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Determination of Catalyst Wetting Fraction on the Molecular Level

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Introduction

Recently it was reported that catalyst wetting under reactive conditions could be recognized by nuclear magnetic resonance imaging (MRI) (Koptyug et al. 2002). However, the catalyst internal wetting data were not reported, since the authors (Kirillov and Koptyug, 2005) only estimated the external wetting efficiency of the catalyst particle and assumed that the particle was isothermal with the inner porous volume completely filled with liquid. This work presented fundamental data on liquid wetting fraction of a catalyst from adsorption/desorption isotherm experiments. Adsorbed multilayer thickness of benzene over γ-Al_2O_3 was obtained experimentally and was correlated by the modified Halsey equation. The nonisothermal critical molecular thickness for vapor condensation was obtained for the first time. Liquid wetting fraction and molecular layer number were characterized for the catalysts in a hydrogenation reactor. It was revealed that the reaction rate was controlled by the catalyst wetting degree and molecular-layer thickness, rather than by the liquid flow rate.

Characterization of catalyst wetting condition is essential to modeling and control of trickle-bed reactors since most reactions like hydroprocessing of petroleum fractions and saturation of organic compounds are usually accompanied with substantial reaction heats. In these cases, a large fraction of liquid stream can be vaporized and leaves the internal space of catalyst pellets partially wetted. Since the reaction rate is substantially affected by the catalyst wetting degree, transition from liquid-phase into gas-phase can cause severe operation problems.[1,2] On the other hand, phase transition can be developed as a trickle-bed intensification technology since the reaction heat can be counterbalanced by the latent heat of liquid vaporization, which also increases the reaction rate by decreasing the liquid content in the catalyst.[3,4] It is, thus, of significant importance to estimate the catalyst internal wetting condition during the reaction, however, this can only be attained previously from weighing the loss of the catalyst. It was only recently that the distribution of liquid within a cylindrical pellet could be measured under reacting condition by nuclear magnetic resonance imaging (MRI).[5] Since the spatial resolution of the equipment was 230×140 μm^2, only the spatial map of the liquid phase in the catalyst could be reported, and the authors had to assume that the particle was isothermal with the inner porous volume completely filled with liquid.[6] Therefore, identification of liquid distribution in a partial-wetting catalyst on the molecular level is essential.

Development of this Work

Determination of the adsorbed molecular layer thickness

In the mesopores the vapor gas is first adsorbed on the pore wall as monolayer and followed by more other layers. When the relative vapor pressure is high enough, gas to liquid phase transition will take place. Therefore, there is a gas-solid equilibrium between the bulk gas and the adsorbed gas, and there is also a gas-liquid equilibrium between the bulk gas and the condensed liquid, which are described by the density functional theory, or by an appropriate adsorption equation or the Kelvin equation.[7–9] Experimentally, they can be measured conventionally by the adsorption methods,[10–14] or in some cases by the solid-state nuclear magnetic resonance.[15] In this work, an adsorption method will be used, since it can not only provide the amount of adsorption, more importantly it can provide the critical point of capillary con-

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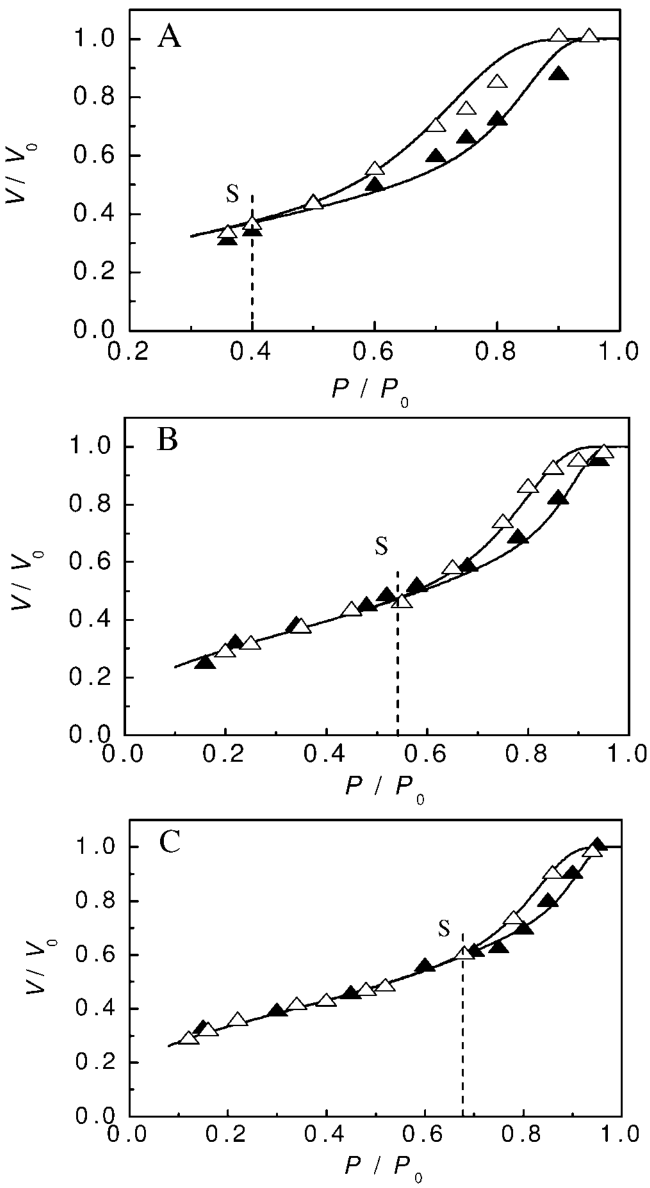


Figure 1. Adsorption/desorption isotherm of benzene in hydrogen over γ-Al_2O_3.

▲, △- Experimental value; — Prediction ▲- Adsorption; △— Desorption; A-393K; B-433K; C-453K.

densation from the interaction of the hysteresis loop formed by the adsorption and desorption isotherms.

In this work, benzene hydrogenation into cyclohexane was used as the working system. The catalyst was 0.5% Pd supported on the γ-Al_2O_3 spheres of 4 mm in diameter, which has an average pore diameter of 6.8 nm, with a standard variation of 2.51 nm, and is well described by the single gamma function. The pore volume is measured to be 0.47 $cm^3 \cdot g^{-1}$, and the surface area is 276 $m^2 \cdot g^{-1}$.

Since the adsorption/desorption isotherm data using TG (Thermogravimetry) is not available under 1.0 to 3.0 MPa, in this work such data were obtained on the inert catalyst support from breakthrough profile measurements with benzene and hydrogen as the vapor phase.[16] The isotherm data shown in Figure 1 featured hysteresis loops under all the simulated reaction conditions at 393K, 433K and 453K, which clearly indicate the occurrence of capillary condensation.

By denoting V as the volumetric adsorption amount of benzene according to Figure 1, and A as the surface area of the catalyst support, the statistical molecular thickness will be V/A, which was correlated satisfactorily by the Halsey equation shown in Eq. 1

$$t = t_m\left(\frac{5}{ln(P_0/P)}\right)^{1/3}\left(\frac{P}{P_0}\right)^{0.4} \qquad (1)$$

where t is in nm, P and P_0 are, respectively, the partial and saturated vapor pressures of benzene, t_m is the monolayer molecular thickness of benzene and is obtained from:

$$t_m = \frac{10^{21}}{\rho \cdot N_A \cdot a} \qquad (2)$$

where t_m is in nm, ρ is the density of benzene in g/cm^3, N_A is the Avogadro number 6.02×10^{23}, and α is the cross sectional area of benzene being 0.38 nm^2/molecule.

Since ρ varies with temperature, and t_m will also be a function of temperature. In this work, t_m was correlated with temperature in Kelvin as

$$t_m = 0.1 + 7.57 \times 10^{-4}T \qquad (3)$$

The dependence of adsorbed layer thickness t as a function of relative vapor pressure P/P_0 under different temperatures is shown in Figure 2. It is found t increases with P/P_0 constantly, and passes through the phase transition points which were measured to be 0.613, 0.732, and 1.022 nm at 393 K, 433 K, and 453 K, respectively.

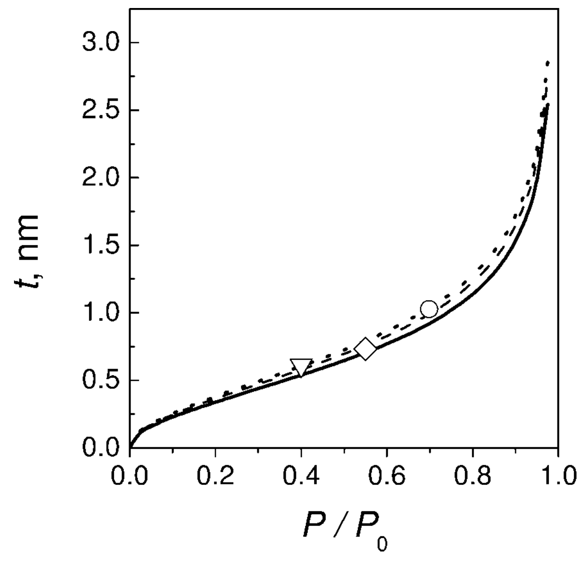


Figure 2. Prediction of adsorbed multilayer thickness of benzene over γ-Al_2O_3.

Experimental data at phase transition: ▽ - 393K; ◇-433K; ○ - 453K Correlation by Eq. 1: —— 393K; ---- 433K; ...... 453K.

Determination of the catalyst internal wetting fraction

From Figure 1 it is found when the relative vapor pressure is larger than a critical value indicated by the point "S", the vapor will condense into liquid over the adsorbed molecular layers. Since the catalyst pore is occupied by both liquid phase and the adsorbed phase, the wetting fraction of the catalyst pellet will be defined in different manners.

If the total pore volume is considered as the basis, an absolute wetting fraction is obtained

$$F_w = \int_t^{t+r_K} V(r)dr \Big/ V_0 \tag{4}$$

On the other hand, if the volume of the adsorbed layers are not taken into account, a relative wetting fraction is obtained

$$f_w = \int_t^{t+r_K} V(r)dr \Big/ \int_t^{r_{max}} V(r)dr \tag{5}$$

Where, V_0 is total volume of the catalyst pores, V(r) is the pore volume distribution, r_{mas} is the upper limit of the pore radius, r_k is the Kelvin radius which is evaluated from the classical Kelvin equation and Cohan equation, respectively

$$r_K = \begin{cases} \dfrac{2M_w\sigma}{R_g T\rho ln(P_0/P)} & \text{(6a)} \\ \dfrac{M_w\sigma}{R_g T\rho ln(P_0/P)} & \text{(6b)} \end{cases}$$

Where, M_w is the molecular weight of benzene, R_g is the ideal gas constant, and σ is the surface tension of liquid benzene. Since F_w is always less than 1 even if the catalyst is completely filled with liquid, therefore, it does not properly describe the wetting condition of catalyst. Comparatively, the relative wetting fraction defined by Eq. 5 satisfies this requirement. The experimental wetting fraction of the catalyst pellets in this meaning is obtained

$$f_w = \frac{V - V_S}{V_0 - V_S} \tag{7}$$

The experimental and predicted liquid wetting fractions are compared in Figure 3, which are in close agreement. Therefore, in a trickle-bed reactor, the catalyst wetting fraction along the flow direction can be predicted through Eqs. 1, 2 and 5 only if the temperatures and relative vapor pressures are given.

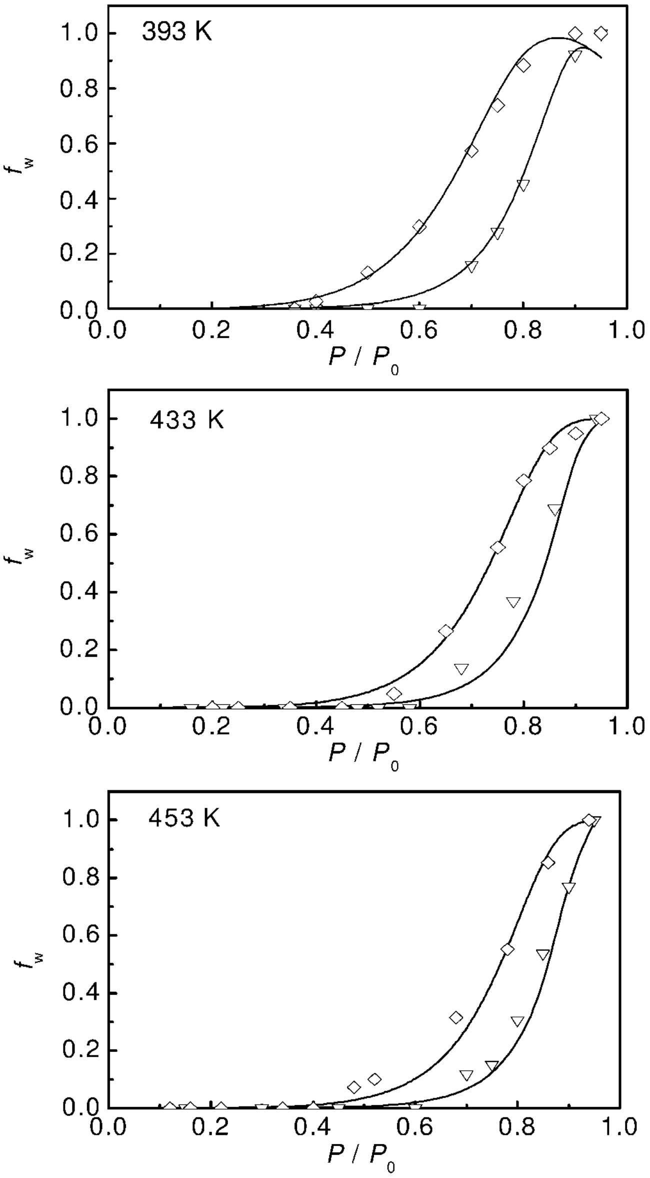


Figure 3. Liquid wetting fraction of catalyst under different vapor pressures.

◇,▽-Experimental data. ▽- Adsorption; ◇- Desorption — Prediction.

Results and Discussion

The influence of liquid flow rate on hydrogenation of benzene was studied in this work. The reactor was 20 mm in inside diameter, while the catalyst was packed to a height of 1.0 m with a void fraction of 0.41. The reactor was operated adiabatically under concurrent upward flow of the gas and liquid phases at 1.0 MPa at an inlet temperature of 150°C. Benzene was premixed with cyclohexane as the liquid feed to give an inlet concentration of 31.5 wt %. The hydrogen flow rate was kept at 15.5 NL/min, and the liquid flow rates were varied at 1.24, 2.16, 3.24, and 4.74 kg/hr, which gave a molar ratio of H_2 to benzene as 8.3, 4.55, 3.17 and 2.17.

Corresponding to the temperature profiles measured in Figure 4A, the estimated catalyst wetting condition was shown in Figures 4B, C, and D. It can be realized from these figures that the wetting condition of the catalyst bed is related to the conversion of the reactant:

1. At liquid flow rates of 1.24 and 2.16 Kg $\cdot$ hr^{-1}, the reactant conversions were 100% and 53.6%, respectively. The residence-time ratio under the two liquid flow rates was 1.7:1, while the ratio of the two conversions was 1.8:1. Obviously, the conversion was almost proportional to the residence time of the reactant, and such a result can only be obtained under similar catalyst wetting conditions. From

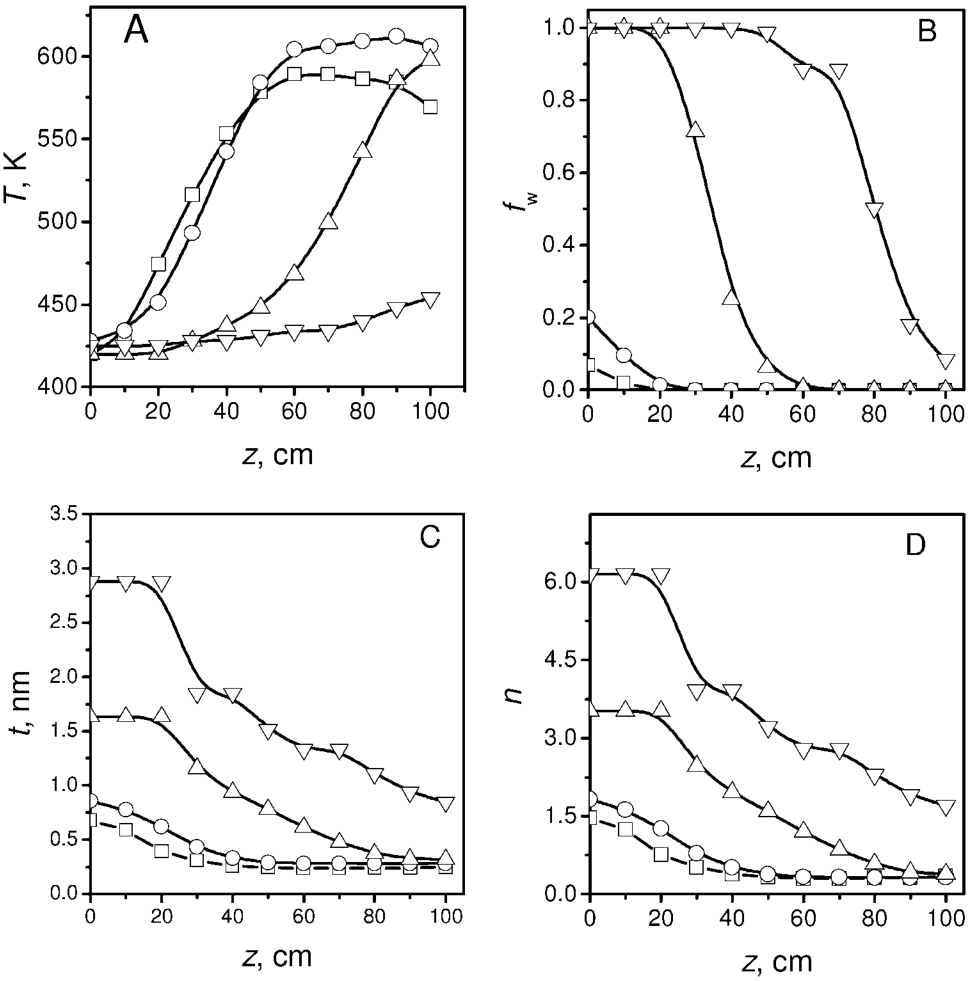
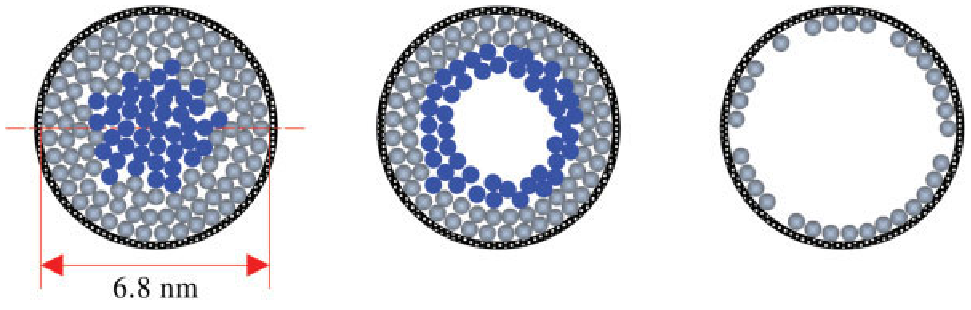


Figure 4. Estimation of catalyst wetting condition in a hydrogenation reactor.

A—Temperature profile; B— Catalyst wetting degree; C— Thickness of adsorbed layers; D— Number of adsorbed layers, Liquid flow rate: □—1.24, ○—2.16, △—3.24, ▽—4.74 kg/h, Conversion: □—100%, ○—53.6%, △—41%, ▽—14%.

Figure 4B and 4C, it was found that the catalyst wetting condition under these two liquid flow rates are very similar over the reactor length, which verifies the relationship between residence time and conversion.

2. At liquid flow rates of 2.16 and 3.24 Kg · hr^{-1}, the reactant conversions were 53.6 and 41%, respectively. The residence-time ratio under the two liquid flow rates was 1.5:1, while the conversion ratio was 1.8:1, which was a little



$n = 3.51; f_w = 100$ %
$z = 20$ cm; $T = 420$ K

$n = 1.95; f_w = 25$ %
$z = 40$ cm; $T = 437$ K

$n = 0.85; f_w = 0$
$z = 70$ cm; $T = 499$ K

Figure 5. Phase distribution of benzene in the catalyst pore.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

higher than residence time ratio. This can be explained that at $L = 3.24$ Kg $\cdot$ hr^{-1} the catalyst bed became evacuated from liquid in the middle of the reactor, thus the overall reaction rate was not much different from the case of $L =$ 2.16 Kg/h.

3. At liquid flow rates of 3.24 and 4.74 Kg $\cdot$ hr^{-1}, the conversions were 41 and 14%, respectively. The residence-time ratio under the two liquid flow rates was 1.5:1, while conversion ratio was 2.9:1, which was much larger than the residence time ratio. This result should be explained from the much different catalyst wetting conditions shown in Figures 4B, C, and D. Besides, it should be noted that the reaction rate is primarily dominated by the liquid wetting fraction in the catalyst, since it is found the reactor temperature does not rise until f_w is lower than 0.2, when liquid flow rates of 3.24 and 4.74 Kg $\cdot$ hr^{-1} are examined.

The distribution of molecules in the catalyst pores in above hydrogenation reactor is illustrated in Figure 5. Near the reactor inlet the catalyst pore wall is covered with 3.51 layers of reactant molecules, and the pore is entirely filled with liquid. Further downstream in the reactor, the reactor temperature increases with a reduction of the adsorbed layer thickness and partial vaporization of the liquid. Near the reactor exit, there is no liquid condensate, and only 0.85 layers of reactant molecules are adsorbed on the pore wall. Since only the reactant molecules adsorbed in the form of monolayer directly participate in the reaction, the other layers and the condensed liquid will only impose mass-transfer resistance to the diffusion of hydrogen in arriving at the catalyst surface.

Conclusions

Adsorption method was introduced to characterize the catalyst wetting condition in a hydrogenation reactor, and it shows that:

1. With the adsorption method, both the adsorbed molecular layer thickness, and the liquid wetting fraction in a catalyst under simulated reacting condition can be determined on the molecular level.

2. The reaction rate of the catalyst depends primarily on its internal wetting condition. Although it is difficult to account accurately the contribution of the adsorbed phase, and the liquid phase on the overall reaction rate, it is still possible to identify that the influence of liquid phase is larger than the adsorbed phase since significant temperature rise was not observed unless the wetting fraction was less than a small value such as 0.2.

Acknowledgments

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