

A THERMOGRAVIMETRIC ANALYSIS OF CATALYTIC HYDROPROCESSING OF A COAL-DERIVED LIQUID

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INTRODUCTION

Thermogravimetric analysis (TGA) has normally been used to study thermal behaviours of solid materials. The extension of this technique to materials in fluid phases is less common. So far there have been very few reports dealing with the application of TGA to solid-catalyzed gas-phase reaction system. Massoth and Cowley [1] described the use of a stirred flow microbalance in studying the catalytic hydrogenation of 1-butene under steady-state reaction conditions. More recently, TGA was combined with techniques such as online MS or GC analysis to study catalytic reactions [2,3]. However, the use of TGA in studying a solid-catalyzed gas-liquid reaction, especially when the liquid is a relatively non-volatile complex feedstock, is very limited.

Laboratory-scale experiments on the hydroprocessing of complex feedstocks such as coal-derived liquids (CDLs) involve considerable preparation and time as well as chemical analysis to obtain useful information. The application of TGA to studies of such a complex reaction system appears appealing because of its small sample size requirement, short running period, simple operation and thus low running expense. In the present work, an attempt was made to explore the usefulness of TGA to catalytic hydroprocessing of a CDL. A programmed heating of an organic complex such as a CDL usually involves vaporization and chemical reactions such as thermal cracking, coking, etc., depending on temperature and operation conditions. If the system contains an active solid catalyst, the process will be more complicated. We found that many operating parameters have significant effects on the TGA data of CDL-catalyst mixture samples. For such a complex system, it is essential to set-up standardized operating conditions. The effects of various operating parameters on TGA curves were investigated in order to establish a reliable procedure. This paper reports TGA results of catalytic hydroprocessing of a CDL, the influence of TGA atmosphere (carrier gas) on CDL weight loss, and the comparison of performances of different catalysts in TGA of CDL.

EXPERIMENTAL

TGA experiments were carried out using a Perkin Elmer TGS-2 Thermogravimetric Analyzer. In most runs, the amount of CDL in a CDL-catalyst mixture sample was about 20 mg. H₂ or N₂ was used as a carrier gas (100 ml/min, atmospheric pressure). Temperature was programmed from 50 °C to 450 °C at a heating rate of 5 °C/min. The weight loss of a catalyst itself due to removal of moisture was obtained under these conditions, and was usually less than 5%. The weight loss of CDL in contact with the catalyst was obtained by subtracting the weight loss of the catalyst from total weight loss of the mixed sample.

RESULTS AND DISCUSSION

In our preliminary experiments, we found that many TGA operating conditions such as heating rate, sample weight, pan material and carrier gas flow rate significantly influenced TGA data. Efforts were therefore made to find reasonable conditions, and the following were chosen: heating rate = 5 °C/min; CDL sample weight = 20 mg; pan material = quartz; carrier gas flow-rate = 100 ml/min.

Effect of catalyst particle size What occur in the samples under our operating conditions involve gas-liquid-solid heterogeneous reactions, such as thermal/catalytic cracking, hydrogenation, coking, etc. Weight loss percentage and weight loss rate can be considered as measurements of overall conversion and conversion rate, respectively. Conversion is strongly dependent on the contact among gas (carrier gas), liquid (CDL) and solid (catalyst). In the present work, the mixed samples of CDL and catalyst were made by simply immersing a catalyst into CDL. Particle size of the catalyst will influence the contact among the three phases, and thus conversion. Fig. 1 shows the influence of catalyst (Ni-Mo/Al₂O₃) particle size on weight loss of CDL, where the weight of CDL in the mixed samples (catalyst content 50 wt%) was 20 mg and hydrogen was used as the carrier gas. It can be noted that the presence of the catalyst has a significant effect on CDL weight loss. Compared to the data obtained in the absence of the catalyst, CDL in contact with the catalyst has an increased weight loss at lower temperatures and a decreased weight loss at higher temperatures. The finer the catalyst particles, the greater the CDL weight loss (Fig. 1a). In addition, the presence of catalyst brings about a lower temperature at which maximum CDL weight loss rate occurs (maximum weight loss rate temperature). The finer the catalyst particles, the greater the maximum of CDL weight loss rate (Fig. 1b).

In order to examine whether the difference between the curve for pure CDL and the curves for CDL in contact with the catalyst resulted from the catalysis (a chemical factor) or from the better contact between CDL and atmosphere (H₂) provided by CDL dispersion on fine solid catalyst

particles (a physical factor), a mixture of fine glass beads (0.10 - 0.12 mm) with CDL was subjected to TGA. It was found that TGA curves with and without glass beads almost overlapped, indicating that inert materials such as glass beads cannot result in substantial change in TGA curve of CDL. In other words, the increased CDL weight loss at lower temperatures and the decreased at higher temperatures in the presence of a catalyst is mostly caused by the interaction between CDL and active sites on the catalyst surface, not by a larger exterior area exposing to hydrogen. Finer catalyst particles resulted in a greater CDL weight loss and a greater weight loss rate. This is because there are more accessible catalytic sites for CDL to reach on smaller catalyst particles.

An anomalous observation is that, at relatively high temperatures the presence of catalyst always suppresses CDL weight loss. The coke formation on catalyst surface at higher temperature is the most probable reason for the phenomenon. To examine this speculation, following calcination was carried out. A residue in a sample pan was calcined at 600 °C in air in a muffle furnace for 30 minutes after TGA. The residue was weighed before and after the calcination respectively. The weight loss of the residue during the calcination accounts for the coke formed during the TGA run. CDL weight loss was obtained by subtracting catalyst weight loss from total weight loss of the sample. The results listed in Table 1 indicates that coking on catalyst surface does occur at higher temperatures. This may result from the high content of aromatics in the CDL. In subsequent runs, the catalyst particles finer than 0.12 mm were used.

Influence of the catalyst content in CDL-catalyst mixture Fig. 2 shows the influence of catalyst content in a mixture sample on CDL weight loss. Hydrogen was used as a carrier gas. CDL weight in the sample was 20 mg. The important point is that the presence of a catalyst in the feedstock resulted in an increased CDL weight loss at low temperatures. This increased weight loss is shown in Fig. 3, which was obtained by subtracting CDL weight loss observed in the absence of the catalyst from that in the presence of the catalyst. It is seen from Fig. 3 that a high catalyst content (> 50%) or a low one (< 40%) is not favourable for CDL weight loss. The fact that too high a catalyst content suppresses weight loss suggests that the weight loss is affected not only by catalytic effects but also by adsorption of CDL on the catalyst surface. When the catalyst content is increased to a certain extent (> 50%), enhanced adsorption causes somewhat stabilized adsorbed species on the catalyst surface. On the other hand, when catalyst content is too low (< 40%), it is difficult to make a uniformly mixed CDL-catalyst sample. Therefore, an intermediate catalyst content is suggested in order to obtain reliable data. In subsequent runs, a catalyst content of 40% or 50% is used.

Reproducibility of TGA results The above discussions indicate that the TGA data of CDL strongly depend on the operating conditions. Strictly controlled operating conditions are essential because of the small sample size and high sensitivity of the TGA system. Several operating parameters have been chosen. Using these standardized parameters, tests of TGA reproducibility for CDL without and with a catalyst were carried out, and the maximum deviation in CDL weight loss observed among three independent runs is 0.7% for pure CDL sample and 1.2% for CDL-catalyst mixture sample, respectively.

Effect of gas atmosphere This series of runs was carried out with Ni-Mo/Al₂O₃ catalyst. CDL weight and the catalyst content in the feedstock were 20 mg and 40 wt% respectively. Fig. 4a shows that CDL weight loss is higher when the sample is heated in hydrogen than in nitrogen. This observation is in agreement with that of Kordulis et al. [4] for Safaniya asphaltene. A lower maximum weight loss rate was also observed in an inert atmosphere (Fig. 4b). The same tendency was observed in the presence of a catalyst. In both hydrogen and nitrogen, the effect of the catalyst was displayed at lower temperatures (< 300°C), as evidenced by the higher weight loss and the lower temperature for maximum weight loss rate. At temperatures above 300 °C, weight loss was suppressed by the catalyst because of coke formation as discussed earlier. The fact that a hydrogen atmosphere is conducive to weight loss suggests that contacting the CDL plus catalyst with H₂ suppresses the formation of coke on the catalyst to some extent. Comparison between curves 2 and 4 indicates that, for CDL feedstock which is of high aromaticity, catalytic *hydroprocessing* is much more effective than catalytic processing without the participation of hydrogen.

Comparison between different catalysts Fig. 5 summarizes the results obtained from CDL with three different catalysts at identical TGA conditions. A comparable run with pure CDL is also included. All the experiments were run in hydrogen (100 ml/min). Mixed samples contained 20 mg of CDL and 40 wt% of catalyst. Compared to the curve for pure CDL (Fig. 5, curve 1), all three curves for catalyst presence show a similar tendency, i.e., below 300 °C, the presence of catalysts has a positive effect on CDL weight loss, while above 300 °C, it suppresses CDL weight loss. Three residues from these runs were subjected to calcination using the same method as described earlier, and the results are shown in Table 2.

It is indicated in Fig. 5 and Table 2 that the interactions between three catalysts and CDL are different. The retention of CDL on the catalysts while being heated is likely to be caused by the combination of two factors, i.e., (1) surface adsorption affinity for the components present in CDL and (2) the condensation of aromatic compounds. The former predominates at lower temperatures while the latter does at higher temperatures. The additional weight loss of CDL in

the presence of catalysts may be attributed to catalytic (hydrogenation/hydrocracking) activity of the catalysts, which may occur over the whole temperature range tested. The differences between the TGA curves for different catalysts likely represent different catalytic selectivities for competing reactions such as thermal and catalytic cracking, hydrocracking, hydrogenation and coking. Coking is favoured at higher temperatures with a deficiency of H₂. Among the three commercial catalysts tested, Co-Mo/Al₂O₃ exhibits the maximum retention of CDL mass over the entire programmed temperature range. One may deduce that there is a stronger interaction between CDL and Co-Mo/Al₂O₃, which brings about somewhat stabilized adsorbed species. Because of the stable adsorption, on the one hand, it becomes more difficult for volatile components to evaporate and for reactive heavier species to be converted into lighter ones, and on the other hand, it becomes easier for aromatic species to condense on active sites of the catalyst.

If the catalyst which exhibits the minimum retention of CDL mass during the temperature-programmed heating to 450 °C is considered to be the superior one, the Ni-Mo/Al₂O₃ appears to be the best for hydroprocessing of CDL. The TGA curves have shown a different extent of CDL weight loss for each catalyst. These real differences in weight loss suggest that TGA may be useful as a tool for a quick but rough evaluation of hydrocracking catalysts.

A comparison between hydrocracking catalyst test results using the TGA method and from high-pressure batch tests To evaluate the ability of TGA to indicate the relative activities of catalysts for hydroprocessing CDL, additional runs at 13.9 MPa and 400 °C were carried out in a catalytic stirred tank reactor operated in a closed (batch) mode [5]. The following comparisons were obtained from analysis of the product liquid:

Hydrodesulfurization activity:	Ni-Mo/Al ₂ O ₃ > Ni-W/Al ₂ O ₃ > Co-Mo/Al ₂ O ₃
Hydrodenitrogenation activity:	Ni-Mo/Al ₂ O ₃ > Ni-W/Al ₂ O ₃ > Co-Mo/Al ₂ O ₃
Hydrodeoxygenation activity:	Co-Mo/Al ₂ O ₃ > Ni-Mo/Al ₂ O ₃ > Ni-W/Al ₂ O ₃
Aromaticity-reducing ability:	Ni-Mo/Al ₂ O ₃ > Ni-W/Al ₂ O ₃ > Co-Mo/Al ₂ O ₃
H/C ratio of the product liquid:	Ni-W/Al ₂ O ₃ > Ni-Mo/Al ₂ O ₃ > Co-Mo/Al ₂ O ₃
Conversion to gas-oil (343-524 °C):	Ni-Mo/Al ₂ O ₃ > Ni-W/Al ₂ O ₃ > Co-Mo/Al ₂ O ₃

While some of the above differences may be small, these results suggest that the Ni-Mo/Al₂O₃ catalyst provided the best overall performance. The TGA results yielded the weight loss in the following sequence (see Fig. 5):

Ni-Mo/Al₂O₃ > Ni-W/Al₂O₃ > Co-Mo/Al₂O₃.

Thus there may be some qualitative relation between overall catalyst performance and weight loss during a temperature-programmed TGA experiment.

SUMMARY

Because of small sample size and high sensitivity of TGA, its results will be significantly affected by operation conditions, especially when the sample involves a complicated system like the mixture of a relatively non-volatile CDL and a solid catalyst. In order to ensure reproducibility and to make valuable comparisons of experimental data, strictly standardized procedures need to be pre-defined in applications such as catalytic hydroprocessing (gas-liquid-solid systems).

TGA can provide useful information about solid-catalyzed relatively non-volatile liquid phase reaction systems. Such an application to hydroprocessing of a CDL was demonstrated in the present work. The weight loss of CDL as a function of increasing temperature is increased at lower temperatures and lowered at higher temperatures when a catalyst is present, irrespective of whether the atmosphere is H₂ or N₂. Preliminary results suggest that the catalyst most active for hydroprocessing of the CDL tested is the catalyst producing the greatest weight loss.

Our experimental results suggest that many of the molecular fragments are strongly adsorbed on the surface of the catalyst. In a batch-type experiment such as in a TGA weighing pan, this adsorption may persist over the entire range of temperature tested and its magnitude may vary with the type of catalyst tested. At higher temperatures (>300 °C), the reactions involving coking increasingly dominate.

What occurs during TGA of CDL in H₂ atmosphere in the presence of a catalyst is so complicated that some ambiguities in TGA results exist. So far it is not yet possible to comment in depth about the chemistry involved because TGA only provided a mass-temperature record of the process. Additional work using TGA combined with some means of identifying the chemical character of the evolved gases seems to be valuable. Recent designs of TGA equipment available enable mass changes as large as ten grams to be monitored. Access to such equipment would enable chemical analysis of the residue as well as the evolved gases to be determined.

REFERENCES

- [1] F.E. Massoth and S.E. Cowly, *Ind. Eng. Chem. Fund.*, 15 (1976) 218.
- [2] J.W. Dean and D.B. Dadyburjor, *Ind. Eng. Chem. Res.*, 27 (1988) 1754.
- [3] D.E. Rogers and L.M. Parker, *Appl. Catal.*, 51 (1989) 181.
- [4] C. Kordulis, F.M. Faus and B. Delmon, *Appl. Catal.*, 23 (1986) 367.
- [5] I.G. Dalla Lana, "Hydroprocessing of Coal-Derived Liquids", Final Report to Alberta Office of Coal Research and Technology, (1990).

Table 1 Coke formation from pure CDL and from CDL-catalyst mixture

Sample for TGA	Weight loss after TGA (wt%)	Weight loss after calcination (wt%)	Coke formed during TGA (wt%)
pure CDL	82.38	98.80	16.42
CDL-catalyst mixture	77.47	98.79	21.32

Table 2 Coke formation on three commercial catalysts

Mixture samples for TGA	Ni-Mo/Al ₂ O ₃ & CDL	Co-Mo/Al ₂ O ₃ & CDL	Ni-W/Al ₂ O ₃ & CDL
Weight loss of CDL after TGA (%)	77.47	74.08	75.44
Weight loss of CDL after calcination (%)	98.79	98.82	98.78
Coke formed during TGA (%)	21.32	24.74	23.34

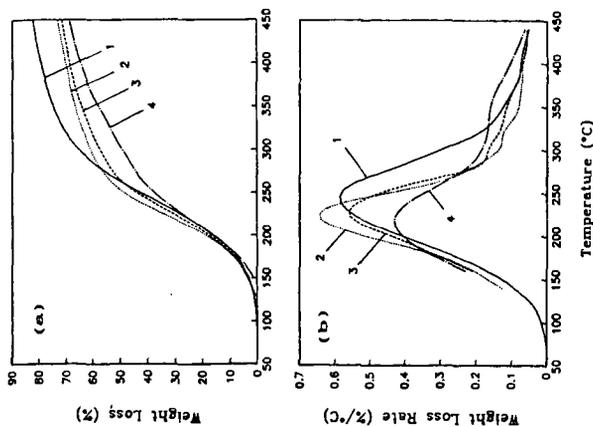


Fig. 1 Effect of catalyst particle size on TGA curve of CDL: (1) no catalyst; (2) <math>< 0.12\text{ mm}</math>; (3) 1.59 mm; (4) 3.18 mm. Catalyst content = 50 wt%; carrier gas = H₂.

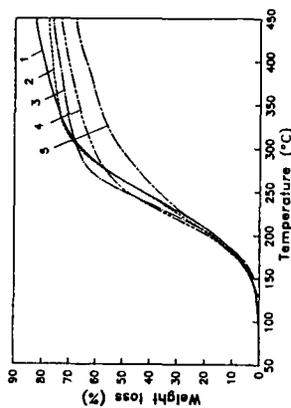


Fig. 2 Influence of catalyst content (wt%) in mixture sample: (1) 0%; (2) 25%; (3) 40%; (4) 50%; (5) 60%. Carrier gas = H₂.

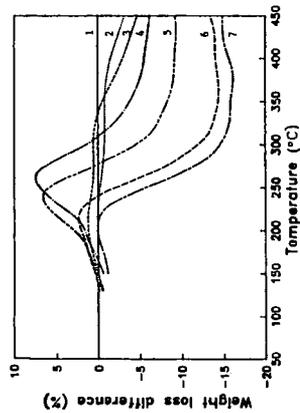
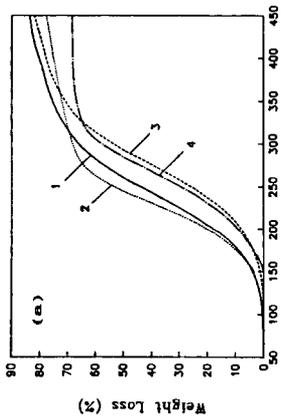


Fig. 3 The difference between CDL weight losses in the presence of the catalyst and that in the absence of the catalyst. Catalyst content: (1) 0; (2) 10%; (3) 25%; (4) 40%; (5) 50%; (6) 57%; (7) 60%.

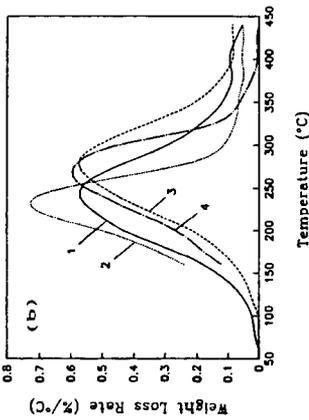


Fig. 4 Effect of atmosphere on TGA curve of CDL with and without the catalyst: (1) H_2 , without catalyst; (2) H_2 , with catalyst; (3) N_2 , without catalyst; (4) N_2 , with catalyst. Catalyst content = 40%.

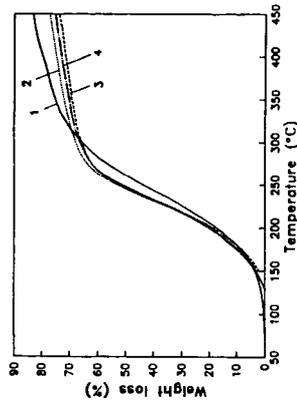


Fig. 5 TGA curves of CDL in the presence of different commercial catalysts: (1) no catalyst; (2) Ni-Mo/ Al_2O_3 ; (3) Co-Mo/ Al_2O_3 ; (4) Ni-W/ Al_2O_3 . Carrier gas = H_2 .