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Kinetics of the water-gas shift reaction over Rh/Al_2O_3 catalysts

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ABSTRACT

The kinetics of the water-gas shift (WGS) reaction over Rh/Al_2O_3 catalyst is studied experimentally and numerically. Using the experimentally determined conversion in WGS, reverse WGS, and preferential oxidation of CO over a catalytically coated disk and over a honeycomb monolith, a thermodynamically consistent multi-step reaction mechanism with the associated rate expressions was developed. Both the experimental configurations were numerically simulated coupling models for the flow field with this heterogeneous reaction mechanism. The main reaction path for CO_2 formation on this catalyst is concluded to be the direct oxidation of CO with O species at high temperatures, whereas the formation of the carboxyl (COOH) group is significant at temperature below 600 °C. The reaction kinetics reproduced the experimental observations, also for the subsystems of hydrogen and CO oxidation.

1. Introduction

The water-gas shift (WGS) reaction (Eq. (1)) is industrially important in many chemical processes.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298} = -40.4\,\text{kJ/mol} \tag{1}$$

In conversion of hydrocarbons by total and partial oxidation, steam reforming, and dry reforming, WGS is one of the crucial reactions that determine the overall product selectivity [1–4]. WGS technology is used to purify reformates from CO to operated low-temperature fuel cells and ammonia synthesis plants with hydrogen [5–8]. In exhaust-gas after-treatment, WGS occurs in the catalytic converter with significant effects on the reduction of CO emissions and thermal stability of the catalysts [4,9,10].

1.1. Low temperature applications: synthesis gas purifications

In commercial applications, in which the removal of CO from the synthesis gas stream is necessary, the WGS reaction takes place in two steps, involving high-temperature shift (HTS) and low-temperature shift (LTS) processes [8]. Iron oxide and chromium oxide catalysts are used for the HTS in the temperature range of 310–450 °C [11]. For the LTS reaction, usually carried out as a second step after HTS, the catalysts are based on zinc and copper oxides operated between 200 °C and 250 °C [11,12].

There is an interest in alternative robust WGS catalysts, because LTS catalysts are sensitive to air and steam and they are easily poisoned by sulfur [10]. Besides, conventional catalysts imply large reactor volumes, in which mostly a packed-bed reactor configuration is used. The large size limits their application to on-board reforming technologies where smaller systems are required [13].

Noble metal-supported catalysts show promising activity because of their high stability in low and high temperature regimes and high tolerance capacity to impurities [4,10]. Pt, Rh, Pd, and Au-promoted catalysts on different supports (ceria, La_2O_3) have been investigated for WGS reactions [4,6]. Among these metals, Rh is a promising catalyst exhibiting high turnover frequencies (TOF) and stability. In understanding the reaction mechanism of WGS over Rh, the interaction of the catalyst with the support needs to be considered for support materials like ceria as well [5,14,15].

Many theoretical and experimental studies are conducted to elucidate the reaction kinetics of WGS resulting in three general reaction mechanisms. The first one relies on the assumptions that the redox mechanism is dominant and that CO_2 is generated by a reaction of CO, which is adsorbed on the metal and CeO_2 support, and that H_2 is formed via re-oxidation of Ce with H_2O [1]. In the second one, it is assumed that a carboxyl species plays a decisive role [5]. For supports containing CeO_2, regardless of the metal type (Pt or Rh), subtraction of H from water leads to OH formation on the support, which is a slow step, and CO_2 is primarily formed via a carboxyl (COOH) intermediate. The reaction between the chemisorbed CO and O is negligible [5]. In the third mechanism

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proposed, a formate species (HCOO) is the decisive intermediate formed by adsorbed CO and OH.

Olympiou et al. studied WGS reactions at 350–550 °C on Pt, Pd, and Rh supported on γ-Al_2O_3 with similar noble metal dispersions [8]. According to their study carried out at steady state conditions, adsorbed HCOO is formed upon surface diffusion of H and OH present on the alumina support. This reaction is considered as a slow step in WGS and the intermediate HCOO resides on the alumina support and/or the metal. A variety of other studies proposed the presence of a formate species on the reduced ceria, e.g., on Au/CeO_2 [6], Rh/MgO, Rh/ZnO, and Rh/CeO_2 [16], Pt/MgO and Pt/ZrO [17], and Pt/CeO_2 [18].

HCOO and the carboxyl species (COOH) are isomers and both the structures were detected experimentally using FTIR and DRIFTS and steady-state isotropic transient kinetic analysis (SSITKA) analysis [19,20]. However, there is a disagreement in the interpretation of the experimental data as to whether it is a carboxyl or a formate species. According to Hilaire et al. [21], the band in the spectra, which appears in the range of 1000–1700 cm^{-1} originates from OCO asymmetric and symmetric stretching vibrations. Therefore, it is difficult to distinguish whether the bands in this region correspond to carbonates or formates, because both species contain OCO vibrations. Besides, theoretical calculations favor the formation of the carboxyl species [2,3].

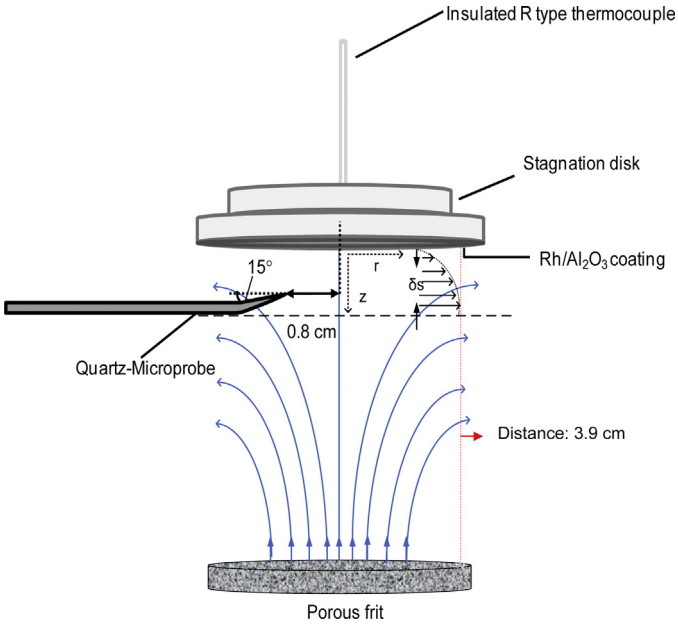

Fig. 1. Stagnation-flow field and microprobe sampling technique.

1.2. High temperature applications: effect of WGS reaction on synthesis gas production

For high-temperature applications, Rh supported on Al_2O_3 is a well-known catalyst for synthesis gas production from hydrocarbons [22–24]. Two routes to synthesis gas are proposed [25–28]. The direct route postulates the formation of H_2 and CO via partial oxidation of CH_4 in the presence of gas-phase O_2 [29], whereas, the indirect route favors a two-zone model, in which first total oxidation takes place followed by steam reforming of hydrocarbons and WGS [28,30].

The literature addresses different types of mechanism for WGS reaction and its effect on catalytic partial oxidation (CPOx) and reforming of hydrocarbons depending on the reactor types, in which the kinetic investigations are carried out, and on operating conditions and analytics used [23,28,31–33]. Horn et al. [22] studied the effect of the WGS in CPOx over a Rh catalyst monitoring concentration and temperature profiles along the catalyst bed under transient and steady-state conditions. They concluded that WGS has only a minor effect since the amount of CO_2 does not change in the absence of O_2 and that the contribution of the WGS varies with the C/O feed ratio. Michael et al. [34] have studied the effects of H_2O and CO_2 as co-reactants on CPOx by also resolving spatial concentration profiles. They found that feeding of H_2O as a co-reactant has no effect on conversion of CH_4, however, the selectivity is affected due to WGS. Maestri et al. [23] proposed that WGS is in equilibrium and the adsorbed OH species is the main oxygen source to form CO via adsorbed carbon generated by pyrolysis of methane. It was concluded that steam reforming (SR) and dry reforming (DR) of methane always occur with WGS and that the formation of CO_2 is mainly due to the dissociation of the carboxyl (COOH) species. Wang et al. [33] studied the WGS reaction over Rh/Al_2O_3 at 600 °C and 800 °C under vacuum by using a TAP (Temporal Analysis of Products) reactor. They concluded that CO_2 formation mainly occurs via fast oxidation of CO with adsorbed oxygen or via a nucleophilic attack of adsorbed OH groups on the alumina support, which has an inverse spill-over effect because the water can dissociatively adsorb on alumina by producing O(s) and OH(s) species; the suffix (s) denotes adsorbed species in this article. The isotopic tracer studies of Wei et al. show that H_2O dissociation is quasi-equilibrated, i.e., H(s) and OH(s) species recombine rapidly to form gas-phase hydrogen and water [32].

1.3. Reactors for kinetic studies

There are many different reactors used for kinetic studies; only few remarks will be made here. Despite their simplicity, kinetics derived from integral, tubular flow reactors containing powders, pellets, foams or honeycomb monoliths as catalysts are usually difficult to be interpreted on a mechanistic level because of the overlapping of mass and heat transfer in at least two dimensions with catalytic reactions. Gas-phase concentration and also temperature can strongly vary within a millimeter in radial and axial directions. Surface coverages may strongly vary as well in flow directions [22,28,35,36]. In modeling of these reactors, simplifying assumptions are usually made to describe the heat and mass transport effects [37,38]. These simplifications can be crucial in deriving the intrinsic kinetics as soon as parallel and/or sequential catalytic reactions as well as gas-phase reactions occur.

As an alternative to tubular flow reactors, the TAP reactor is used to investigate the reaction kinetics under isothermal conditions. The only transport process here is realized by Knudsen diffusion. However, the TAP reactor is usually operated under low-pressure with small amount of reactive mixtures [33,39].

The stagnation-flow reactor (SFR) (Fig. 1) is another useful concept to investigate catalytic kinetics. Even though the flow field of the entire reactor is two-dimensional (2D) with axial and radial spatial coordinate, a potential flow can be established leading to a one-dimensional (1D) boundary-layer over the catalyst [40,41]. Hence, the entire catalyst (except at the edges) is exposed to the identical gas-phase leading to no lateral variations of the catalyst surface coverage in general. A number of groups have studied catalytic kinetics in stagnation-flow reactors to better understand catalytic combustion [42–46], partial oxidation and steam reforming on noble metals [47–49] as well as diamond growth [50]. Recently, McGuire et al. [49] studied dry reforming of methane over Rh supported on strontium-substituted hexaaluminates. They used a microprobe sampling technique which enables a resolution of the concentration profiles in the gas-phase boundary-layer adjacent to the catalytic surface.