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COKE DEPOSITION ON Co-Mo/Al_2O_3 AND Co-Mo/C CATALYSTS

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ABSTRACT

A commercial Co-Mo/Al_2O_3 HDS catalyst displayed catalytic activity towards the coking of anthracene. This is related to its hydrogenation/dehydrogenation activity. The Al_2O_3 support without metals displayed little coking activity but there was a linear increase in the amount of coke deposited with increasing Mo loading.

As with the Al_2O_3 support, little or no coking activity was displayed by a carbon black composite. Following the addition of Co and Mo to the carbon black composite, some enhancement in the coking of anthracene was observed, but to a much lesser extent than for the Co-Mo/Al_2O_3 system. Given that some carbon-supported HDS catalysts have initial HDS activities higher than those with Al_2O_3 supports, the potential exists for carbon based catalysts to better resist deactivation due to coke deposition and maintain their activities over longer periods of operation.

INTRODUCTION

During the processing of heavy petroleum residues and coal-derived liquids, an upgrading step is often required to reduce N and S levels in order to meet the stringent environmental requirements associated with the combustion of these fuels. In general, upgrading requires, or at least is aided by, the use of heterogeneous catalysts. Development of catalysts for specific applications in this regard is not particularly advanced, relying to some extent on progress made in other areas of petroleum refining and on the early German work on coal hydrogenation.

One principal area of concern is that of maintaining catalytic activity over extended periods of time. Initial activity declines significantly after several hours or days on-stream depending on

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the feed composition and processing conditions (1). This can be attributed to several factors including the deposition of carbonaceous material, the deposition of metals, and chemisorption of molecules from the feed on the catalytically active surface.

Hydrotreatment of heavy liquids is usually carried out over a catalyst containing Mo promoted by Co supported on γ-Al_2O_3. However, this formulation catalyzes cracking and hydrogenation reactions as well as hydrogenolysis reactions. The current work addresses the question of coke deposition on these catalysts from reactions involving polynuclear aromatic hydrocarbons. Coke deposition leads ultimately to catalyst deactivation.

A further aim of the research was to develop catalysts which were less susceptible to deactivation via coke formation. It has been suggested that coking rates are associated with the acidic nature of Al_2O_3-supported catalysts (2). The approach adopted in the current research was to replace the acidic Al_2O_3 support by a less acidic carbonaceous support. In particular, a carbon black composite support was used. These carbons have low surface acidities and were expected therefore to have low coking propensities. Moreover, carbon-supported hydrodesulfurization (HDS) catalysts have been shown to have catalytic activities, in some cases, higher than similar Al_2O_3 supported catalysts for the hydrodesulfurization of thiophene (3). The method used in this work was to evaluate, using liquid anthracene and stringent coking conditions, the relative coking rates of Al_2O_3 and carbon-supported HDS catalysts. Relative HDS activities and coking propensities from the vapor phase cracking of propylene have been reported elsewhere (4).

EXPERIMENTAL

Selection of Materials

Petroleum residues and coal-derived liquids contain significant quantities of polynuclear aromatic hydrocarbons composed of three condensed rings (5). Anthracene and phenathrene have been identified as major constituents. Upon carbonization, both anthracene and phenanthrene produce highly anisotropic mesophase and subsequently graphitizable cokes (6), but at different rates. Anthracene carbonizes at a rate considerably in excess of that for phenanthrene (7). For example, under 3 MPa H_2 anthracene produces coke at 430°C while phenanthrene is relatively unreactive. Anthracene was chosen, therefore, as the coke precursor material because of its greater coking propensity.

An Al_2O_3 support and a Co-Mo/Al_2O_3 HDS catalyst in the form of 1 mm diameter cyclindrical extrudates were supplied by The Gulf Research and Development Company. The cobalt molybdate catalyst contained 3 wt% Co and 10 wt% Mo in their oxidic states supported by γ-Al_2O_3.

Preparation of Carbon Black Supports

A carbon black, Monarch 700, was supplied by Cabot Corporation from which carbon black composite supports were fabricated. Some properties of the carbon black are given in Table 1. Furfuryl alcohol was polymerized to produce a thermosetting binder by using concentrated sulfuric acid as a polymerization catalyst. Pellets were made from a mixture of the carbon black and partially polymerized binder. The mean particle size of the carbon black, 18 nm, was commensurate with producing a composite with a pore size distribution similar to that of the Al_2O_3 support. Details of the fabrication procedure are given by Schmitt et al. (8). In essence, the composites were made using 25 wt% poly(furfuryl alcohol) binder based on the weight of carbon black. Use of higher amounts of binder increases the strength of the pellets but produces lower pore volumes. Cylindrical pellets were dry-pressed to a diameter of 0.5 cm in a Stokes Pellet Press. The composites were heat treated to 600 and 1200°C at a heating rate of 10°C/min and were held at maximum temperature for 1 h. The heating and cooling cycles were performed under a N_2 atmosphere.

Table 1
Properties of Monarch 700 Carbon Black

Mean particle size, nm	18
N_2 surface area, m^2/g	206
Diamagnetic susceptibility, 10^6 emu/g	0.93
Interlayer spacing, nm	0.474
Av. crystallite height, nm	0.89
Volatile matter, wt%	1.5

Properties of the CB-composites are given in Table 2 for both heat treatment temperatures (HTT). Heat treating to 600°C was not sufficient to eliminate the fine microporosity associated with the binder. This can be inferred from the CO_2 to N_2 surface area ratio (9), 1.88 for the 600°C treatment and 1.05 for the 1200°C treatment. Microporosity is essentially eliminated by the 1200°C heat treatment. The average diameter of pores accessible to Hg at 207 MPa was not altered significantly upon heating to the higher temperature nor was the total pore volume accessible to Hg. All coking data were obtained with the composite heat treated to 1200°C.

Table 2

Properties of the Carbon Black Composite as a Function of Heat Treatment Temperature

	HTT, °C	
	600	1200
N_2 surface area, m^2/g	220	215
CO_2 surface area, m^2/g	415	225
Pore volume accessible to Hg, cc/g	0.79	0.86
Av. pore diameter from Hg intrusion, nm	26	25

Coking Experiments

The coking experiments were performed in batch tubing reactors similar to those used previously in coal liquefaction studies (10). The reactors had an internal volume of 15 cm^3 and were fitted with a valved sidearm to allow evacuation and pressurization.

For the coking tests, anthracene and catalyst were added to reactors which were then sealed. The reactors were evacuated through the valved sidearm to less than 30 Pa, then pressurized to an operating pressure 6.9 MPa of N_2 at reaction temperature. Rapid and uniform heating of the reactors and their contents were accomplished by plunging them into a preheated fluidized-bed sandbath. Following reaction, the reactors and contents were quenched in a water bath. Heating and cooling times were less than 3 min.

Coke was determined by Soxhlet extraction with boiling pyridine. The use of pyridine insolubility has been adopted conventionally in the petroleum industry. Extractions were performed under a N_2 atmosphere to minimize oxidation of the samples. Following extraction for 24 h, which was sufficient time to ensure complete extraction, residual pyridine was expelled in vacuum at 105°C for 48 h.

RESULTS AND DISCUSSION

Coking of Anthracene Over Co-Mo/Al_2O_3

Mass Transfer Effects. For a multiphase system involving anthracene liquid and vapor and porous catalyst pellets, it is necessary to test for the effect of the rate of anthracene diffusion through the pore system of the catalyst on the measured coking rates. Diffusion effects must be eliminated before meaningful comparisons of coking rates can be made. This was achieved by comparing the coking rate over as-received pellets (1 mm diameter) and catalyst crushed to a smaller particle size (-60 mesh or < 0.25 mm diameter).

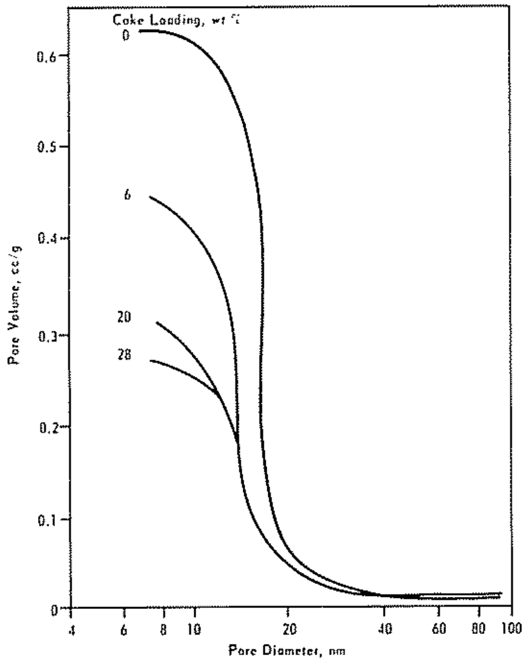
Data are shown in Table 3 for the coking of 4 g anthracene over 2 g Co-Mo/Al_2O_3 at 445°C for 2 h. The data represent weight percentages of coke to catalyst. There was no observed effect of the reduction in catalyst particle size. This is in agreement with an absence of diffusional effects. The data illustrate also that the reproducibility of the experimental procedure is within 2%.

Table 3

Effect of Co-Mo/Al_2O_3 Catalyst Particle Size on the Coking of Anthracene: 4 g Anthracene, 2 g Catalyst, 405°C, 2 h

	coke loading, wt%	
Run	1 mm diameter pellets	-60 mesh particles
1	15.6	15.9
2	15.5	15.6
3	15.9	16.0
4	16.0	15.8

The pore volume distribution within the CoO-MoO_3/Al_2O_3 pellets down to a diameter of 7 nm is given in Figure 1, as determined by Hg porosimetry up to a pressure of 207 MPa. Pore diameters were distributed narrowly around a mean of 17 nm. The total pore volume was 0.6 cc/g.



1. Pore volume distributions as measured by Hg porosimetry for the Co-Mo/Al_2O_3 catalyst containing coke loadings of 0, 6, 20 and 28 wt%.

Assuming cylindrical pores, the following relationship obtains,

$$S.A. = 4000\ V/D$$

where S.A. = specific surface area, m^2/g

V = pore volume, cc/g

D = mean pore diameter, nm.

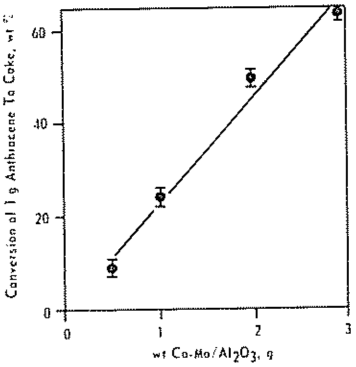
Use of this equation produces a calculated surface area for the $CoO\text{-}MoO_3/Al_2O_3$ pellets of 140 m^2/g. The surface area measured by N_2 adsorption at 77 K was 130 m^2/g, which is in reasonable agreement with the calculated value. It was deduced, therefore, that the catalyst did not contain significant microporosity which, if present, may not have been affected by the reduction in particle size.

Even for pores of 17 nm in diameter, the particle size reduction may not have been sufficient to detect intraparticle mass transfer effects. It was observed at short reaction times, however, that the anthracene filled the catalyst pore system prior to the onset of coking. Hence, an absence of diffusional effects was expected.

The reactors were agitated during each run at a rate of 60 cycles/min to enhance heat and mass transfer. Conversion was independent of agitation rates which were varied from 0 to 200 cycles/min. It was deduced, therefore, that coking rates were not masked by mass transfer effects.

The Effect of $Co\text{-}Mo/Al_2O_3$ to Anthracene Ratio. The effect of the initial $Co\text{-}Mo/Al_2O_3$ to anthracene ratio on the conversion of 1 g anthracene into coke is shown in Figure 2 for reaction at 425°C for 1 h. In the absence of added $Co\text{-}Mo/Al_2O_3$ and in the presence of the Al_2O_3 support without metals, no measurable amount of coke was produced from anthracene under these coking conditions. The conversion of anthracene to coke increased, however, as the weight of $Co\text{-}Mo/Al_2O_3$ was increased. This indicates that the $Co\text{-}Mo/Al_2O_3$ HDS catalyst was also a catalyst for the coking of anthracene under the conditions employed.

The data of Figure 2, when expressed as weight percentages of coke to catalyst, indicate that the coke loading was 23 ± 3 wt%, and was independent of the initial $Co\text{-}Mo/Al_2O_3$ to anthracene ratio. In addition, the coke loading for a given $Co\text{-}Mo/Al_2O_3$ to anthracene ratio was independent of the total weight of sample charged to the reactor. This was illustrated in Table 4 for a catalyst to anthracene ratio of 3:1 for coking at 405°C for 1 h. The coke loading was 18.8 ± 0.4 wt% for these conditions. In all subsequent experiments, 3 g catalyst and 1 g anthracene were used.



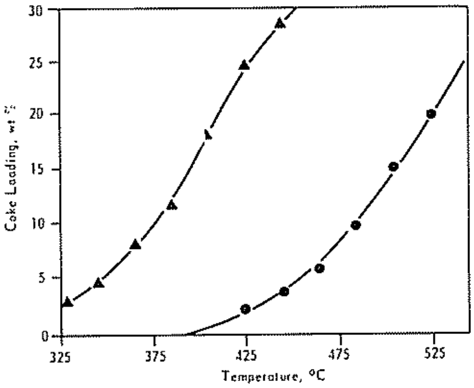
2. Effect of Co-Mo/Al_2O_3 to anthracene weight ratio on conversion to coke at 425°C for 1 h.

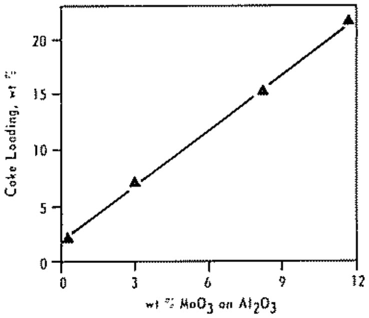
Table 4
Effect of Sample Weight on the Coking of Anthracene Over Co-Mo/Al_2O_3 at 405°C for 1 h

wt Co-Mo/Al_2O_3, g	3.0	2.25	1.50	0.75
wt anthracene, g	1.0	0.75	0.50	0.25
catalyst/anthracene	3:1	3:1	3:1	3:1
coke loading, wt%	18.7	18.4	18.9	19.1

Coke Distribution. The Co-Mo/Al_2O_3 catalyst and the catalyst containing various levels of coke were characterized with respect to their surface areas and pore volume distributions. Coke was deposited on the catalyst to levels of 6, 20 and 28 wt%. The deposition temperatures were 325, 385 and 445°C, respectively.

The change in pore volume distribution as a function of coke loading is shown in Figure 1, as determined by Hg porosimetry. For a coke level of 6 wt%, the pore volume accessible to Hg was reduced from 0.61 to 0.44 cc/g. If it is assumed that coke occupied the volume rendered inaccessible to Hg, then the calculated coke density would be 0.34 g/cc. The density of anthracene-derived coke formed in the absence of added catalysts was measured by He displacement to be 1.5 g/cc. Cokes leached from catalysts with concentrated KOH solution have been reported to have similar densities (11). It appears, therefore, that the low calculated density is due to the fact the pore volume excluded to Hg was not occupied by the coke alone. That is, either the coke contained significant microporosity not accessible to Hg at a pressure of 207 MPa and/or significant pore mouth blocking in the Al_2O_3 occurred.





3. Comparative coke loadings after 1 h on the Al_2O_3 and Co-Mo/Al_2O_3 as a function of temperature; ● Al_2O_3, ▲ Co-Mo/Al_2O_3.

4. Effect of MoO_3 loadings on Al_2O_3 on anthracene coking for 1 h at 425°C.

The surface area data of Table 5 indicate that while Hg was excluded from a significant pore volume for coke loadings up to 20 wt%, N_2 at 77 K was not. For a coke loading of 20 wt%, the N_2 surface area had been reduced by only 10 m^2/g to 120 m^2/g. This is consistent with significant coke microporosity in pores from about 0.5 to 7 nm and/or partial pore mouth blocking by apertures < 7 nm in diameter.

Table 5

Effect of Coke Loading on the Surface Area of Co-Mo/Al_2O_3

wt% coke on Co-Mo/Al_2O_3	surface area N_2 (77 K)
	m^2/g
0	130
6	125
20	120
28	95

Effect of Metals Loading. A comparison between the coking of anthracene over the Co-Mo/Al_2O_3 catalyst and the Al_2O_3 support is given in Figure 3 for a reaction time of 1 h at various temperatures. Coke loadings increased with increasing temperature in both cases but were always much greater in the presence of the Co-Mo/Al_2O_3 catalyst than in the presence of the Al_2O_3 support.

Comparison between the Co-Mo/Al_2O_3 and the Al_2O_3 is made on a weight basis since both have approximately the same surface areas as measured by N_2 adsorption at 77 K. Incorporation of the CoO and

MoO_3 on to the Al_2O_3 reduced its surface area by only 10 m^2/g from an initial value of 140 m^2/g. In addition, an error of only 1% would be associated with a possible reduction of MoO_3 to MoO_2 by hydrogen liberated during reaction. However, both of the above would have an effect of underestimating the difference in behavior between Al_2O_3 and Co-Mo/Al_2O_3 on the coking of anthracene.

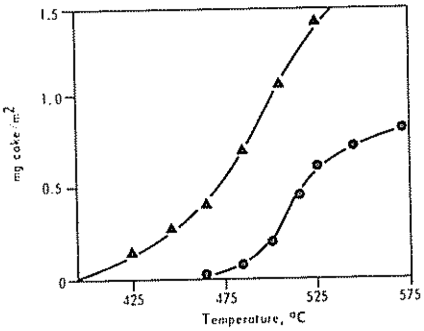
The higher activity of the Co-Mo/Al_2O_3 catalyst compared to Al_2O_3 towards coking parallels its behavior towards dehydrogenation. As discussed by Zdrazil (12), for tetrahydrothiophene in the absence of hydrogen, the ratio of dehydrogenation producing thiophene to H_2S elimination is higher on Co-Mo/Al_2O_3 than on Al_2O_3. Furthermore, the elimination of H_2S is by far the dominant reaction on Al_2O_3 indicating that Al_2O_3 has almost no dehydrogenation capacity. Gases produced from the coking of anthracene over the Co-Mo/Al_2O_3 and Al_2O_3 at 425 K for 0.75 h were measured. In both cases, H_2 was the principal gaseous species produced. However, its concentration in the presence of Co-Mo/Al_2O_3 was 20 times greater than in the presence of Al_2O_3 alone. This is in agreement with previous findings that in the absence of added H_2, Co-Mo/Al_2O_3 is a good dehydrogenation catalyst.

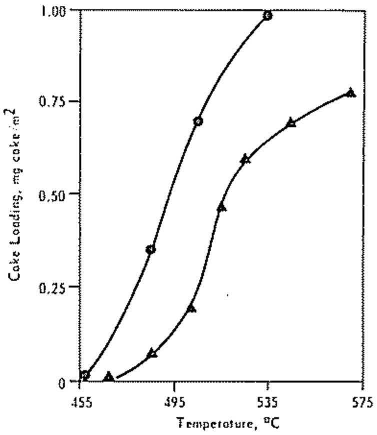
The effect of the addition of MoO_3 to the Al_2O_3 on the coking of anthracene is shown in Figure 4 for MoO_3 loadings up to 12 wt%. Data were generated at 425°C for reaction times of 0.5 h. Coke loadings increased linearly with increasing MoO_3 loading up to 12 wt%.

The dehydrogenation activity of MoO_3/Al_2O_3 catalysts has been found to increase linearly with increase in MoO_3 loading. Above a certain MoO_3 loading, however, the dehydrogenation activity remains constant with further increase in the MoO_3 loading (13). The MoO_3 loading above which no further increase in dehydrogenation activity occurs has been related to the equivalent monolayer capacity of the catalyst surface. In the present investigation, the highest loading of 12 wt% Mo (as MoO_3) was only slightly in excess of the loading required for monolayer coverage of the Al_2O_3 surface by MoO_3. The linearity of Figure 4, therefore, can be related to the linear increase in dehydrogenation activity with increasing MoO_3 loading.

Coking of Anthracene Over Carbon Black (CB) Composites

A comparison between the coking of anthracene over the CB composite and the Al_2O_3 is shown in Figure 5 as a function of temperature. Coke loadings are expressed as mg coke/m^2 of total surface area (N_2, 77 K). The validity of a comparison based on total surface area depends upon uniform distribution of coking sites over the surface.



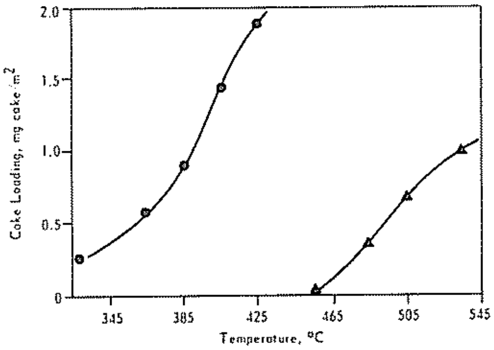


5. Comparative coke loadings after 1 h on the Al_2O_3 and CB supports as a function of temperature: ▲ Al_2O_3, ● CB.

6. Comparative coke loadings after 1 h on the CB support and Co-Mo/CB catalyst as a function of temperature, ▲ CB, ● Co-Mo/CB.

The carbon black composite showed no significant activity towards the coking of anthracene.

The effect of the addition of 10 wt% MoO_3 and 3 wt% CoO to the carbon black composite on the coking of anthracene is shown in Figure 6. Coimpregnation of the metals from an aqueous solution of ammonium molybdate (VI) tetrahydrate and cobalt nitrate was performed by incipient wetness. The catalyst was then dried in air for 24 h at 110°C. With the addition of the CoO and MoO_3 to the carbon black composite there was a significant enhancement in the coke concentration formed on the CoO-MoO_3/CB catalyst for 1 h. However, the enhancement was



7. Comparative coke loadings after 1 h on the Co-Mo/Al_2O_3 and Co-Mo/CB catalysts: ● Co-Mo/Al_2O_3, ▲ Co-Mo/CB.

much less pronounced than in the case of the $CoO\text{-}MoO_3/Al_2O_3$ catalyst. This is illustrated in Figure 7, which shows a significantly greater coking propensity for the $Co\text{-}Mo/Al_2O_3$ catalyst than for the Co-Mo/CB catalyst.

As published elsewhere (4), the addition of metals, particularly Co and Mo, effectively introduces hydrogenation and desulfurization activity to both carbon and alumina. However, as shown here, it also causes an increase in coking activity of both carbon and alumina. The smaller increase in coking propensity for the carbon than the alumina upon metals addition may be associated with an attendant smaller increase in the number and strength of acid sites. Consequently, carbon supported catalysts may be prepared to have high HDS activities and low propensities for coking.

ACKNOWLEDGMENT

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