

Kinetics of hydrogen oxidation on Rh/Al₂O₃ catalysts studied in a stagnation-flow reactor



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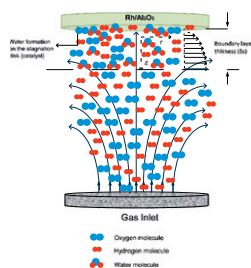
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HIGHLIGHTS

- ▶ A stagnation-flow reactor set-up is proposed for studying catalytic kinetics.
- ▶ H₂ oxidation over Rh/Al₂O₃ is studied experimentally and numerically.
- ▶ A thermodynamically consistent multi-step reaction mechanism is proposed.
- ▶ The reaction mechanism is successfully tested in a continuous annulus flow reactor.

GRAPHICAL ABSTRACT



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ABSTRACT

A newly established stagnation flow reactor with analysis of spatially resolved concentrations profiles is presented as useful tool for the investigation of heterogeneously catalyzed gas-phase reactions. The simplicity of this laboratory-scale reactor enables detailed modeling of the diffusive and convective transport within the one-dimensional gas-phase boundary-layer coupled with elementary-step homogeneous and heterogeneous reaction mechanisms. This set-up is applied to study the kinetics of hydrogen oxidation over Rh/Al₂O₃. By combining experimental and modeling results for a wide range of temperature and fuel/oxygen ratios, a thermodynamically consistent set of kinetic data for a 12-step surface reaction mechanism is derived. The applicability of the mechanism is further tested by the model prediction of experimentally derived ignition temperatures in a stagnation flow reactor and oxygen conversion in H₂-rich hydrogen oxidation in an annular flow reactor at varying flow rate and temperature.

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1. Introduction

Since Döbereiner's discovery of the catalytic effect of Pt on H₂ and O₂ mixtures in 1823, heterogeneous oxidation of H₂ on transition metals has been studied extensively (Löber and Hennig, 1997; Padowitz and Sibener, 1991; Rinnemo et al., 1997; Rinnemo et al., 1993; Thiel et al., 1979b; Verheij et al., 1990; Völkening et al., 1999;

Warnatz et al., 1994; Yates et al., 1979a, b). Besides its simplicity, with only a few reaction steps of adsorption and desorption of the reactants and products, it is one of the key reactions in many catalytic processes of industrial importance (Treviño, 2011; Wilke et al., 2000). In microreactor technology, H₂ oxidation is carried out to test the flexibility of the reactor at different operating conditions without the occurrence of a flame (Choi et al., 2008; Vesper, 2001; Zhou et al., 2009). Due to the low ignition temperature of H₂/O₂ mixtures, small amounts of H₂ can be applied in CH₄/O₂ systems to decrease the light off temperatures, e.g. for catalytic combustor and turbine applications (Deutschmann et al., 2000). Furthermore, this reaction has a strong impact on exhaust gas after-treatment.

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During sudden acceleration of a car, the formation and consequently oxidation of small amounts of H₂ in the exhaust gas may cause hot spot formations in the catalyst and lead to altering of catalytic converters (Whittington et al., 1995; Yakhnin and Menzinger, 2002).

There is also a continued interest in developing a better understanding of hydrocarbon fuel processing technologies for syngas (H₂+CO) production in a wide range of operating conditions in order to increase reaction efficiency and reduce pollutants (Beretta et al., 2011; Chakrabarti et al., 2011; Chin et al., 2011; Hartmann et al., 2011; Holladay et al., 2009; Horn et al., 2007; Nogare et al., 2011). All fuel processing technologies i.e., partial oxidation, steam reforming, or auto thermal reforming, include the formation and/or oxidation of H₂ in their reaction pathways (Holladay et al., 2009).

Development of a detailed kinetic mechanism for such complex reaction schemes necessarily begins with a H₂-O₂ sub-system which is also a critical step as the overall reaction efficiency is determined by H₂ selectivity to H₂O (Hartmann et al., 2011).

1.1. H₂ oxidation on Rh

Among the catalysts belonging to group VIII transition metals (Rh, Pt, Ru, Ni), Pt and Rh are the most effective catalysts for synthesis gas production (Horn et al., 2007; Thiel et al., 1979b; Wilke et al., 2000). Although the reaction pathways and the existing surface species of H₂ oxidation on Pt and Rh are quite similar, the kinetic parameters differ considerably. Pt shows higher water formation activity than Rh as the energy barrier for the formation of formate hydroxyl species is lower than for Rh. This makes Rh a better catalyst for syngas production (Wilke et al., 2000; Zum Mallen et al., 1993). Although H₂ oxidation kinetics on Pt surfaces has been studied extensively, the work on Rh is limited (Anton and Cadogan, 1990; Cho and Law, 1986; Deutschmann et al., 1994, 2000; Germer and Ho, 1989; Ikeda et al., 1995; Ljungström et al., 1989; Mantzaras et al., 2009; Rinnemo et al., 1993; Verheij et al., 1990; Williams et al., 1992).

In 1979, Yates, Thiel and Weinberg published a series of papers to examine the adsorption, desorption, and surface reactions of H₂ and O₂ on Rh(111) surfaces using low-energy electron diffraction (LEED) and thermal desorption (TDS) studies. They explained the H₂ and O₂ adsorption as coverage-dependent where oxygen pre-coverage blocks surface sites, and this inhibits subsequent H₂ adsorption. If O₂ is co-adsorbed with H₂, the activation energy for H₂ desorption is decreased. Due to the LEED technique, their experiments were limited to temperatures below 375 K (Thiel et al., 1979a, b; Yates et al., 1979a, b).

Padowitz and Sibener proposed an elementary-step reaction mechanism on Rh(111) surfaces by following the approach of Yates, Thiel and Weinberg. Using molecular beam technique, they were able to examine the reactions at temperatures of 450–1250 K for reactant pressures below 10⁻⁴ Torr. In their mechanism, they introduced oxygen dissolution into bulk metal at high temperatures and showed that water formation mainly follows the path of combination of adsorbed O and H species to yield hydroxyl intermediates, and that the reaction of H is sequenced. The reaction mechanism does not assume any dissociation of water, although all other elementary steps are reversible. They concluded that the adsorption of H₂ and O₂ was coverage dependent. For high temperature regimes with high oxygen and low hydrogen coverage conditions, the reaction regime shows linear, nonlinear, and possibly oscillatory behavior (Padowitz and Sibener, 1991).

Zum Mallen et al. studied H₂ oxidation on polycrystalline Rh foils and compared it with Pt. In their study, they measured the OH formation rate for surface temperatures between 1000 and 1800 K by laser-induced fluorescence (LIF), and proposed a potential-energy diagram which emphasizes that the oxygen desorption energy is

slightly higher on Rh than on Pt, and that OH surface species are less stable on Rh. In this diagram, it was shown that the high OH formation activation energy (83.6 kJ/mol) via the reaction of O and H is higher than Pt (10.5 kJ/mol) (Zum Mallen et al., 1993).

Further, Wilke et al. (2000) presented a theoretical study of H₂ oxidation kinetics on Rh and Pt surfaces using density-functional theory (DFT) to create the potential-energy diagram for water formation. In their study, they succeeded in reproducing the potential-energy diagram for Rh with little difference compared to Hickman and Schmidt (1993). This difference was attributed to the execution of real experiments in industrial working conditions as compared to computer experiments simulated under high vacuum and on a single crystal.

Dewaele et al. (1999) studied the adsorption of H₂ and O₂ on supported (γ-Al₂O₃) Rh catalysts to point out the effect of real catalyst properties with low amounts of active metal on support. In their study, they examined the desorption kinetics of H₂ and O₂ using a TAP (Temporal Analysis of the Products) reactor. They concluded that their kinetics data derived was in good agreement with the predicted adsorption and desorption rate of H₂ with respect to the second-order dependency of gas phase H₂ concentration and adsorbed H on the surface. They also estimated the desorption activation energy for H₂ to be 56.6 kJ/mol which is considerably less than reported in the literature (80–100 kJ/mol) (Dewaele et al., 1999). This difference is attributed to the support effect.

In recent years, Mhadeshwar and Vlachos studied H₂ ignition on Rh foils in a microreactor at atmospheric conditions in fuel-lean regimes. They pointed out that, unlike on Pt catalysts, ignition temperature decreases with increasing H₂ concentration in the fuel mixture (Mhadeshwar and Vlachos, 2005). Using the ignition data, they proposed a H₂ oxidation reaction mechanism as well. In their mechanism, they emphasized that desorption activation energies of oxygen and hydrogen are coverage dependent. Maestri et al. (2007, 2008) used this heterogeneous reaction mechanism to examine the effect of H₂/O₂ homogeneous reactions at moderate temperature ranges in H₂-rich regimes for varying flow rates. They used an annular duct reactor for kinetic investigations and showed that the gas phase reactions are negligible in a temperature range of 323–873 K. They pointed out that the heterogeneous model overestimates the measured O₂ conversions at intermediate temperatures and at the lowest flow rate (2 Ni/kg cat). On the other hand, at high temperatures, the model underestimates the experimental O₂ conversion values. The difference between the experiments and predicted values becomes more evident with increasing flow rates. Besides the mass transfer limitations due to the reactor behavior, they explain these differences as a result of possible non-uniformity of the deposits in the boundaries of the catalyst bed and the uncertainty between the beginning and the end of the reactor (Maestri et al., 2008). This conclusion emphasizes the necessity of a well-defined reactor type for kinetic investigations.

1.2. Laboratory-scale reactors for kinetic studies

Although a fixed-bed flow reactor configuration is mostly used in the laboratories, it is usually limited for kinetic investigations because of the exothermic or endothermic nature of the catalytic processes where temperature and concentration gradients can vary within a few millimeter of the catalyst bed (Nogare et al., 2011; Rice et al., 2007). As an alternative, TAP reactor geometry can be used to investigate the reaction kinetics, assuming that adsorption, desorption, and the reaction steps are the processes that occur under isothermal conditions. The only transport mechanism of the molecules is through the Knudsen diffusion. On the other hand, the application of the TAP reactor is not really

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