Mechanism Discrimination for Bimolecular Reactions: Revisited with a Practical Hydrogenation Case Study

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The governing mechanism of surface reactions is a fundamental concern in heterogeneous catalysis. The Langmuir–Hinshelwood (LH) mechanism is widely accepted to control the surface reactions in many catalytic systems. This contribution derives and compares several important surface rate equations to evaluate their quality of fitting to the experimental data collected for a vapor-phase hydrogenation case study to produce furfuryl alcohol over supported copper catalysts. Meanwhile, a few essential but less addressed issues in determining the surface reaction mechanism were underlined. It is established that the Eley-Rideal mechanism would be equally (if not more) viable compared to the LH rate model all with coefficients of multiple determination larger than 97%, a conclusion in some contradiction with the common assumption of the previous publications for this case study. This investigation further highlighted that a good fit to any rate expression should not be taken as a proof of the assumed mechanism unless the opponent cases are tested within adequately wide ranges of concentrations.

**Keywords:** Bimolecular reactions, Hydrogenation mechanism, Langmuir-Hinshelwood, Eley-Rideal, Heterogeneous catalysis

**INTRODUCTION**

Bimolecular reactions are among the most well-known reactions occurring at the surface of heterogeneous catalysts. To understand the nature of the reactions, to design an intensified process, and to predict the time-dependent behavior of the reactants, the knowledge of the governing mechanisms and kinetics of the reactions is inevitable [1]. Hydrogenation process is one of those gas/solid surface reactions in which hydrogen atoms react with adsorbate-covered surfaces. The mechanisms and kinetics of these gas/solid surface reactions from theoretical and experimental points of view have been investigated over the last few decades. Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) scenarios are two well-known mechanisms evaluated for the gas/solid reaction systems.

The former is more frequently reported and accepted as the reaction mechanism in different processes [2-3]. In all versions of the LH model, the reactant molecules bind to and are thermally accommodated by the surface prior to the reaction, while the ER suggests that some gas-phase species collide with adsorbed species of another type and directly react to form products. Although rarely reported as a viable hydrogenation mechanism in the literature, the real conditions of this type of reactions are more close to this mechanism [2-8].

Before proceeding to the analysis of the experimental data, it is worthwhile to note that distinction has to be made between the governing mechanism of the reactions and the quality of fitting of the experimental data with a kinetic model. More strictly, due to the inclusion of the hydrogen equilibrium constant in the LH models, the number of LH
parameters is more than those of ER in which this constant is absent. Hence, one can predict that the LH mechanism should almost always fit the experimental data better than ER, even if some appropriate criteria such as the adjusted $R^2$ coefficient are employed to assess the goodness of fit. In other words, the inclusion of an additional predictor in the model is normally expected to enhance the quality of correlation. As also stressed in the relevant textbooks [2], when the Langmuir-Hinshelwood kinetic model is fitted on a set of experimental data, prior to proposing this mechanism for the reactions, discussion of the constant parameters obtained from this fitting is a must to figure out how certainly the LH could be the probable mechanism for the reactions. Sometimes, basic but important issues are overlooked in fundamental evaluation of experimental data. An example of such misconceptions can be found in a paper which explains frequent flaws in thermodynamic description of adsorption data compiling several inaccurate enthalpies of adsorption reported in experimental works [9]. The same cautions have to be exercised in mechanistic deductions (vide infra).

Furfural hydrogenation [10-13] is one of the most profitable industrial hydrogenation processes. In spite of its importance, only a few studies have addressed the viable mechanisms and kinetics of this process, particularly in the vapor phase. All relevant studies performed up to now [14-20] have applied a Langmuir-Hinshelwood kinetic scheme to describe the reactions and found a very good agreement with the experimental data. The deductions and assumptions of the previous reports [14-20] in favor of the LH mechanism is therefore questionable in light of the fact that the amount of $K_{H2}$ was as small as it could be ignored in comparison to $K_{FAL}$ in the developed kinetic schemes (vide infra). This short paper questions a priori assumption of the almost widely-accepted choice in favor of the LH mechanism in the bimolecular reactions using the experimental data from the literature on the vapor-phase hydrogenation of furfural as a case study.

Case Studies

In order to probe the controlling mechanism of surface hydrogenation of furfural over copper catalysts, the results of fitting different LH and ER models to the experimental data reported by Rao et al. [16] for three carbon-supported copper catalysts, and those of Sitthisa et al. [15] for a silica-supported Cu catalyst for the vapor-phase hydroconversion of furfural are discussed. The Cu/C catalysts [16] are called herein as Cat#1 to Cat#3, respectively, for the 5.1% Cu/GF-WI, 4.8% Cu/AC-HNO₃, and 5.1% Cu/DM samples. In addition, the kinetic data collected at 230 °C over Cu/SiO₂ [15] was named Cat#4 in this paper.

Total of seven bimolecular and multi-component models were selected including ER1 (involving the associative adsorption of furfural), ER2 (with the multi-component associative adsorption of furfural (FAL), methyl furan (MF) and furfuryl alcohol (FOL) molecules), LH1 (the dissociative sequential addition of hydrogen atoms to FAL on the same adsorption sites), which was derived in [14] with an erroneous power in the denominator, and corrected in the derivation part of the present study (see Supplementary A), LH2 (invoking the noncompetitive dissociative adsorption of hydrogen molecule on two different types of sites) as derived in [16], LH3 (with the associative adsorption of hydrogen molecule), LH4 (including the multi-component associative adsorption of FAL, MF and FOL molecules and also dissociative adsorption of H₂ molecule on equivalent sites), and finally LH5 (described as a model with complex features of both ER and LH mechanisms) derived in [15]. The models are listed in Eqs. (1)-(7), respectively.

$$r(ER1) = \frac{kK_{FAL}P_{FAL}P_{H2}}{1 + K_{FAL}P_{H2}}$$  \hspace{1cm} (1)

$$r(LH1) = \frac{kP_{FAL}P_{H2}}{(1 + K_{H2}P_{H2}^{eq} + K_{FAL}P_{FAL}^{eq})^{\gamma}}$$  \hspace{1cm} (2)

$$r(LH2) = \frac{kP_{FAL}P_{H2}}{(1 + K_{H2}P_{H2}^{eq} + K_{FAL}P_{FAL}^{eq})^{2}}$$  \hspace{1cm} (3)

$$r(LH3) = \frac{kP_{FAL}P_{H2}}{(1 + K_{H2}P_{H2}^{eq} + K_{FAL}P_{FAL}^{eq})^{3}}$$  \hspace{1cm} (4)

$$r(ER2) = \frac{kK_{FAL}P_{FAL}P_{H2} - kP_{FAL}K_{H2}}{(1 + K_{FAL}P_{H2} + K_{MF}P_{MF} + K_{FAL}P_{FOL})}$$  \hspace{1cm} (5)
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\[ r(LH4) = \frac{kK_{FOL}P_{FOL}}{(1 + K_{FOL}P_{FOL} + K_{FOL}P_{FOL} + K_{FOL}P_{FOL})} - \frac{kP_{FOL}}{K_{eq}} \]

\[ r(LH5) = \frac{kK_{FOL}P_{FOL}}{(1 + K_{FOL}P_{FOL} + K^{0.5}P_{FOL} + K_{FOL}P_{FOL})} - \frac{kK_{FOL}P_{FOL}}{K_{eq}} \]

The underlying parameters are defined in the nomenclature.

As shown in this figure, when the proposed models are plotted in a wide range of FAL and hydrogen concentrations, their differing trends become obvious, particularly in the case of FAL concentrations. However, the lack of sufficiently scattered experimental data makes any mechanism designation difficult. More specifically, the two models of LH1 and LH3 behaved almost similarly while being different from the behavior of the two LH2 and ER1 mechanisms. Moreover, the former two models were optimized with higher adjusted correlation coefficients of 99.19% and 99.50%, respectively. This indicated that the FAL hydrogenation reaction slightly preferred to occur with adsorption of both hydrogen and FAL molecules on the same active sites (see Eqs. (2) and (4)). The distinction between these two models would be more confident if there were more experimental data in the high concentration range of FAL (see Fig. 1, the lower panel). Although acceptably correlating, ER1 and LH2 which respectively represent the molecular collision of hydrogen from gas phase without adsorption on the catalyst surface and adsorption of both hydrogen and FAL on different active sites, were slightly less successful than LH1 and LH3 to predict the trend of experimental data (see Table 1).

According to the stoichiometry of furfural hydrogenation to furfuryl alcohol defined in Eq. (8), the Langmuir-Hinshelwood mechanism would be ideally predominant if the adsorption contributions of furfural and hydrogen were close to each other or the corresponding constants were of the same order of magnitude assuming that an equimolar (stoichiometric) composition of the reactants was used [21]. As observed in Table 1, the amounts of the equilibrium constants of furfural adsorption in all of the fitted LH models were several hundred to several thousand times larger than those of hydrogen adsorption for the carbon-supported copper catalysts. Obviously, this significant difference between the amounts of equilibrium adsorption constants makes the LH mechanism less probable to occur in reality. In other words, the LH model was not controlling the reactions as a prevalent mechanism. In contrast, the low rate of hydrogen adsorption on the catalyst surface points to the ER as the governing mechanism over the Cu/C catalysts where hydrogen collides directly with furfural to form the corresponding alcohol (Eq. (8)).

\[ C_5H_4O_2 + H_2 \rightarrow C_5H_6O_2 \]

A similar discussion holds true for the Cu/SiO₂ catalyst with the furfural equilibrium constant being larger than that of hydrogen. More precisely, the amount of hydrogen equilibrium constant in this multi-component adsorption scheme has to be compared with those from all competing
components having a chance to adsorb on the surface. Thus, the equilibrium constant obtained for H\textsubscript{2} is even much smaller than those for its rivals in the LH4 model, as shown in Table 1. Moreover, the number of experimental points for a multi-component regression was too low. These make the original assumption of a LH-type reaction mechanism by the authors [15] questionable.

From a purely mathematical point of view, the LH models had a good fit on the experimental data for the Cu/C samples (see Table 1). As pointed out previously, however, the goodness of fit for a model does not guarantee that it reflects the most predominant mechanism of the reactions. Moreover, the predominance of a LH1-type mechanism requires [21] that the rate plot passes through a maximum in

<table>
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<th>Constants</th>
<th>k or k'</th>
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<th>K\textsubscript{FAL}</th>
<th>K\textsubscript{MF}</th>
<th>K\textsubscript{FOL}</th>
<th>K\textsubscript{eq}</th>
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<th>SD</th>
<th>R\textsuperscript{2adj}</th>
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<td>-</td>
<td>-</td>
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<td>0.00022</td>
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<td>0.19883</td>
<td>9.150</td>
<td>99.76</td>
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\*The kinetic parameters of k, k', K\textsubscript{H2}, K\textsubscript{FAL}, K\textsubscript{MF} and K\textsubscript{FOL} are respectively in [µmol (g\textsuperscript{-1} s\textsuperscript{-1} atm\textsuperscript{-1})], [µmol (g\textsuperscript{-1} s\textsuperscript{-1})], and the rest in [1/atm] for all of the catalysts except Cat#4 for which they are in [mmol (g\textsuperscript{-1} h\textsuperscript{-1} Torr\textsuperscript{-1})], [mmol (g\textsuperscript{-1} h\textsuperscript{-1})], and the rest in [1/Torr]. The coefficients of determination are expressed as % values.
Fig. 1. Hydrogenation rate of the Cu/C catalyst (Cat#2) vs. partial pressure of hydrogen (upper panel) and furfural (lower panel). The experimental points were obtained from Rao et al. [16] (The adjusted correlation of coefficients for ER1, LH1, LH2 and LH3 are 98.57%, 99.19%, 98.89%, and 99.50%, respectively. Please, refer to Table 1 for further statistical data).
terms of the partial pressures of both reactants including that of hydrogen. This is while the corresponding plots of the Cu/C catalyst (Fig. 1) had a monotonic upward trend over the whole range of hydrogen pressure as expected from an ER-type mechanism. Since the experimental data scattered over a wide range of hydrogen partial pressure (0-1 atm) and only limited values of FAL partial pressure (much lower than 0.05 atm) were available, the graph drawn in terms of the changes in the hydrogen partial pressure is more suitable to distinguish the reaction mechanism. In fact, for any deduction from the plots of rate vs. furfural pressure, the experimental results over higher concentrations of FAL should be available as practiced in several studies [22-23]. Otherwise, the ER1 and LH models would overlap in a local range of data thus making the determination of the true mechanism unreliable as in this case study (Fig. 1). Another interesting observation which is not addressed in the previous reports is that the plots of ER1 and LH2 mechanisms coincided almost identically (Fig. 1 and Table 1). Although this coincidence becomes anticipated from the mathematical description of Eqs. (1) and (3), we note that the classical schemes of linearity or curved behaviors for a discrimination between ER and LH mechanisms do not apply universally, emphasizing that the general notions of these mechanisms which are often learnt in graduate studies should be applied carefully and critically. An example of a blind and wrong use of some ubiquitous rules to real adsorption data can be found elsewhere [9]. An overlap is also apparent for LH1 and LH3 mechanisms at low concentrations of furfural. As observed in Fig. 1, both mechanisms with their different concepts were found to have equal chances to occur on the surface of the catalyst (both with correlation coefficients of ~99.6%). This indicates that a fundamental distinction between these two mechanisms is not essentially feasible and caution should be exercised in any designation in favor of one of them without further evidences. However, more scattered experimental data can more certainly point out to any of the models.

The essential difference between the LH1 and LH2 mechanisms was not explained by Rao et al. [16] who concluded that both of the equations fitted the experimental data very well. They warned, however, that one is not able to select between the two models with the limited data presented. Indeed, an inadequate scatter of experimental data (in this case, assembled in low concentration range of reactants) as well as a limited number of them has led to an increased uncertainty with the designation of the sound surface mechanism. The inherent behaviors of the ER1 and LH2 models are the same giving no maximum rate at different conditions. In contrast, the essence of the LH1 and LH3 models enables volcano-type behaviors in terms of concentration. These two categories of behaviors would be born in mind for use in analyzing any surface kinetic data.

Also shown in Table 1 are the results of the multivariable regression of the models with the experimental data for the Cu/SiO2 catalyst (Cat#4) based on Eqs. (5) and (6). As evident, both of the models (ER2 and LH4) showed excellent fits (with coefficients of multiple determination being larger than 98% within the investigated range). The partial pressure of hydrogen in the conducted experiments was kept fixed at 1 atm (excess amount of hydrogen). Actually, the data used to train the kinetic models lacked any variance in $P_{H2}$ as a key predictor to spot the Eley-Rideal mechanism. As such, the estimated equilibrium constant for hydrogen adsorption in such a case could be merely an adjusted factor and convey no true physical meaning. Therefore, any judgment in favor of the Langmuir-Hinshelwood kinetic model is an unproven postulation and all of the trends beyond the experimental range could be an artifact. These conflicts prompt the crucial question of whether the attribution of the LH kinetics to this process is correct. Additional diagnostic tests, such as chemisorption tests of pure components or measurements of the transient responses to the feed stream changes, would also be required to discriminate between the competing mechanisms [2]. In addition, the pure forms of ER and LH could be both adequate and simplifying assumption for the excess hydrogen amount in the original work was not necessary.

As a complementary discussion, the degree of fitting of the original models could also be reexamined. The results of fitting of the experimental data for the Cu/C catalyst to the original kinetic models are illustrated in Fig. 2 with their corresponding constants given in Table 2 where the asterisks in LH1* (with the original formula derived in [14]) and LH2* stand for the corresponding Langmuir-Hinshelwood models with constants presented by Rao et al.
Fig. 2. Hydrogenation rate vs. partial pressure of hydrogen (upper panel) and furfural (lower panel) for Cat#2. The experimental points and regression models were obtained from Rao et al. [16] (The adjusted correlation of coefficients for LH1* and LH2* are 72.29% and 97.69%, respectively. Please, refer to Table 2 for further statistical data).
Beside the fact that LH1* and LH2* behaved quite differently as also anticipated from our previous discussion, the LH1* gave a poorer match with the experimental data compared to LH2* (Table 2) and also compared to LH1 (Fig. 1), most probably due to the insufficient computational tools at 1990s. However, the impressive difference between the amounts of furfural and hydrogen adsorption constants was also common between the original models.

The outcome of the correlating experimental data collected over the Cu/SiO₂ catalyst (Cat#4) with the original kinetic model (LH5) and the embodied parameters determined by Sitthisa et al. [15] are listed in Table 2. As it is clear, the model is incapable of a good prediction of the real data most possibly due to the typographical error(s) in the reported parameters.

Table 2. Quality of Fitting of the Experimental Data with the Original Models and Parameters by Rao et al. [11] and Sitthisa et al. [10]

<table>
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<th>K₅₁₆</th>
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<th>K₉₁₆</th>
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<td>93</td>
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<td>-</td>
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<td>0.18</td>
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<td>b</td>
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*The coefficients of determination are expressed as % values. The regression was very weak.

Using hydrogenation case studies, we underscored that in order to correctly attribute any particular mechanism to the reaction results, the experimental data have to be collected over an adequately wide range of concentrations rather than a limited range of data. Furthermore, the candidate mechanisms should all be tried and tested against the experimental data to reject other counterparts of the model, particularly when the models emerge from opposing concepts. In this context, the sole reliance upon a good regression can be troublesome. Taking into account these important issues, we demonstrated for a number of furfural hydrogenation cases that the Eley-Rideal mechanism was ignored or excluded inaccurately by the previous reports while the analysis of the kinetic constants connoted that an ER-type mechanism would be the most probable event to govern the catalytic reactions. It was further highlighted that in order to firmly support any model for the reactions, more systematic changes in the partial pressures of both reactants are also required.

**NOMENCLATURE**

- $k'$: Product of $kK_{FAL}K_{H2}$ [µmol (g⁻¹ s⁻¹)]
- $k$: Rate constant [µmol (g⁻¹ s⁻¹ atm⁻¹) or mmol (g⁻¹ h⁻¹)]
- $K_{FAL}$: Equilibrium adsorption constant [–]
- $K_{H2}$: Furfuryl alcohol adsorption constant [1/atm or 1/Torr]
- $K_{FOL}$: Hydrogen adsorption constant [1/atm or 1/Torr]
- $K_{MF}$: Methyl furan adsorption constant [1/atm or 1/Torr]
- MSE: Mean squared error
- $P_{FAL}$: Furfural partial pressure [atm or Torr]
- $P_{FOL}$: Furfuryl alcohol partial pressure [atm or Torr]
- $P_{H2}$: Hydrogen partial pressure [atm or Torr]
- $P_{MF}$: Methyl furan partial pressure [atm or Torr]
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\[ r \] Rate of reaction \([\mu \text{mol} (\text{g}^{-1} \text{s}^{-1})\) or \(\text{mmol} (\text{g}^{-1} \text{h}^{-1})]\)

\[ R^2 \] Coefficient of multiple determination [-]

\[ R_{adj}^2 \] Adjusted coefficient of determination [-]

\[ \text{SD} \] Standard deviation [-]

REFERENCES


