

## Deactivation of a Hydrogenation Catalyst: Importance of Mass Transfer

Arthur R. Tarrer, Hyon H. Yoon, Vinay P. Wagh  
Chemical Engineering Department, Auburn University, AL 36849

### Introduction

Over the past few years, a study for a private company has been ongoing at Auburn in parallel with its coal liquefaction program, that involves the development of a hydrogenation process using feedstocks that can be derived from coal. For economic reasons this hydrogenation process had to be done at low severity conditions, i.e., at low temperatures ( $\sim 100^{\circ}\text{C}$ ) and at low hydrogen partial pressures ( $\sim 100$  to  $200$  psi.). It was found that the hydrogenation could be done in the required low pressure and temperature ranges only after a variety of design and operational changes had been made to increase hydrogen gas/liquid mass transfer rates. A new hydrogenation reactor design was developed for the purpose of facilitating hydrogen gas/liquid mass transfer, such that gas compression requirements and gas (VOC) emissions could be kept a minimum.

In this research project, as in coal liquefaction processes, the need exists to reduce process severity by minimizing hydrogen partial pressure requirements. Reducing hydrogen partial pressures can change the relative rates of different reactions (condensation versus hydrogenation) and can result in catalyst deactivation and low conversions. The relative roles that gas/liquid mass transfer and transport mechanisms play in this is important. Design and operational changes can be made, as were done in the above work, to increase mass transfer rates and overcome limitations caused by the mass transfer. Whereas, limitations caused by kinetics, can be overcome by using a more active and selective catalyst. In reducing process severity, mass transfer related parameters and kinetic activity related parameters (e.g., catalyst activity/selectivity) must be changed simultaneously.

In the following discussion, first it will be shown that both a reduction in hydrogen partial pressure and an increase in temperature for the hydrogenation of a heavy coal-derived fraction (SRC) lead to catalyst deactivation. This reaction data for model compound hydrogenation at high severity conditions and at low severity conditions will be presented. In so doing, the responses in catalyst activity/deactivation to changes in kinetic and mass transfer parameters will be examined. A comparison will then be made between the observed responses and governing mechanisms at high severity conditions, and some conclusions will be drawn regarding the importance of mass-transfer parameters--particularly gas/liquid mass transfer--in maintenance of catalyst activity at low severity conditions.

### Effect of Hydrogen Partial Pressure and Temperature on Catalyst Activity/Deactivation

Coking is generally accepted to be the chief cause of catalyst deactivation during the hydrogenation of coal liquids. Like any other reaction, coking reactions proceed at a faster rate and to a greater extent at elevated temperatures. The effect of reaction temperature on deactivation rate has been studied here by measuring the activity of a hydrogenation catalyst (Shell 324 Ni-Mo-Al<sub>2</sub>O<sub>3</sub>) deactivated at different temperatures while hydrogenating a coal liquid (SRC fraction). Naphthalene hydrogenation activity is used here as an indicator of catalyst activity (1) and is given in terms of percent hydrogenation of the naphthalene. Percent hydrogenation (or catalyst activity) is plotted versus the coal liquid (SRC) hydrogenation temperature in Figure 1. As to be expected, present hydrogenation decreases rapidly with increasing temperature.

The effect of hydrogen partial pressure on the extent of deactivation is studied similarly by charging a microreactor with hydrogen at different pressures at room temperature. Naphthalene hydrogenation activity is plotted against reactor charge pressure in Figure 2. The plot shows that percent hydrogenation decreased as the hydrogen pressure in the reactor was decreased.

The above observation--that catalyst was deactivated to a greater extent at reduced hydrogen pressures--agrees with the findings reported for hydrotreating petroleum residue. Sie (2) found that the steady-state carbon level on a catalyst depends on the hydrogen partial pressure in the reactor; an approximate inverse linear relationship between these two parameters was observed. Similarly, in aromatizing cyclohexane, Ruderhausen and Watson (3) observed a linear relationship between the amount of carbon deposition and hydrogen partial pressure. Donath (4) observed that decalin splitting activity for a WS<sub>2</sub> catalyst was decreased considerably at lower pressures. A decrease in hydrogen partial pressure may cause a decrease in the amount of adsorbed hydrogen on the catalyst surface, due to lower mass transfer rates or because the dissolved hydrogen concentration in the reactant is lower, as will be discussed later. As a result, there would probably be an increase in the rate of condensation over that of hydrogenation. This would cause more coke formation at the lower hydrogen pressures.

### High Severity Hydrogenation Studies

In this section, naphthalene hydrogenation is used as a model reaction to demonstrate the relative importance of kinetic and mass-transfer parameters on catalyst activity/deactivation. It is to be shown that under high severity conditions, for certain catalysts, naphthalene hydrogenation follows an apparent first-order kinetics, depending on both naphthalene concentration and dissolved hydrogen concentration (i.e., hydrogen partial pressure). Also, gas-liquid mass transfer does not appear to have any significant influence on hydrogenation rates, and no significant deactivation appears to occur for this model reaction as long as the sulfide state of the catalyst is maintained.

A series of naphthalene hydrogenations were done in a microreactor at different hydrogen partial pressures. During hydrogenation, it was assumed that the hydrogen pressure was maintained constant at the mean value of the initial hydrogen pressure and the hydrogen pressure recorded at the end of the

reaction. Figure 3 gives a first-order plot relating hydrogen partial pressure to naphthalene conversion,  $x$ . Apparently, naphthalene rates vary with hydrogen partial pressure (thus, dissolved hydrogen concentration) in a first-order manner, under these conditions. The intrinsic rate constant,  $k$ , obtained from the slope of the figure for naphthalene hydrogenation on a presulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at 380°C has a value of  $4.5242 \times 10^{-3}$  g liquid/(g catalyst min. psia of H<sub>2</sub>).

The reaction parameter used most often to evaluate the relative importance of gas-liquid mass transfer is agitation rate. Varying the agitation rate changes the observed reaction rate only when gas/liquid mass transfer is at least partially rate controlling (5). A plot of naphthalene conversion versus agitation rate is shown in Figure 4. A microreactor was used here. In the absence of steel balls, given by curve 1, the effect of agitation on conversion was marginal up to 500 cpm; however, there was a sudden increase in the conversion in the agitation range 500-550 cpm, and further increase in agitation had no significant effect on conversion which remained constant at about 40 percent. It should be noted that the drop in conversion in the low agitation range (<500 cpm) may be due to poor catalyst dispersion (6). Obviously, in the higher agitation range (>500 cpm), as was used in collecting the deactivation data with coal liquids shown earlier, Figure 1, gas/liquid mass transfer does not appear to be controlling (7).

Catalyst deactivation rate during naphthalene hydrogenation was evaluated by performing successive hydrogenations with a presulfided catalyst in the absence of CS<sub>2</sub> and in its presence. The catalyst activity in terms of percent hydrogenation is given in Figure 5. Since hydrogen was consumed in the hydrogenolysis of CS<sub>2</sub>, the amount of hydrogen in the reaction vessel had to be increased in order to maintain the amount of hydrogen available to the reaction at a level equivalent to those reactions without CS<sub>2</sub>. In the CS<sub>2</sub> reactions, the percent of excess hydrogen was 1340%, as compared to 1400% without CS<sub>2</sub>. The amount of CS<sub>2</sub> added was equivalent to five times the amount used ordinarily to sulfide shell 324 NiMo catalyst.

Apparently, the activity of the catalyst remained essentially constant in all the reaction cycles, with and without CS<sub>2</sub> added. The sulfur content of aged catalysts was measured after the final naphthalene hydrogenation in the successive reaction series. The fresh presulfided catalyst, presulfided/no CS<sub>2</sub> catalyst, and presulfided/CS<sub>2</sub> catalyst had sulfur contents of 8%, 7%, and 7.6% respectively. The presulfided/no CS<sub>2</sub> catalyst as well as the presulfided/CS<sub>2</sub> catalyst had a slightly lower sulfur content compared to that of the fresh presulfided catalyst. Also, the presulfided/no CS<sub>2</sub> catalyst had a slightly less wt.% sulfur than the presulfided/CS<sub>2</sub> catalyst. However, the activity of the presulfided catalyst was nearly the same in the presence as well as in the absence of CS<sub>2</sub>. It should be noted that the amount of bulk sulfur may not be a true indication of the extent of sulfiding. In summary, the data show that no significant catalyst deactivation occurred under the reaction conditions used here.

#### Low Severity Hydrogenation Studies

In all of the above hydrogenations, the reaction severity was relatively high (temp. >300°C, pres. > 800 psi H<sub>2</sub>). The hydrogenations to be considered in the following section were those done for a private company and were at

relatively low severity conditions. Here, again using model reactants (naphthalene and *o*-methyl styrene), it will be shown that gas/liquid mass transfer must be considered, because of the high catalyst activity. High catalyst activities are required here in order to attain high conversions under the low severity hydrogenation conditions. A comparison will be made between activities observed with a reactor having poor mass transfer characteristics and one having good mass transfer characteristics. By altering the reactor having poor mass transfer characteristics and making appropriate changes, activities are shown to improve and under these conditions--at which mass transfer becomes no longer controlling--no appreciable catalyst deactivation will be shown to occur.

Hydrogenation of naphthalene was performed at 90°C and 100 psi of H<sub>2</sub> at 25°C in a microreactor (Table 1). Six weight percent catalyst loading of Raney nickel 2800 was used. After 15 min of reaction naphthalene conversion was 100% to tetralin; no significant decalin formation was observed. Assuming first-order kinetics with respect to naphthalene concentration, the kinetic rate constant was about 0.8 min<sup>-1</sup> based on 15 min. of hydrogenation required to attain 100% conversion.

To study the influence of gas/liquid mass transfer on low severity naphthalene hydrogenation, a different type of reactor--a 300 cc. autoclave--was used. The gas/liquid mass transfer rates in this autoclave were known to be poorer than that in the microreactor used in the above studies. Figure 6 gives a plot of the mass transfer parameters  $k_L a$  versus the mixing parameter,  $M$ . These values were obtained using sulfite oxidation. The maximum  $k_L a$  values in the bubble column, the stirred tank, and the microreactor (TMBR) were 0.1, 0.25, and 3.8 s<sup>-1</sup>, respectively. Coefficients as high as 0.15 and 0.5 s<sup>-1</sup> have been reported in literature in bubble columns, and stirred vessels (Van't Riet, 1979), respectively, but none approached the value obtained here for the microreactor (TMBR). From Figure 6 it is observed that the gas-liquid mass transfer rate in the TMBR was roughly an order of magnitude greater than in the autoclave and the bubble column reactors (7).

A comparison is made in Table 2 between the naphthalene conversion observed in the microreactor (TMBR) and that in the 300 cc autoclave. In general, while performing the hydrogenation in the autoclave, a steady state catalyst activity could not be obtained. The reproducibility of the reaction rates was consequently poor. This was observed to be true also for low severity *o*-methyl styrene (AMS) hydrogenation at low severity conditions using a relatively high activity catalyst. With AMS, in the microreactor as well as the autoclave, the reaction rate was observed to increase with increased agitation, indicating that mass transfer resistances were the controlling factors (Table 3).

The following changes were made to improve the gas/liquid mass transfer rates in the autoclave: 1) baffles were installed 2) the hydrogen partial pressure was increased (100 to 600 psi) 3) toluene was used instead of hexadecane to reduce the reaction mixture viscosity 4) the maximum stirring rate (2800 rpm) was used. Once these changes were made, the naphthalene conversion was the same in the autoclave as it was in the microreactor. A series of hydrogenations were also made in the autoclave to evaluate catalyst deactivation (Figure 7). Under these conditions of high mass transfer rates, no significant catalyst deactivation was observed.

### Summary

Catalyst deactivation was observed to occur while hydrogenating coal liquids under high severity conditions. The rate of catalyst deactivation increased as the hydrogen partial pressure was reduced and as the reaction temperature was increased. For the model reactant naphthalene, however, under high severity conditions, no catalyst deactivation was observed to occur; gas/liquid mass transfer was not controlling; and the hydrogenation appeared to be kinetically controlled having a first-order dependency on dissolved hydrogen concentration (i.e. hydrogen partial pressure) and on naphthalene concentration. Under low severity conditions when a higher activity catalyst was required, on the other hand, mass transfer was observed to be controlling factor both for naphthalene and AMS hydrogenation. Also, with high mass transfer rates no significant catalyst deactivation was observed, but with low mass transfer rates significant catalyst deactivation was observed.

The implications of these observations are that mass transfer as well as kinetic related parameters must be addressed in searching for lower severity coal liquefaction processes. The observed catalyst deactivation with coal liquid hydrogenation cannot be attributed solely to kinetics--catalyst selectivity etc. Poor hydrogen mass transfer could have been a major factor in causing the observed deactivation, even though, for the model reactant naphthalene, mass transfer was not observed to be limiting. Many of the coal liquefaction reactions have higher hydrogenation rates than does naphthalene, and when the hydrogen transport mechanism is not able to meet these higher rate demands, deactivation can occur. To achieve lower severity conditions, higher activity catalysts are needed as was true here with naphthalene, and for higher activity catalysts, higher gas/liquid mass transfer rates are required to minimize deactivation. Higher mass transfer rates can be achieved as was shown here for naphthalene hydrogenation through reactor design changes and appropriate operational changes. In the study done for the private company referred to here, a novel reactor design was developed for their specific purpose.

### References

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Table 1. Conversion of Naphthalene to Tetralin Using Raney Nickel 2800 and Different Reaction Times (Microreactor)

Reaction time, min	Conversion of Naphthalene to Tetralin, area %
5	31
15	100
30	100
60	100
90	100

Reaction Mixture:

Naphthalene - 0.3 g  
 Tetralin - 2.7 g  
 Raney Nickel - 0.1 g

Reaction Conditions:

Temperature - 90°C  
 H<sub>2</sub> Pressure - 100 psi at 25°C  
 Reactor Volume - 45 cc  
 Agitation - 860 cpm

1st Order Reaction Rate,  $k = 0.8 \text{ min}^{-1}$ , based on 15 minute reaction time.

Table 2. Comparison Between Naphthalene Conversion in Microreactor with High Mass Transfer Rates and in 300 cc Autoclave with Low Mass Transfer Rates.

Reaction Time, min	Reactor Type	Conversion of Naphthalene, area %
15	Microreactor	100
60	Autoclave	65

Reaction conditions were the same as those shown in Table 1.

Table 3. Molar Reaction Rates in Alpha-Methyl Styrene Hydrogenation

RPM	Autoclave r, g-moles/hr.lit.	CPM	TBMR r, g-moles/hr.lit.
650	0.025	400	0.75
1050	0.3	600	0.9
1650	0.74	800	1.15
2150	0.84	1000	1.5
		1200	1.75

Experimental Conditions:

Temperature - 20°C  
 Catalyst loading - 13.1 g/l (TBMR)  
 - 6.6 g/l (Autoclave)

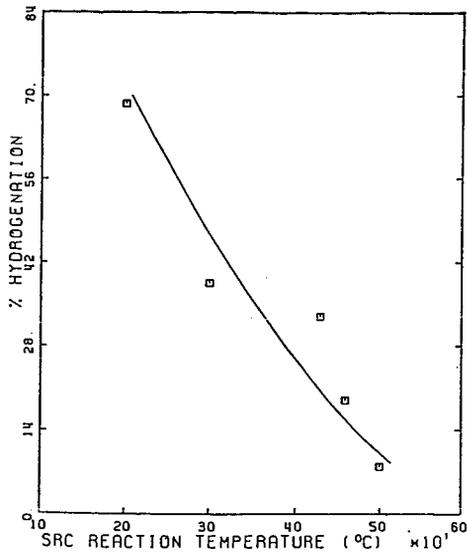


Figure 1. Effect of SRC Reaction Temperature on Catalyst Deactivation (NiMo/Al<sub>2</sub>O<sub>3</sub>). (1)

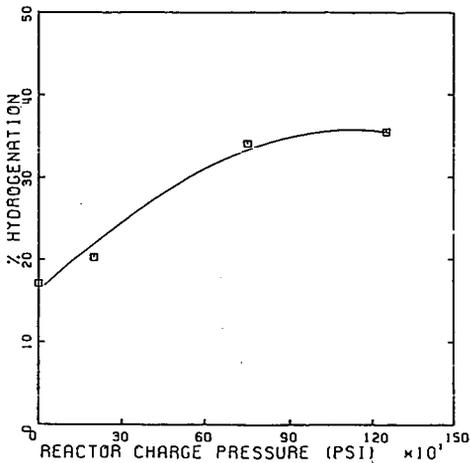


Figure 2. Effect of Hydrogen Pressure on Catalyst Deactivation (NiMo/Al<sub>2</sub>O<sub>3</sub>). (1)

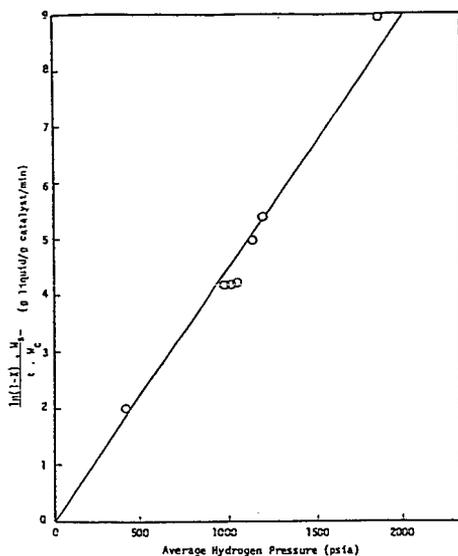


Figure 3. Effect of Hydrogen Pressure on Naphthalene Reaction Rate (CoMo/ $\text{Al}_2\text{O}_3$ ). (6)

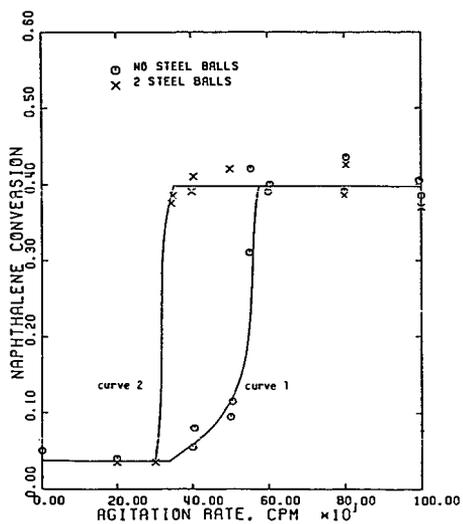


Figure 4. Naphthalene Conversion to Tetralin as a Function of Agitation Rate (CoMo/ $\text{Al}_2\text{O}_3$ ). (7)

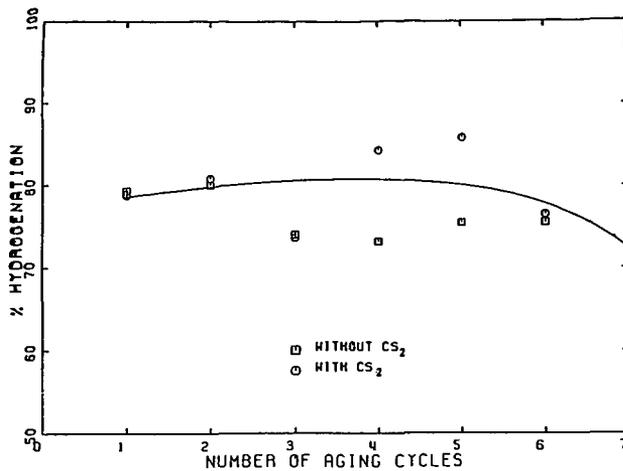


Figure 5. Comparison of the Activity of the Presulfided Catalyst in Successive Naphthalene Hydrogenation Reactions with/without the Addition of CS<sub>2</sub> (NiMo/Al<sub>2</sub>O<sub>3</sub>). (1)

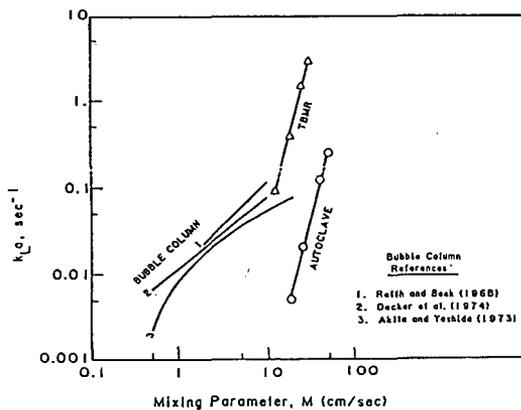


Figure 6. Comparison of  $k_L$  in different Reactor Types. (7)

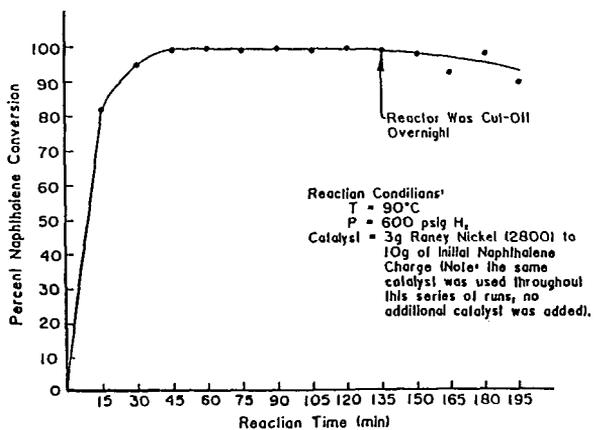


Figure 7. First Series, Batch Hydrogenation of Naphthalene to Tetralin in a 300 cc Autoclave.