kinetic parameters of coke burnoff reported in the scientific literature.

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Table 1 - Experimental conditions and carbon and sulphur content
in regenerated catalysts.

Catalyst	O ₂ in Gas % vol	Flow L/min	Weight g	Final temp. of burnoff, °C		C wt %	S wt %
				in steps	one step		
<u>Fresh presulphided</u>	-	-	-	-	-	-	6.30
	20	1.00	0.20	-	210	-	2.77
	20	1.00	0.20	-	325	-	0.73
	20	1.00	0.20	-	360	-	0.77
	20	1.00	0.20	-	410	-	0.24
	20	0.23	0.50	-	-	-	-
<u>Spent sulphided</u>	-	-	-	-	-	2.5	6.07
	20	1.00	0.20	550	-	0.2	0.44
	20	0.23	0.60	500	-	0.1	1.02
	20	0.50	0.60	500	-	0.1	1.18
	20	0.50	0.60	350	-	0.8	1.75
	20	1.00	0.20	500	-	0.2	0.93
	20	0.07	2.00	-	500	0.1	0.56
	20	0.07	2.00	-	500	0.1	0.79
<u>Spent oxidic</u>	-	-	-	-	-	4.4	0
	20	1.00	0.40	500	-	0.2	0
	20	0.22	0.40	550	-	0.1	0
	20	0.50	1.00	550	-	0.0	0

Table 2 - Data constants (L/min atm) for TGA
and fixed bed burnoff

Temperature °C	TGA		Fixed bed	
	oxid.	sulph.	oxid.	sulph.
300	-	-	0.54	0.965
350	0.095	1.64	-	-
400	0.37	2.00	1.08	3.01
450	0.65	2.46	-	-
500	1.52	2.60	10.30	18.90

FIGURE CAPTIONS

Fig. 1 - Weight loss versus time during TGA analysis at 350°C.

Fig. 2 - Product distribution during burnoff of the sulphided catalyst at 400°C in the fixed bed.

Fig. 3 - Cumulative yields of CO₂ from stepwise burnoff (0.5 L/min of reactive gas).

Fig. 4 - Cumulative yields of SO₂ from stepwise burnoff of the fresh sulphided and spent sulphided catalyst (0.6 g catalyst; 0.5 L/min reactive gas)

Fig. 5 - Effect of temperature on the cumulative amount of carbon and sulphur removed in stepwise burnoff.

Fig. 6 - Effect of Fo/W ratio on the amount of carbon removed during burnoff as CO₂.

Fig. 7 - Cumulative amounts of CO₂ produced during single step burnoff versus time.

Fig. 8 - The log k versus 1/T correlations for burnoff performed in the fixed bed and TGA reactors.















