Predicting the kinetics of catalytic oxidation of multicomponent organic waste gases

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HIGHLIGHTS

- Predict the kinetics of catalytic oxidation of multicomponent waste gases.
- Explore the influence of reaction rate constants on a competitive oxidation.
- Build a prediction approach for the design and operation of a catalysis reactor.
- Obtain easily the optimal operation conditions for air pollution control.

GRAPHICAL ABSTRACT
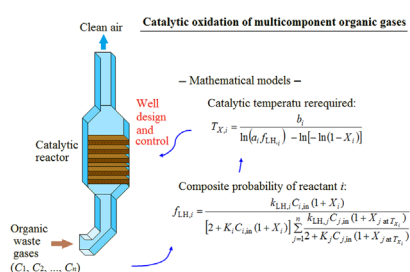
ABSTRACT

This study proposes an approach developed for predicting the conversion–temperature curve of catalytic oxidation of multicomponent organic waste gases. The mathematical models of these catalytic oxidations for the Langmuir–Hinshelwood, Eley–Rideal, and Mars–van Krevelen kinetic mechanisms were developed. The results of three case studies involving five commonly industrially used hydrocarbons showed that the constructed mathematical model was accurate; the range of average absolute relative error between the modeling and experimental temperatures of the five hydrocarbons in catalytic oxidations of mixtures was 2.5–6.8%. The biases of conversion–temperature curves obtained through modeling decrease with increasing conversion rates. The reaction rate of a hydrocarbon during competitive oxidations of multicomponent organic gases was controlled through composite probabilities of their reaction rates and adsorption equilibrium constants on a catalyst surface. This study also investigated the effects of the apparent reaction rate and adsorption equilibrium constants on catalytic oxidation.

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1. Introduction

A mathematical model of reaction kinetics can describe the characteristics of a chemical reaction to yield information on the rates, mechanism, and transition states of chemical processes. Most researchers use the power-law rate, Langmuir–Hinshelwood (LH), Eley–Rideal (ER), or Mars–van Krevelen (MVK) models, to test the applicability accurately, expressing the reaction rate under differential reactor conditions. Bahlawane (2006) indicated that the experimental data of the catalytic combustion of methane over cobalt oxide data fitted well to the MVK model, and can be approximated using a power rate law in oxygen-rich mixtures. Grabowski (2004) reported that the ER model is more appropriate for describing the oxidative dehydrogenation of propane over VTiO and VRbTiO catalysts during steady-state adsorption. Gracia et al. (2009) reported that the mechanism for CO hydrogenation to methane on iron carbides resembles the MVK mechanism for oxidation reactions. Kim and Hong (2002) successfully applied the LH model to correlate the obtained data of photocatalytic degradations of trichloroethylene, acetone, methanol, and toluene over

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a thin-film TiO₂ photocatalyst. The results from kinetic studies have provided valuable information for designing a catalytic system.

A power-law rate model is the simplest model, which is experimentally evaluated and can be used to predict the relationship between the rate of a reaction and the concentrations of reactants. This model can accurately describe experimental results under specific and well-controlled operating conditions (Hla et al., 2011). However, power-law rate equations do not represent any fundamental or exhaustive reaction mechanisms (Gökaliler et al., 2012). LH, ER, and MVK mechanisms are the three main reaction mechanisms for investigating the adsorption and desorption of gas molecules and their interactions on a catalytically active surface. Vannice (2007) indicated that the MVK rate expression for heterogeneously catalyzed oxidation reactions reveals several inconsistencies. The expression as derived is appropriately applicable only for a reaction involving molecular oxygen adsorbed on a single site; however, the model assumes that lattice O ions or atoms react with the substrate being oxidized. The steps describing the model are not elementary, and the competitive adsorption of intermediates and products is not considered. Doornkamp and Ponec presented a detailed discussion on less common reactions associated with the MVK mechanism (Doornkamp and Ponec, 2000). The LH catalytic sequence can typically provide similar or identical rate equations, which can fit rate data more accurately compared with the MVK expression. The distinction between the LH and ER mechanisms is that only one or two molecules adsorbed on a catalytically active surface undergo a bimolecular reaction. These mechanisms provide rate parameters that can be evaluated for thermodynamic consistency.

Among several kinetic models tested for heterogeneous catalytic reactions, the simple LH model is the best-fit model, particularly in the treatment of volatile organic compounds (VOCs) (Abbas et al., 2011; Tseng and Chu, 2001; Yu et al., 2006; Hamoudi et al., 2001; Doucet et al., 2006). The LH kinetic expression is the most commonly used expression for explaining the kinetics of heterogeneous catalytic processes, and determining the relationship between the oxidation rate and the concentration of an organic substrate (Khezrianjoo and Revanasiddappa, 2012; Kumar et al., 2008; Stoltze, 2000).

The selection of the most efficient catalyst and optimum reactor geometries presents two main challenges in designing a catalytic reactor. The first challenge can be overcome by analyzing each catalytic reaction in paths, mechanisms, products, efficiencies, and so on. The second challenge can be overcome by analyzing the reaction kinetics and methods for different reactor types. A kinetic study of the catalytic oxidation is crucial for the accurate design and field operation of a catalytic oxidizer, particularly in the treatment of industrial and vehicular organic waste gases. Industrial and vehicular exhaust emissions contain complex organic waste gases. When multicomponent organic waste gases undergo catalytic oxidation, the reactions of different components proceed at different rates, and the components compete for catalytic oxidation over the catalyst. Therefore, predicting the kinetic parameters of the catalytic oxidation of multicomponent organic waste gases is crucial. However, few studies have identified the kinetic parameters required for designing and optimizing catalytic reactors.

For this study, an approach for predicting the temperature required for the catalytic oxidations of multicomponent organic waste gases was developed. This approach integrated the Arrhenius law with the LH, ER, or MVK rate expression to establish kinetic prediction models. The competitive oxidation of multicomponent organic gases over the catalytic sites and characteristic parameters of each reactant were considered. Furthermore, the present work is a pilot study for using perovskite-type oxides as a

catalyst and dielectric barrier materials in plasma-catalytic techniques on waste gases with complex components treatments. Perovskite-type oxides were chosen because the properties of high temperature resistance, high dielectric value ($\varepsilon = 2000–10{,}000$) (Ogata et al., 1999, 2001), ferroelectricity, and certainly the high oxidation/reduction catalytic ability (Maluf and Assaf, 2010; Merino et al., 2005; Li et al., 2004; Liang and Nien, 2008). Therefore, $La_{0.7}Sr_{0.3}MnO_3$ perovskite-type catalyst was used as the representative catalyst in this study.

2. Methodology

In following case study, the gas-phase oxidations of five commonly industrially used hydrocarbons, namely butanone, xylene, toluene, hexane, and benzene, over a prepared perovskite-type catalyst were carried out. Perovskite-type oxides exhibit favorable catalytic activities (Maluf and Assaf, 2010; Merino et al., 2005). These oxides have an ABO_3 stoichiometry and a cubic crystal structure (Li et al., 2004). The $La_{0.7}Sr_{0.3}MnO_3$ perovskite-type catalyst was used as the representative catalyst because of its excellent activity (Liang and Nien, 2008). The catalyst was prepared using an alkaline coprecipitation method: 0.18 M potassium carbonate was used as the precipitant in a stirred-flask reactor at an agitation speed of 600 rpm; the precipitate was filtered, washed (i.e., the potassium ions were washed out by using deionized water), dried at 110 °C, and calcined in air for 6 h at 960 °C. The catalytic oxidation data were obtained using a packed-bed reactor at atmospheric pressure. A quartz tube with an inner diameter of 1.2 cm was used as the reactor. A furnace with a proportional–integral–derivative (PID) temperature controller (Shinko MCD-100) was used to heat the reactor. Catalyst powder (40–60 mesh, 0.3 g) and mixed quartz powder (40–60 mesh, 1.2 g) were placed on a 100 mesh stainless steel screen in the middle of the tube. The upper and lower portions of the tube were packed with quartz powder (0.5 and 1.0 g) to disperse the reaction gas.

In this study, the five liquid hydrocarbons were injected into an evaporator by using a syringe pump (Stoelting, Model-100), and air was fed to the reactor as the carrier gas. The initial concentrations of the five VOCs and their mixtures were maintained at 4000 ± 100 ppmv to acquire the rate expression. Another PID temperature controller was used to maintain the temperature of the vaporizer (Shinko, MCD-100) at 10 °C more than the boiling point of each hydrocarbon. A pressurized air tank and a mass flow controller (Tylan, FC-260) were used to control the flow rate of air through the evaporator and reactor, respectively, at a flow rate of 120 mL min⁻¹. The weight hour space velocity (WHSV) was maintained at 24,000 mL h⁻¹ g⁻¹. The gas at the inlet and outlet of the reactor was analyzed using a gas chromatograph (Shimadzu, GC 14B–FID) with a 30-m capillary column (Supelco, fused silica column, internal diameter 0.25 mm) at 100 °C.

3. Results and discussion

3.1. Predicting kinetic parameters

The reaction rate of catalytic oxidation is expressed as follows:

$$\frac{dC}{dt} = -kSC = -k_{app}C \qquad (1)$$

where C is the concentration of the reactant, S is an adsorption site on the catalyst surface, and the apparent rate constant $k_{app} = kS$.