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Applications of Chemical Kinetics in Heterogeneous Catalysis

Zhenhua Zhang, Li-Ping Fan and Yue-Juan Wang

Abstract

Chemical kinetics is a key subdiscipline of physical chemistry that studies the reaction rate in every elemental step and corresponding catalytic mechanism. It mainly concludes molecular reaction dynamics, catalytic dynamics, elemental reaction dynamics, macrodynamics, and microdynamics. Such a research field has wide applications in heterogeneous catalysis. Based on the Arrhenius plot fitted by the catalytic conversions below 15% without the mass transfer effect and heat transfer effect, the apparent activation energy echoing with the intrinsically catalytic sites and the pre-exponential factor echoing with the relative number of active sites can be, respectively, derived from the slope and intercept of the Arrhenius plots, which can be used to compare the intrinsically catalytic activity of different catalysts and the relative amount of active sites. Reaction orders of both reactants and products are derived from the reaction rate equation and also fitted by the catalytic conversions below 15% without the mass transfer effect and heat transfer effect. According to the acquired reaction orders, the reaction mechanism can be proposed and even defined in some simple reactions. Therefore, investigations of chemical kinetics are of extreme importance and meaning in heterogeneous catalysis.

Keywords: Arrhenius equation, reaction rate equation, apparent activation energy, reaction order, heterogeneous catalysis

1. Introduction

Chemical kinetics, also known as reaction kinetics or chemical reaction kinetics, is a key branch of physical chemistry. Its main task is to investigate the rate during chemical process and to propose the catalytic mechanism of chemical process by a method of research object acting as a nonequilibrium dynamic system whose properties change with time [1, 2]. Through the study of chemical kinetics, it can reasonably guide us to know how to control the reaction conditions and improve the main reaction rate, in order to increase the production of chemical products, and also guide us to learn how to suppress or slow down the reaction rate of side reactions to reduce the consumption of raw materials, reduce the burden of separation operations, and eventually improve the product quality. Chemical kinetics can provide general knowledge on how to avoid explosion of dangerous goods, material corrosion, and aging and deterioration of products. It can also carry out optimal design and control for the industrialization of scientific research results and select the most suitable operating conditions for the existing production. Generally speaking, chemical kinetics is one

of the main theoretical bases of chemical reaction engineering, accompanied by the chemical thermodynamics for the improved study of chemical reactions.

Chemical kinetics is of great antiquity with continuous improvements. Date back to the first half of the twentieth century, a great deal of research was devoted to the parameter determination, theoretical analysis, and using these parameters to study the reaction mechanism. However, investigation of the reaction mechanism was extremely difficult at that time, which was dominantly limited by the abilities of probe and analyze reaction intermediates. As time goes on, the study of free radical chain reaction kinetics was generally carried out in the late twentieth century, which brought two development trends for chemical kinetics. One was for the study of elemental reaction dynamics, and the other was to urgently establish a method for detecting active intermediates. Such researches were accompanied by the development of electronics and laser technology. Notably, Herschbach, Lee, and Polanyi, three famous scientists in this field, were awarded the Nobel Prize in chemistry in 1986, which marked the importance of chemical kinetics and indicated the current progress and the achieved level.

Nowadays, chemical kinetics has become an indispensable tool in both chemical discipline development and scientific research. The application in heterogeneous catalysis is a typical example [3]. Heterogeneous catalysis, possessing most of the catalytic reactions in the industry, refers to the catalytic reaction that occurs at the interface of two phases. The heterogeneously catalytic reaction generally occurs on the catalyst surface on which the reactant molecular adsorbs, diffuses, activates, reacts, and desorbs to acquire the final products. Therefore, the surface compositions and structures of catalytic materials are extremely critical in determining the catalytic properties [4]. The adsorption center on catalyst surface is often the center of catalytic activity, which is denoted as active site. The reactant molecule bonds to the active site to form surface adsorption complex, which is denoted as active intermediate species. The existence of active site on catalyst surface can affect the formation and activation of active intermediate species, thus altering the reaction path and consequently the required activation energy [5, 6].

In this chapter, two important kinetic equations, the Arrhenius equation and the reaction rate equation, were comprehensively introduced, accompanied by the applications in heterogeneous catalysis. Through the introduction of the Arrhenius equation, the apparent activation energy (E_a) and pre-exponential factor (A) can be calculated based on the Arrhenius plots fitted by the catalytic conversions below 15% without the mass transfer effect and heat transfer effect, which can reflect the intrinsically catalytic sites and relative number of active sites, respectively. The reaction mechanism involving rate-determining elementary reaction step can be proposed by the reaction order derived from reaction rate equation plotted by the catalytic conversions below 15% without the mass transfer effect and heat transfer effect. Understanding the structure and number of active sites and catalytic mechanism, it can guide us insights into the understanding for a catalytic reaction and thereby provide a research fundamental for the design and synthesis of high-performance catalysts.

2. Applications of kinetic equations in heterogeneous catalysis

2.1 The Arrhenius equation and its applications in heterogeneous catalysis

The Arrhenius equation is an empirical formula with chemical reaction rate changing with temperature, which was established by Svante August Arrhenius, a famous scientist in Sweden. This equation can be expressed in different forms

containing the differential expression (Eq. (1)), antiderivative form expression (Eq. (2)), derivative form expression (Eq. (3)), and exponential form expression (Eq. (4)), as listed below. Among them, k represents the rate constant, R represents the gas molar constant, T represents the thermodynamic temperature, E_a represents the apparent activation energy, and A represents the pre-exponential factor. The Arrhenius equation can be used to calculate the apparent activation energy, the optimal reaction temperature and time, and the reaction rate constant in a chemical reaction.

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (1)$$

$$\ln k = \frac{-E_a}{RT} + \ln A \quad (2)$$

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

$$k = e^{\frac{-E_a}{RT}} \quad (4)$$

As shown in the above listed equations, it shows a wide applicability in catalytic reactions, including not only gas-phase reactions but also liquid-phase reactions, as well as most of complex catalytic reactions. However, the precondition of this equation in use is to assume that E_a is an independent constant without relating to temperature. Therefore, the results derived from this equation is well agreeing with the real experiment results within a certain temperature range.

This equation is of wide applications in heterogeneous catalysis. Typical in the catalytic oxidation of CO, a representative probe reaction in heterogeneous catalysis [7–12], the Arrhenius equation is often used as an evaluation standard to compare the intrinsic activity of different catalysts and relative amount of active sites. Bao et al. [7] reported a crystal-plane-controlled surface restructuring and catalytic performance of Cu_2O nanocrystals in CO oxidation with excess O_2 . As shown in **Figure 1**, the relationships of catalyst structure and catalytic property were deeply explored. Based on the microscopic and spectroscopic characterization results (detailed descriptions shown in Ref. [7]), the surface compositions and

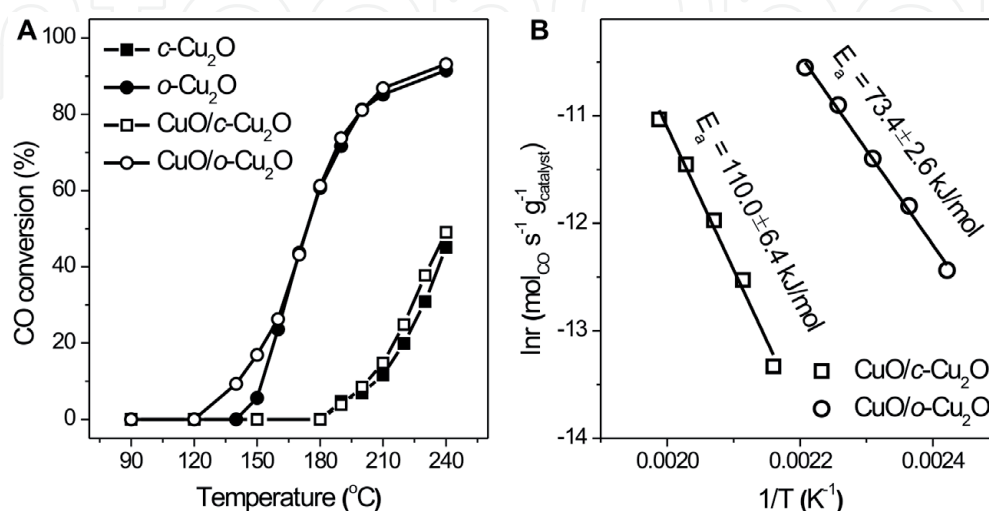


Figure 1. (A) Catalytic performance of $c\text{-Cu}_2\text{O}$, $o\text{-Cu}_2\text{O}$, $\text{CuO}/c\text{-Cu}_2\text{O}$, and $\text{CuO}/o\text{-Cu}_2\text{O}$ in CO oxidation reaction and (B) the Arrhenius plot of CO oxidation catalyzed by $\text{CuO}/o\text{-Cu}_2\text{O}$ and $\text{CuO}/c\text{-Cu}_2\text{O}$ [7]. Copyright © 2011, Wiley-VCH Verlag GmbH & Co.

structures of the restructured CuO/Cu₂O catalysts were distinctly identified. Their corresponding catalytic performance in CO oxidation with the plotted Arrhenius equation was also conducted. The derived E_a value plays a key role in comparing the intrinsic activity of surface sites on different catalysts based on the slope of the Arrhenius plots. CuO/Cu₂O octahedra (denoted as CuO/o-Cu₂O) show a lower E_a value of $73.4 \pm 2.6 \text{ kJ mol}^{-1}$ than CuO/Cu₂O cubes (denoted as CuO/c-Cu₂O) with a E_a value of $110.0 \pm 6.4 \text{ kJ mol}^{-1}$, indicating that CO oxidation catalyzed by the CuO of CuO/o-Cu₂O surface is more intrinsically active than the CO oxidation catalyzed by the CuO of CuO/c-Cu₂O surface. Density functional theory (DFT) calculations results demonstrate that they exist in different catalytic reaction mechanisms involved in different CuO/Cu₂O surface structures. The CuO/Cu₂O(100) surface is terminated with two-coordinated oxygen (O_{2c}) atoms, which result in a typical Mars-Van Krevelen (MvK) mechanism proceeded, while three-coordinated Cu (Cu_{3c}) and three-coordinated oxygen (O_{3c}) atoms are terminated on the CuO/Cu₂O(111) surface, which results in a Langmuir-Hinshelwood (LH) mechanism proceeded. These results clearly establish the catalyst structure-catalytic property relationships based on experimental observations and DFT simulations.

Similar results have been extensively reported in many other heterogeneous catalytic reactions, which were used by the calculated E_a values derived from the Arrhenius plots to compare the intrinsic activity [13–15]. Another example is in the identification of the most active Cu facet for low-temperature water gas shift reaction (**Figure 2**) [13]. Three types of Cu nanocrystals were prepared by a morphology-preserved reduction strategy from corresponding Cu₂O nanocrystals. Microscopic structural characterization results and in situ diffuse reflectance infrared Fourier transformed spectra (DRIFTS) of CO adsorption at 123 K confirm the Cu cubes (denoted as c-Cu), octahedra (denoted as o-Cu), and rhombic dodecahedra (denoted as d-Cu), respectively, enclosed with {100}, {111}, and {110} crystal planes (detailed descriptions shown in Ref. [13]). A morphology-dependent catalytic performance was observed on Cu nanocrystal catalyzed low-temperature water gas shift reaction, and the catalytic activity follows an order of c-Cu > d-Cu > o-Cu (**Figure 2A**). However, various Cu nanocrystals are different in particle sizes and surface structures and thus lead to the differently specific BET surface areas and catalytic sites in water gas shift reaction, respectively. As a result, it is difficult to compare the intrinsic activity of c-Cu and d-Cu nanocrystals in

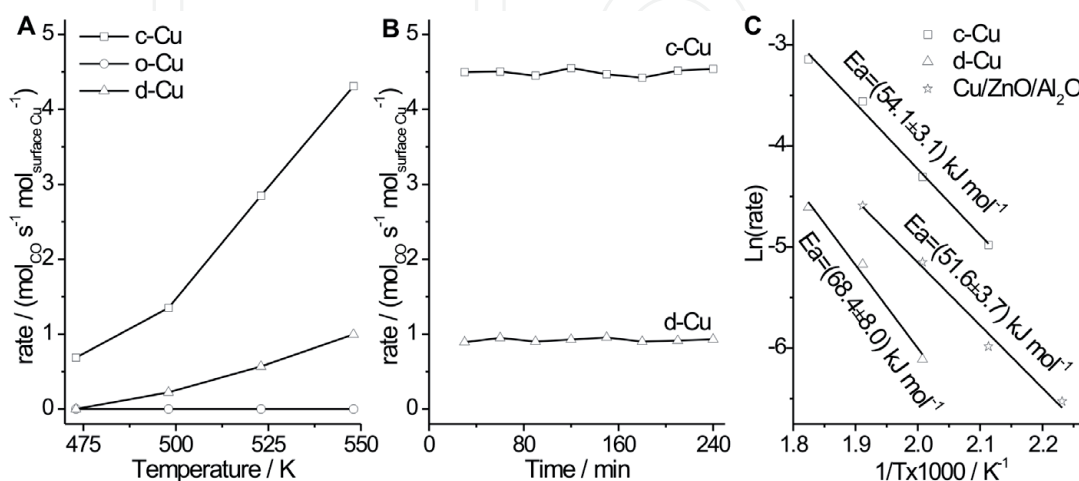


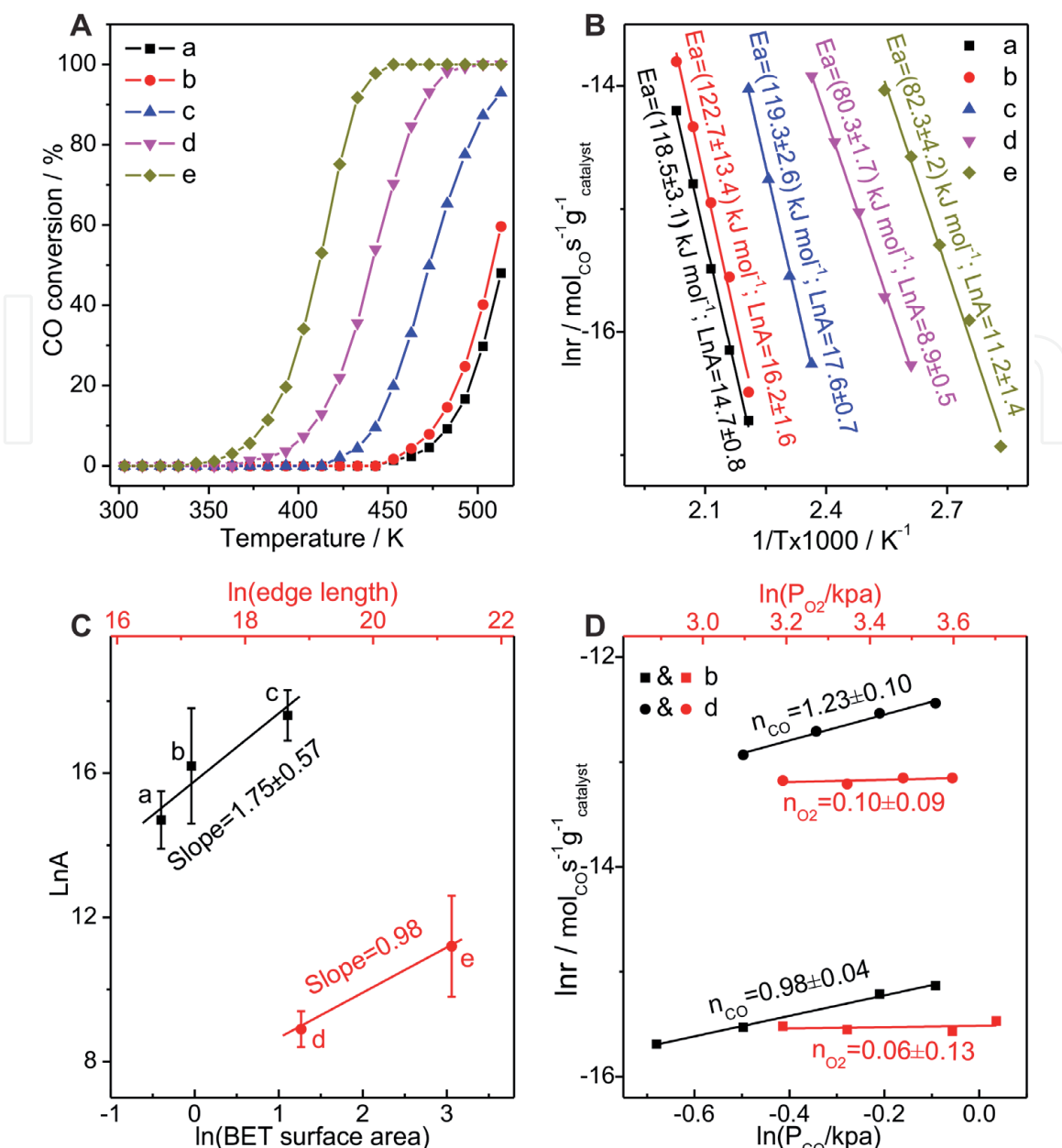
Figure 2.

(A) Reaction rate ($\text{mol}_{\text{CO}} \text{s}^{-1} \text{mol}_{\text{surface Cu}}^{-1}$) of Cu cubes, Cu octahedra, and Cu rhombic dodecahedra in the water gas shift reaction as a function of reaction temperature; (B) reaction rate ($\text{mol}_{\text{CO}} \text{s}^{-1} \text{mol}_{\text{surface Cu}}^{-1}$) of Cu cubes and rhombic dodecahedra at 548 K in the water gas shift reaction as a function of reaction time; (C) the Arrhenius plots of Cu cubes, rhombic dodecahedra, and commercial Cu/ZnO/Al₂O₃ catalyst in the water gas shift reaction [13]. Copyright © 2017, Nature Publishing Group.

water-gas shift reaction except o-Cu nanocrystals due to its catalytically inert under the reaction conditions. Subsequently, the Arrhenius equation was plotted based on the catalytic conversions below 15% without the mass transfer effect and heat transfer effect to compare the catalytic performance of intrinsically active sites. The calculated E_a value is $54.1 \pm 3.1 \text{ kJ mol}^{-1}$ for c-Cu nanocrystals, which is lower than d-Cu nanocrystals with a E_a value of $68.4 \pm 8.0 \text{ kJ mol}^{-1}$ and similar to commercial Cu/ZnO/Al₂O₃ catalyst with a E_a value of $51.6 \pm 3.7 \text{ kJ mol}^{-1}$ (**Figure 2C**). This indicates that the catalytic reaction proceeds more facile on c-Cu nanocrystals enclosed with {100} crystal planes, and thus, c-Cu nanocrystals are the most active Cu facet for low-temperature water gas shift reaction.

The above-mentioned results are a relatively straightforward and convenient method in the use of the Arrhenius equation. For more in-depth use, the Arrhenius equation can also have been utilized to identify the role and contribution of different active sites of a catalyst nanoparticle to the catalytic reaction based on the calculated E_a and pre-exponential factor A values derived from the Arrhenius equation [8]. c-Cu₂O nanocrystals in different sizes were synthesized by the established methods and subsequently evaluated in the oxidation of CO with excess O₂. The catalytic activities of the restructured CuO/c-Cu₂O catalysts increase with the size decrease (**Figure 3A**), apparently in consistent with their specific BET surface areas. However, their corresponding E_a values are distinctly different. c-Cu₂O nanocrystals in large sizes show a higher E_a value of about 120 kJ mol^{-1} than those in fine sizes with a E_a value of about 80 kJ mol^{-1} (**Figure 3B**), indicating that they exhibit different structures of active sites. Until here, it is still unclear which site contributes to the catalytic performance; thus, the relative relationships of different surface sites to the number of active sites, including facet sites and edge sites, are plotted in order to identify the structure of active sites on different c-Cu₂O nanocrystals. Under the same catalytic reaction conditions, the calculated A values derived from the intercept of the Arrhenius equation are positively related to the density of active sites. Thereby, the calculated $\ln(A)$ values of the CuO/c-Cu₂O catalysts were, respectively, plotted as a function of $\ln(\text{BET surface area})$ and $\ln(\text{edge length})$. As shown in **Figure 3C**, the $\ln(A)$ values of CuO/c-Cu₂O-1029, CuO/c-Cu₂O-682, and CuO/c-Cu₂O-446 are proportional to $\ln(\text{BET surface area})$ with a slope value of 1.75 ± 0.57 , and the $\ln(A)$ values of CuO/c-Cu₂O-109 and CuO/c-Cu₂O-34 are proportional to $\ln(\text{edge length})$ with a slope value of 0.98. These results are in consistent with the kinetic analysis results of DFT calculations, in which the calculated reaction rate expression based on the elementary reactions exhibits a slope value of 2 between $\ln(\text{reaction rate})$ and $\ln(\text{CuO/Cu}_2\text{O}(100) \text{ surface site})$ and a slope value of 1 between $\ln(\text{reaction rate})$ and $\ln(\text{CuO/Cu}_2\text{O}(110) \text{ surface site})$. Furthermore, the reaction orders of CO and O₂ derived from reaction rate equation (described below) in two representative CuO/c-Cu₂O catalysts are calculated (**Figure 3D**), whose values are also in consistent with the DFT calculation results. These kinetic analysis results in combination with DFT calculations successfully demonstrate the structure of active sites with the switch of dominant surface sites contributing to the catalytic activity in CO oxidation reaction from face sites for large c-Cu₂O nanocrystals to edge sites for fine c-Cu₂O nanocrystals.

The Arrhenius equation is also suitable for some complex reactions [16–18], such as the oxidative dehydrogenation of propane (ODHP) to selectively produce propene. You et al. [16] reported that the NbO_x/CeO₂-rod catalysts applied for such a reaction and the calculated E_a values derived from the Arrhenius plots with stable C₃H₈ conversions below 15% without the mass transfer effect and heat transfer effect are dependent on the catalyst structure (**Figure 4**). NbO_x/CeO₂-rod catalysts show a higher E_a value of about 65 kJ mol^{-1} than that of CeO₂ rods with a E_a value of about 45 kJ mol^{-1} , proving that the loading of NbO_x onto CeO₂ rods suppresses their

**Figure 3.**

(A) Stable light-off curves of the CuO/c-Cu₂O structures in different sizes during the oxidation of CO and (B) the corresponding Arrhenius plots; (C) calculated apparent pre-exponential factors ($\ln A$) as a function of the measured BET surface area and the calculated edge length; (D) reaction rates as a function of the partial pressures of CO and O₂: (a) CuO/c-Cu₂O-1029, (b) CuO/c-Cu₂O-682, (c) CuO/c-Cu₂O-446, (d) CuO/c-Cu₂O-109, and (e) CuO/c-Cu₂O-34 [8]. Copyright © 2019, Wiley-VCH Verlag GmbH & Co.

intrinsically catalytic activity. These results clearly demonstrate a wide application for the Arrhenius equation in heterogeneous catalysis. As the science advance, its physical significant is constantly being interpreted with a large amount of analysis of experimental data; therefore, it has a comprehensive guiding significance for chemical kinetics.

2.2 Reaction rate equation and its application in heterogeneous catalysis

Reaction rate equation is an equation of utilizing the concentration or partial pressure of reactants to calculate the reaction rate of chemical reaction. The general expression (Eq. (5)) and differential expression (Eq. (6)) are listed, in which r represents the reaction rate, k represents the rate constant, A and B represent the reactants, and x and y represent the reaction orders of A and B , respectively.

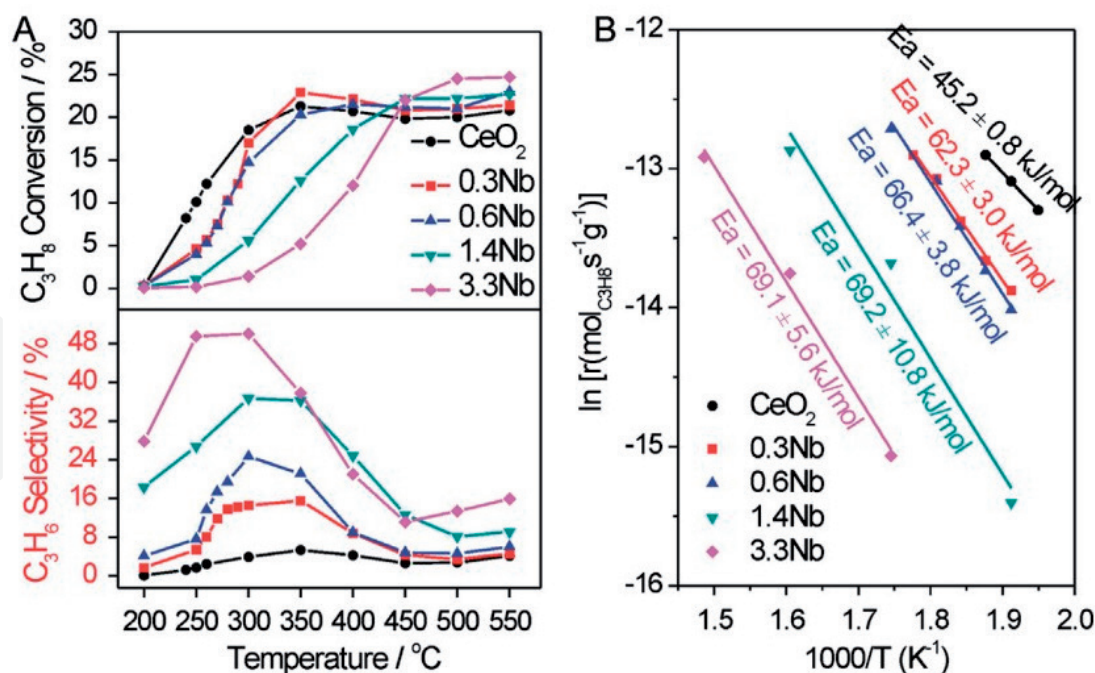


Figure 4. (A) C₃H₈ conversion and C₃H₆ selectivity of CeO₂ rods and NbO_x/CeO₂ catalysts in the oxidative dehydrogenation of propane reaction and (B) the corresponding Arrhenius plots with calculated apparent activation energies (E_a) [16]. Copyright © 2017, Elsevier.

The reaction orders are determined by the reaction process. Normally, the reaction order is equal to the stoichiometric number of chemical reaction in elementary reaction, while the values are generally not equal in nonelementary reaction. Therefore, it has a complex reaction rate expression in many catalytic reactions that lead to a difficult identification of reaction mechanism.

$$r = k [A]^x [B]^y \quad (5)$$

$$\ln \left(\frac{d[A]}{dt} \right) = \ln k + n \ln [A] \quad (6)$$

For a sample heterogeneous catalytic reaction involving a typical MvK mechanism, such as the above-mentioned CO oxidation reaction in **Figure 3D** [8], the calculated reaction orders of CO and O₂ are 1 and 0, respectively, indicating that the catalytic reaction is only dependent on CO but not on O₂. Such dependence suggests the adsorption of CO and O₂ onto catalyst surface proceeded step by step, as well as the rate-determining step prior to the O₂ adsorption process. Thereby, it can be reasonably proposed that the CO oxidation reaction catalyzed by the facet sites and edge sites of CuO/c-Cu₂O catalysts is both proceeding with the MvK mechanism.

But for complex reactions, the reaction mechanism is hardly proposed by the reaction orders [19–21]. However, the reaction orders are still useful to speculate the important catalytic process, especially in determining the rate-determining step of catalytic reaction [22–25]. A typical example is in the preparation of formic acid, an important chemical in the H₂ storage and other industrial applications, from CO₂ hydrogenation. The support plays a key role in determining the catalytic mechanism of CO₂ hydrogenation into formic acid, which has been confirmed in our previous report by using two common metal oxide (CeO₂ and ZnO) supported Pd catalysts dominantly based on the apparent kinetic analysis and in situ DRIFTS results [22]. The calculated E_a values are similar on Pd/CeO₂ catalysts with different Pd loadings but distinctly different on Pd/ZnO catalysts with different Pd

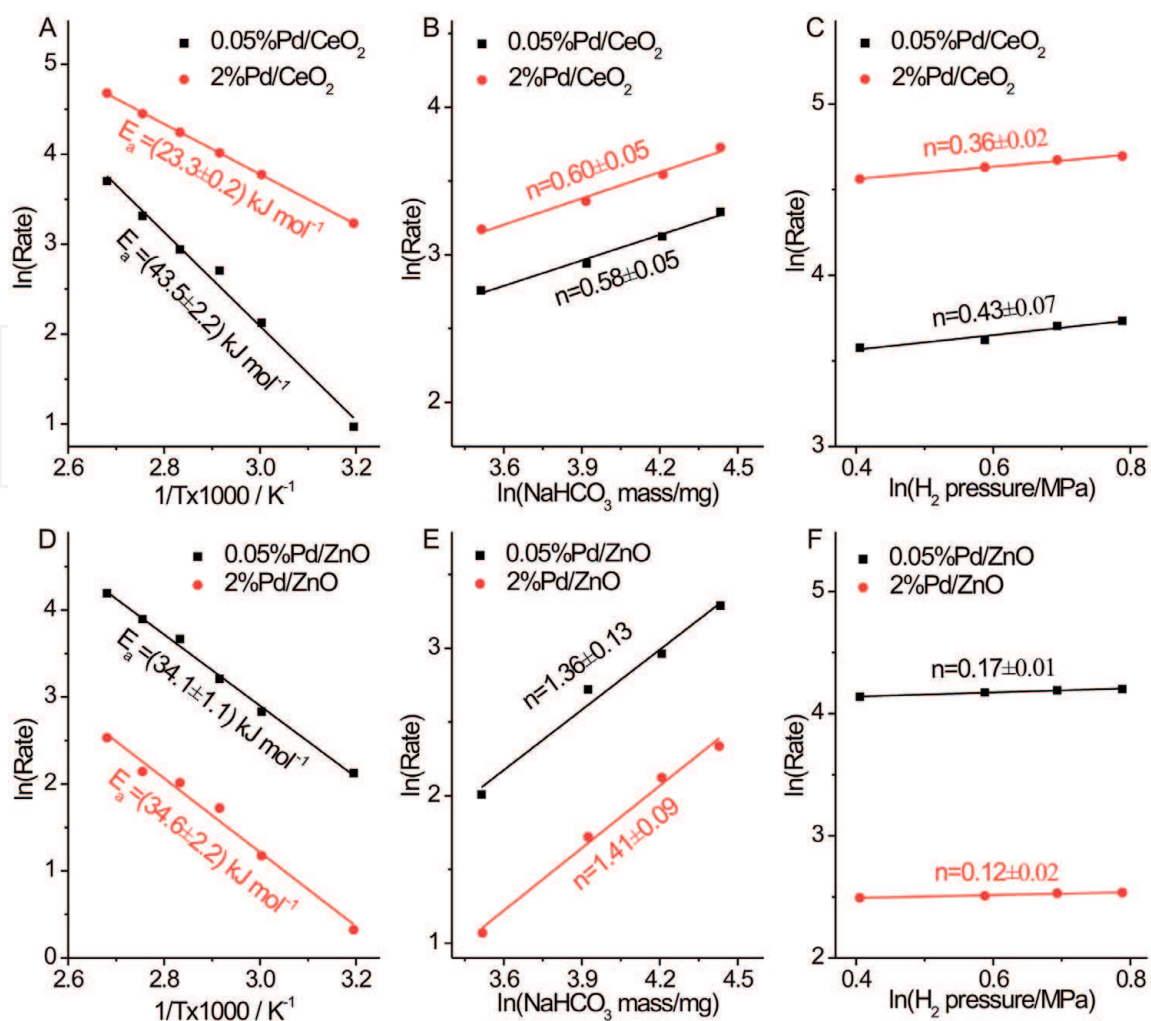


Figure 5.

The Arrhenius plots of (A) 0.05%Pd/CeO₂ and 2%Pd/CeO₂ catalysts and (D) 0.05%Pd/ZnO and 2%Pd/ZnO catalysts; CO₂ reaction orders of (B) 0.05%Pd/CeO₂ and 2%Pd/CeO₂ catalysts and (E) 0.05%Pd/ZnO and 2%Pd/ZnO catalysts at 373 K; and H₂ reaction orders of (C) 0.05%Pd/CeO₂ and 2%Pd/CeO₂ catalysts and (F) 0.05%Pd/ZnO and 2%Pd/ZnO catalysts at 373 K [22]. Copyright © 2019, Elsevier.

loadings (**Figure 5A** and **D**), suggesting that the catalytic performance on Pd/CeO₂ catalysts is affected by the Pd structures. The reaction orders of CO₂ and H₂ clearly demonstrate that the rate-determining step of CO₂ hydrogenation to formic acid on Pd/ZnO catalysts involves a CO₂-contained elementary reaction due to a relatively higher CO₂ reaction order (~1.4) (**Figure 5B** and **E**) and of CO₂ hydrogenation to formic acid on Pd/CeO₂ catalysts involves a H₂-contained elementary reaction due to a relatively higher H₂ reaction order (~0.4) (**Figure 5C** and **F**). H₂ is generally activated on Pd, and thus, the structure of Pd affects the catalytic performance of Pd/CeO₂ catalysts but not that of Pd/ZnO catalysts, in consistent with their calculated E_a results.

This conclusion is further proved by Pd/ZrO₂ catalyzed CO₂ hydrogenation into formate (**Figure 6**) [23]. Experimental observation results in CO₂-TPD profiles (detailed description shown in Ref. [23]) showed the basicity densities following an order of 2%Pd/ZrO₂-T (Tetragonal ZrO₂) > 2%Pd/ZrO₂-M&T (Mixed ZrO₂) ≈ 2%Pd/ZrO₂-M (Monoclinic ZrO₂), in consistent with the intrinsic activity order. Comparing the reaction orders of H₂ and CO₂ on 2%Pd/ZrO₂-T and 2%Pd/ZrO₂-M catalysts, similar H₂ reaction orders were observed, while the CO₂ reaction orders were higher on 2%Pd/ZrO₂-M catalyst than that on 2%Pd/ZrO₂-T catalyst. These results clearly demonstrate that the catalytic performance of Pd/ZrO₂ catalyst in CO₂ hydrogenation into formate is strongly dependent on the

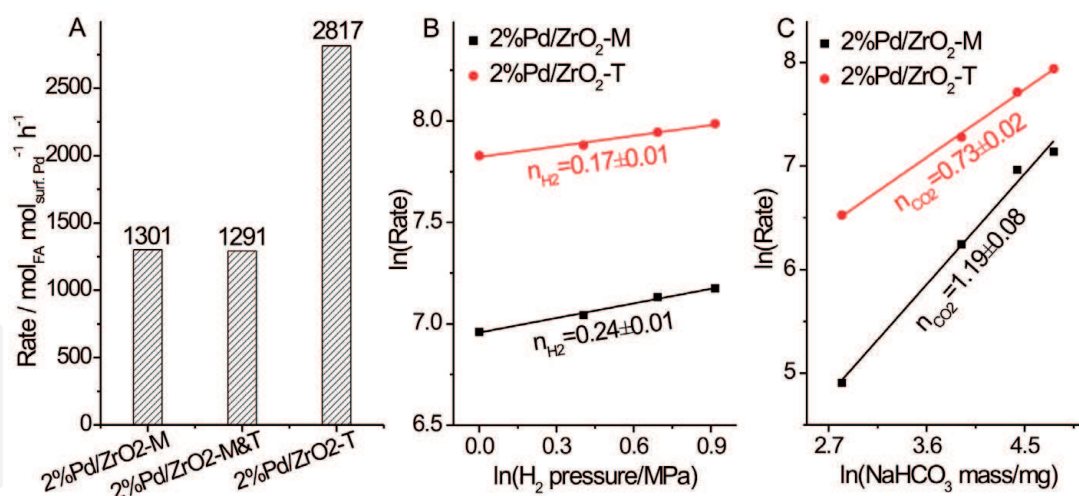


Figure 6.
 (A) Production rate (mol_{HCOO} · mol_{surf. Pd}⁻¹ h⁻¹) of formate on representative various 2%Pd/ZrO₂ catalysts based on the surface Pd atoms; reaction orders of (B) H₂ and (C) bicarbonate of 2%Pd/ZrO₂-M and 2%Pd/ZrO₂-T catalysts [23]. Copyright © 2019, Elsevier.

surface basicity densities, 2%Pd/ZrO₂-T support holds the higher surface basicity densities, and thus, Pd/ZrO₂-T catalyst is more active in catalyzing the formate production.

Reaction rate equation is the real reflection of chemical reaction rate. It has been widely used as an important method in investigating the catalytic mechanism. However, several factors, including temperature, chemical reaction, concentration, pressure, order, solvent, light, and catalyst, strongly affect the rate of a chemical reaction. Among them, temperature usually plays a key factor. Generally, the rate of a chemical reaction increases with an increase in reaction temperature because higher kinetic energy can result in more collisions between the reactant molecules. The increase of collision chance will cause the catalytic reaction more likely to happen. The temperature effect on reaction rate can be quantified by the Arrhenius equation. Notably, some reaction rates are negatively affected by the temperature, while some others are independent of temperature. The chemical reaction, concentration, pressure, and order directly determine the reaction rate. In chemical reaction, the complexity of the reaction and the state of the reactants are important. Such as, the reaction of a powder in a solution always proceeds faster than the reaction of a large chunk of a solid. Concentration, pressure, and order are the important parameters of reaction rate equation and thus directly affect the reaction rate. Solvent, light, and catalyst are the external factors that generally do not participate in a reaction but affect the reaction rate. In familiar with these influence factors, it can guide us to better understand and apply the reaction rate equation.

3. Summary and outlook

In summary, this chapter introduced the Arrhenius equation and reaction rate equation, two important equations in chemical kinetics, and their applications in heterogeneous catalysis in detail. By the analysis of some specific reactions in the documents, the Arrhenius equation could be used to calculate the E_a and A values in catalytic reaction, which were related to the intrinsic activity of the number of active sites, respectively. The reaction rate equation could be used to calculate the reaction order of a single reactant that was useful in speculating the contribution of a single reactant in catalytic reaction. Through these investigations of chemical kinetic equations in catalytic reaction and further combining with DFT

calculations, it well proposed the structure of active sites and the catalytic mechanism in catalytic reaction and thus established the concept of catalyst structure-catalytic property relationships. These would be promising to guide the structural design and controlled synthesis of novel efficient catalytic materials in the future.

Nowadays, the development of chemical kinetics is very rapid and the contained fields gradually enlarged with the research mode from basement state turning to excitation state, from small molecule turning to big molecule, and from gas phase turning to condensed phase. Benefiting from the improvement of advanced characterization skills, especially in the development of surface analysis and intermediate tracking skills, the catalytic science has become the frontier field of chemical kinetics. Furthermore, the progress of basic theory method also accelerates the application and development of chemical kinetics in catalytic science. The combination of theory and experiment can help to gain a deep insight into how various elementary reactions occur. The combination of more precise experimental results with more precise theoretical research is a powerful driving force for the continued development of this research field. Practice once again proves that the close combination of theory and experiment is the only way for the development of science.

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Conflict of interest


The authors declare no conflict of interest.

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