Research Article

The Reactants’ Phase State: A Nonnegligible Factor in Tetralin Hydrogenation Catalysts Evaluation

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The effects of reactants’ phase states (gas-liquid and single gas phase) on tetralin hydrogenation were investigated in the fixed bed. The kinetics of tetralin hydrogenation under different phase states was analyzed. Results showed that, without phase transition, the tetralin conversion increased with the rise of temperature. However, it decreased dramatically around the dew point of the feed at which the reactants’ phase state transferred from gas-liquid phase into gas phase. It was also observed that the gas-liquid phase state was favorable to reduce the deactivation of catalyst in the tetralin hydrogenation.

1. Introduction

The deep hydrodearomatization of diesel fuels has been focused because of the environmental legislation and the clean-fuel production [1–3]. The development of catalytic technology for aromatic saturation and sulfur removal is highly desirable. Since the composition of diesel is complex, model compounds like toluene, tetralin, and naphthalene were commonly used in the evaluation of catalysts’ performances. Without thermodynamic equilibrium limitation, the conversions of these model aromatics should increase with the rise of reaction temperature. However, some studies on the aromatic hydrogenation have found that the conversions of aromatics increased with the rise of temperature at a relatively low temperature but decreased with the further rise of temperature [4, 5]; some others have showed an increase-decrease-increase tendency with the rise of temperature [6–10]; still others showed that hydrogenation depth was deeper at low temperature than at high temperature [5, 10–14]. Generally, these phenomena were ascribed to the exothermal character of the hydrogenation reaction. In other words, the thermodynamic equilibrium constrained the conversion of aromatics [4, 5, 7–9, 11]. Nevertheless, the calculation results showed that the equilibrium conversion of naphthalene to tetralin could approach 100% under 5 MPa and 300°C; even at 350°C and 5 MPa, the equilibrium conversion was also higher than 95% (estimated from the figures in [3]). The hydrogenation of tetralin to decalin had a similar behavior. Furthermore, there were also studies with excellent aromatics conversion under similar reaction conditions [15]. Therefore, further study should be performed to investigate the reasons that caused the decrease of aromatics conversion with the rise of temperature, especially under relatively low reaction temperature.

Another probable reason that affects aromatics conversion is the reactants’ phase state. The liquid phase vaporizes gradually with the rise of reaction temperature. At the dew point of the feed, all liquid phase vaporizes into vapor phase. When the reaction temperature is below the dew point of the feed, the liquid phase is existent, and the hydrogen would dissolve in the liquid phase and react with aromatics on the catalyst surface (gas-liquid-solid reaction mode). When the reaction temperature is above the dew point of the feed, all the liquid phase vaporizes into gas phase and reactants react on catalyst in gas-solid reaction mode. The two reaction modes are intrinsically different. This difference probably affects the
hydrogenation activity of catalyst and leads to the decrease of aromatics conversion. Generally, model compounds are composed of aromatics and inert hydrocarbons; for example, naphthalene dissolves in n-hexadecane [16–19], n-tridecane [20, 21], n-decane [22], n-heptane [5, 10–14, 23], and benzene [4] or tetralin dissolves in n-dodecane [24], n-decane [22, 25, 26], n-heptane [6–9, 12, 15, 27, 28], n-hexane [29], and cyclohexane [30, 31]. The model compounds using light components as solvents are easier to vaporize and have lower dew point. The reaction mode of these model fuels might change from gas-liquid-solid to gas-solid mode. Accordingly, the conversion of aromatics might change during the phase transition.

In this work, tetralin was diluted in n-tetradecane, n-decane, and n-octane and then hydrogenated in a fixed bed under 5 MPa, 220 to 290°C, and different H2/oil ratios. The effects of reactants’ phase states on tetralin conversion and products distribution were discussed.

2. Experimental

A mesoporous MCM-41 (Si/Al = 24, atom ratio) type catalyst containing 1.0 wt.% of Pt was prepared by incipient wetness impregnation of aqueous solution containing required amount of Pt(NH3)4Cl2. After Pt impregnation, the sample was kept at ambient temperature overnight and then dried at 110°C for 3 h and finally calcinated at 400°C for 4 h.

The hydrogenation of tetralin was performed in a fixed bed reactor (inner diameter 12 mm, length 600 mm). 3 g catalyst (20–16 mesh) was placed in the isothermal zone of the fixed bed reactor. The reaction temperature was controlled by 4 thermocouples placed at the reactor wall and monitored with a thermocouple directly placed in the catalyst bed. Before the activity test, the catalyst was in situ reduced with 100 mL/min H2 at 400°C for 4 h. The tetralin (20 wt.%) dissolved in n-tetradecane, n-decane, or n-octane was supplied by a Series II piston pump with the flow rate of 0.3 mL/min. The H2 flow rate (generally 100 mL/min, H2/oil (v/v) = 333) was controlled by a mass flow controller. The reaction pressure (5 MPa) was adjusted by a back pressure valve.

At each reaction condition, the product was collected after 3.5 h in order to achieve steady-state activity. The quantitative analysis of the reaction products was carried out using an Agilent 7890A GC system equipped with a capillary column (HP-ONAs, 50 µm × 0.2 mm × 0.5 µm) and FID detector. The products were preliminarily identified by an Agilent 6890 GC-MS system equipped with a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 µm). The hydrogenation products were t-decalin, c-decalin, C10 products (the ring opening products and the isomers of decalin), and cracking products (C3 to C9 hydrocarbons; these compounds were ignorable at temperature below 270°C). About 0.01%~0.02% of C20 compounds, which were ascribed to the oligomerization of C10 component, were also detected at 290°C. Although the amount of C20 compounds were ignorable, they might affect the deactivation of catalyst.

3. Results

Figure 1 showed the effects of different solvents on the tetralin conversion at the temperature range from 220°C to 290°C. The tetralin conversion in n-tetradecane increased with the rise of temperature. However, there were transition points when n-decane and n-octane were used as solvents. When n-decane was used as solvent, the tetralin conversion decreased at 290°C. When the solvent was alternated to n-octane, the tetralin conversion decreased at 260°C and then increased with the further temperature rise. Tetralin conversions in n-octane and n-decane are similar at 290°C. But the values are much lower than in n-tetradecane. Increasing the H2/oil ratio from 333 to 666 led to the increase of tetralin conversion and resulted in a lower temperature (250°C) at which tetralin conversion began to decrease.

Figures 2 and 3 showed the influence of solvent on the C10 yield and the t-decalin/c-decalin ratio, respectively. Both the C10 yield and the t-decalin/c-decalin ratio increased with the rise of temperature in all the solvents. Differently from the results in n-tetradecane, two increased stages of C10 yield and t-decalin/c-decalin ratio were observed in n-octane. The temperature transition points of the two stages were similar to that of tetralin conversion in Figure 1. The transition of C10 yield and t-decalin/c-decalin ratio in n-decane can also be observed at 270°C, but not as obviously as in n-octane.

Figure 4 showed the tetralin conversion in n-octane under different hydrogen flow rates at 250°C. Firstly, the tetralin conversion increased with the increase of the H2/oil ratio, and then it decreased dramatically between the H2/oil ratios = 555 and 666. Further increase in H2/oil ratio led to the increase in tetralin conversion again. The retested values at H2/oil ratios = 333 and 666 were lower than the values in Figure 1, which indicate the deactivation of the catalyst. The yield of tetralin in naphthalene hydrogenation with the rise
of hydrogen/naphthalene ratio also exhibited the increase-decrease-increase tendency [28].

4. Discussion

4.1. Effect of Phase State on the Catalytic Activity

4.1.1. Relationship of Dew Point and Catalytic Activity. With the rise of temperature, the liquid phase vaporized gradually until all the liquid changed into gaseous phase at the dew point of the feed. The reaction modes below and above the dew point were intrinsically different, as illustrated in Scheme I. Liquid phase exists at the temperature below the dew point of the feed. The hydrogen was dissolved in liquid phase and reacted with tetralin molecule on the catalyst surface. In other words, the reaction took place in the gas-liquid-solid mode or the trickle bed mode. Tetralin and solvents are all vaporized into gas phase at the temperature above the dew point. Thus hydrogen and tetralin molecules diffused to the catalyst surface in gaseous phase, adsorbed on the active sites, and reacted with each other in the gas-solid mode. The difference between these two reaction modes might affect the catalytic activity.

The dew points of reactants under the given conditions of pressures, liquid flow rates, and H2/oil ratios can be calculated by equation of state. PR and SRK [32] equations of states are commonly used in phase equilibria modeling. They were compared in hydrogen-hydrocarbon phase equilibria calculation with experiment data. The SRK equation of state is a little more accurate than the PR equation of state. Thus the dew points were calculated using SRK equation of state (1) as follows and the results were listed in Table I:

$$p = \frac{RT}{V - b} - \frac{a}{V (V + b)},$$

$$a = a_c \cdot \alpha(T, \omega),$$

$$a_c = 0.42748 \frac{p_c^2 T_c}{\rho_c}.$$

Table I: Dew points of feeds with different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n-Tetradecane</th>
<th>n-Decane</th>
<th>n-Octane</th>
<th>n-Octane-666</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dew point, °C</td>
<td>356</td>
<td>297</td>
<td>266</td>
<td>239</td>
</tr>
</tbody>
</table>

aReaction conditions: 3 g catalyst, 5 MPa, 0.3 mL/min tetralin solvent, H2/oil = 333, and bH2/oil = 666.
The dew point of tetralin/n-tetradecane system is 356°C, which is much higher than the experimental temperatures. Liquid phase existed all through the experiment temperature range and only gas-liquid-solid reaction mode takes place. Thus the conversion of tetralin increased with the rise of temperature as shown in Figure 1. The dew point of tetralin/n-tetradecane system is 297°C, which is close to the experimental temperature 290°C. At this temperature the reaction takes place in gas-solid mode, and thus the tetralin conversion decreased. Similarly, the dew point of tetralin/n-octane (H₂/oil ratio = 333) is 266°C, and the conversion of tetralin decreased at 260°C. Further rise in temperature can speed up the reaction and lead to the increase of tetralin conversion again. Increasing the H₂/oil ratio from 333 to 666 would bring down the dew point (from 266 to 239°C). Therefore, the temperature at which tetralin conversion began to decrease also shifted to low (from 260 to 250°C). In Figure 4, the tetralin conversion decreased between the H₂/oil ratio = 555 and H₂/oil ratio = 666. The calculated dew point of the feed at H₂/oil ratio = 555 and pressure 5 MPa was 246.6°C, which was close to the experiment temperature 250°C. These results indicated that there is substantial relationship between the reactants phase state and the catalytic activity.

4.1.2. Kinetic Analysis. The kinetic of tetralin hydrogenation was analyzed to investigate the effects of reactants’ phase state on the catalytic activity. The Weisz-Prater parameter CWP under the experimental conditions is estimated to be about 0.03 (with the method described in [33]); thus, the diffusion limitations can be neglected. The reverse reaction can also be neglected since the tetralin conversions are far from the equilibrium values [3]. With the existence of the liquid phase, the mass balance of tetralin can be expressed as

\[
\dot{\nu}_G C_{\text{THN}} = k_0 e^{-E_a/RT} C_{\text{H}_2G} C_{\text{THN}}^n \text{d}V.
\]  

(2)

Without the existence of the liquid phase, the mass balance of tetralin can be expressed as

\[
\dot{\nu}_L (\nu_G C_{\text{THN}} + \nu_G C_{\text{THNG}}) = k_0 e^{-E_a/RT} C_{\text{H}_2G} C_{\text{THN}}^n \text{d}V.
\]  

(3)

Assuming vapor-liquid equilibrium is achieved at the inlet and every point of the catalyst bed, then the gas phase tetralin concentration \(C_{\text{THN}} = K C_{\text{THN}} \), and \(K = K_0 = \frac{C_{\text{THN}}^0}{C_{\text{THN}}^0} \). The reaction order of the tetralin \(m\) is chosen as 1 according to the previous reports [3, 24, 34, 35]. The variations of \(\nu_L, \nu_G, C_{\text{THN}}, \) and \(T\) are neglected to simplify the discussion, though they vary along the reactor due to the conversion of the reactant and the generation of heat during the reaction. Then the conversion of tetralin can be derived from integrating (2) and (3) with the boundaries \(V = 0\), \(C_{\text{THN}} = C_{\text{THN}}^0\) (or \(C_{\text{THNG}} = C_{\text{THNG}}^0\)), and \(V = V\), \(C_{\text{THN}} = C_{\text{THN}}\) (or \(C_{\text{THNG}} = C_{\text{THNG}}\)). For gas-liquid-solid mode,

\[
-\ln \left( \frac{C_{\text{THN}}}{C_{\text{THN}}^0} \right) = -\ln (1 - x) = k_0 \int_0^1 e^{-E_a/RT} \frac{1}{\nu_L + (C_{\text{THNG}}^0/C_{\text{THN}}^0)} \frac{1}{\nu_G} C_{\text{H}_2G} \text{d}V.
\]  

(4)

and for gas-solid mode,

\[
-\ln \left( \frac{C_{\text{THNG}}}{C_{\text{THNG}}^0} \right) = -\ln (1 - x) = k_0' \int_0^1 e^{-E_a/RT} \frac{1}{\nu_G} C_{\text{H}_2G} \text{d}V.
\]  

(5)

with

\[
k_0' = k_0 V.
\]  

(6)

Equations (4) and (5) imply that the tetralin conversion increases with the increase of the hydrogen concentration in liquid phase \(C_{\text{H}_2G}\) (gas-liquid-solid reaction mode) or hydrogen concentration in gas phase \(C_{\text{H}_2G}\) (gas-solid reaction mode). The tetralin conversion also increases with the decrease of \(\nu_L + (C_{\text{THNG}}^0/C_{\text{THN}}^0) \nu_G\) (gas-liquid-solid reaction mode, affected by volumetric flow rate of liquid and gas phase, and the tetralin concentration in liquid and gas phase) or \(\nu_G\) (gas-solid reaction mode). The \(\nu_L\) and \(\nu_L + (C_{\text{THNG}}^0/C_{\text{THN}}^0) \nu_G\) can be related to the practical residence time of tetralin. The greater the \(\nu_L\) or \(\nu_L + (C_{\text{THNG}}^0/C_{\text{THN}}^0) \nu_G\),

![Scheme 1: Illustration of gas-liquid-solid and gas-solid reaction modes.](image-url)
the lower the practical residence time of tetralin. These values can also be calculated by SRK equation of state [32]. The results were illustrated in Figures 5 and 6. Without phase transfer, the values of hydrogen concentration and \( v_L + (C_{THN}^0/C_{THNL})v_G \) or \( v_G \) change smoothly. The gas phase hydrogen concentrations are about 2∼3 times as large as the liquid phase ones, which benefits the tetralin conversion. However, the \( v_G \) was about 8~25 times as large as the \( v_L + (C_{THN}^0/C_{THNL})v_G \) and had a negative effect on the tetralin conversion. The combined effects of hydrogen concentration and \( v_G \) (or \( v_L + (C_{THN}^0/C_{THNL})v_G \)) lower down the tetralin conversion when all liquid is transferred into gas phase above the dew point.

**Figure 6:** The \( v_L + (C_{THN}^0/C_{THNL})v_G \) and \( v_G \) of different solvents calculated by SRK equation of state.

**Table 3:** Tetralin conversion after gas-liquid-solid or gas-solid reaction manner, %.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Tetralin/n-octane</th>
<th>Tetralin/n-tetradecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>44.51</td>
<td>40.79</td>
</tr>
<tr>
<td>290</td>
<td>49.87</td>
<td>64.84</td>
</tr>
<tr>
<td>250 (after 290)</td>
<td>41.61</td>
<td>39.18</td>
</tr>
</tbody>
</table>

The \( E_a, n, \) and \( k_0' \) of (4) and (5) were listed in Table 2. The activation energy \( E_a \) was set to 50 kJ/mol, which was referred to as the values of most monocyclic aromatics \([3, 36]\). The \( k_0' \) were regressed with experiment data for each reaction system. Without phase transition, the changes of hydrogen concentration can be neglected. Thus the reaction order \( n \) with respect to hydrogen was set to zero in most of the studies \([24, 35]\). The \( n \) was set to 3 in this study because the hydrogen concentrations in liquid phase and gas phase were greatly different. Figure 7 showed the tetralin conversion calculated by (4) and (5). Similar tendencies can be observed in Figures 7 and 1, though the calculation values could not exactly match with the experiment values. The errors might be caused by the error of phase equilibrium calculation. The same activation energies and reaction rate constants that were used for both gas-liquid-solid and gas-solid reaction modes might also cause the deviation.

**Figure 7:** The tetralin conversion calculated by (4) and (5).
the effect of gas-liquid-solid or gas-solid operating mode on catalyst deactivation. The results were listed in Table 3. The tetralin conversion at 250°C decreased from 44.51% to 41.61% after the gas-solid reaction at 290°C (tetralin/n-octane), while it decreased from 40.79% to 39.18% after gas-liquid-solid reaction at 290°C (tetralin/n-tetradecane). The deactivation of triphase mode was much lighter than the previous one.

The decalin dimers were detected in hydrogenation product at 290°C and in the used catalyst (extracted with n-tetradecane, and the obtained liquid was analyzed with GC-MS). They might adsorb on the catalyst surface or active site and cause the deactivation [37, 38]. Figure 8 showed the GC-MS spectra of the C20 components in the hydrogenation product and the used catalyst. The MS results showed that the C20 components were composed of multifyclics and aromatic cycle. This indicated that more than two aromatic molecules condensed into a large molecule during the hydrogenation process. As illustrated in Scheme 1, the liquid solvent might dissolve these large molecules and carry them away. However, with the gas-solid mode, the large molecules were difficult to be desorbed and might occupy the active site. Thus the deactivation in the gas-solid reaction mode was much severer than in the gas-liquid solid one.

![Figure 8: GC-MS spectra of C20 components in product and used catalyst.](image)

Similar to our experiment results, the available literatures which used light hydrocarbon (benzene [4], n-heptane [5–14], or cyclohexane [31]) as solvents are likely to show aromatics conversion transition with the increase of the reaction temperature. Generally, the ones that use heavy hydrocarbons like n-hexadecane, n-tridecane, and n-dodecane as solvents are likely to show that the conversion of aromatics increases with the rise of temperature. In addition, the light hydrocarbons were not the typical components of diesel fuel. We suggest that the model compounds for the evaluation of aromatic hydrogenation catalysts (especially the diesel fuel hydrodearomatization catalysts) should use suitable heavy hydrocarbons as solvents. Otherwise, the reactants' phase state should be taken into consideration during the catalyst evaluation.

5. Conclusions

The reactants' phase state had a significant effect on the catalytic activity of hydrogenation catalyst. The hydrogenation concentration that was available to the catalyst surface of gas-solid reaction mode is 2–3 times as high as that of gas-liquid-solid reaction mode, while the $\nu_T$ (gas-solid mode) is about 8–25 times as large as the $\nu_T + (C_{THNG}^0/C_{THNL}^0)\nu_G$ (gas-liquid-solid mode). The combined effects of hydrogen concentration and $\nu_T$ (or $\nu_T + (C_{THNG}^0/C_{THNL}^0)\nu_G$) cause tetralin conversion to dramatically decrease at the dew point of the feed. The gas-liquid-solid mode was preferred to reduce catalyst deactivation. Model compounds for aromatics hydrogenation catalysts evaluation should be absent in components that might bring in phase transfer under the test condition.
Notations

\[ C: \text{Concentration, mmol mL}^{-1} \]
\[ E_a: \text{Activation energy, J mol}^{-1} \]
\[ k_0: \text{Reaction rate constant, min mmol}^{-1} mL^{-1} \]
\[ k_1: \text{Reaction rate constant, min mmol}^{-1} mL^{-1} \]
\[ R: \text{Ideal gas constant, 8.314 J mol}^{-1} K^{-1} \]
\[ T: \text{Temperature, K} \]
\[ v: \text{Volumetric flow rate, mL min}^{-1} \]
\[ V: \text{Catalyst bed volume, mL} \]

Subscripts

0: Initial condition
G: Gas phase
L: Liquid phase
\( m,n \): Reaction order
\( H_2 \): Hydrogen
THN: Tetralin.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


