CO Methanation on Rh/Al₂O₃: Dynamic in-situ FTIR Experiments and Steady-State Measurements

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Introduction

It is commonly agreed that the dissociation of the C-O bond is the rate-limiting step for CO hydrogenation on supported Rh catalysts [1]; moreover, similar mechanism for CO and CO₂ hydrogenation has been proposed [1,2]. Less generally agreed upon is whether C-O bond cleavage occurs via the direct dissociation of adsorbed CO or through a H*-assisted process. The identity of the most abundant surface intermediates at steady-state reaction condition is also under discussion, thus, a full coverage with CO* contrast with the proposal in which the vacancies and H* (formed by the equilibrated dissociative adsorption of H₂) are also included into the site balance of a L-H model [1,3].

This work shows and discusses the results of dynamic isothermal in-situ FTIR experiments for CO+H₂ reaction on Rh/Al₂O₃ in light of the steady-state kinetic and FTIR measurements at similar reaction conditions and the proposed mechanism for this reaction.

Materials and Methods

The Rh catalysts were prepared by wet impregnation of pure γ-Al₂O₃ (Alfa Aesar, s₇₄/₄₇ = 72 m²/g). The solid was dried at 110°C overnight and later calcined in air at 700°C for 4h. The 1 wt.% Rh loading was confirmed by Atomic Absorption Spectroscopy by using a Hitachi Z-8100 spectrometer with Zeeman polarization. The amount of exposed Rh atoms was measured by irreversible hydrogen chemisorption at 30°C in a homemade volumetric adsorption instrument equipped with a DualGauge controller (TPG 262) and a sensor APR 260 (Pfeiffer Vacuum). H/Rh=1 stoichiometry was assumed to calculate the amount of exposed Rh atoms in the sample. Transmission infrared spectra of Rh/Al₂O₃ wafers were collected in-situ in a reactor cell placed in a FTIR spectrometer (Nicolet 6700, Thermo Scientific) at a resolution of 4 cm⁻¹ and 50 scans/spectrum within the 3500 – 1500 cm⁻¹ range. The IR cell is equipped with KBr windows, connections for inlet and outlet flows, and thermocouples for monitor and control the temperature. The spectra were obtained in absorbance mode after subtraction of the background spectrum of the catalyst disk under He atmosphere at the corresponding temperature. The samples were pretreated in pure H₂ at 280°C. After pretreatment, the catalyst surface was flushed with 100 ml/min of pure He, and the temperature was set to the study conditions. For dynamic assays, sample was firstly exposed to 100 mL/min of a 5kPa CO-He mixture until the steady-state condition was confirmed, then the gas was switched to 6kPa He, 20kPa He and 40kPa He mixtures and constant flow rate of 100mL/min. The integrated adsorption intensity of linear CO peak (at ~ 2045 cm⁻¹) was used to estimate the fractional coverage of Rh surface with CO*, by assuming a value of 3 for the ratio of linear to bridge CO surface concentration.

Results and Discussion

Steady-state kinetic measurements carried out at 200-300°C for CO hydrogenation to produce CH₄ on Rh/Al₂O₃ are consistent with a mechanism in which the quasi-equilibrated CO molecular and H₂ dissociative adsorptions are followed by the first H-addition (also a quasi-equilibrated step) to form HCO*. The C-O bond cleavage is assisted by a second H-addition to form CH²* and OH*. Finally, CH²* species are stepwise hydrogenated to form CH₄.

Fig.1 shows the effect of Pₗ₂ on CO coverage decreasing rate (Eq.1 and 2) for dynamic in-situ FTIR experiments carried out at similar reaction conditions than those of kinetic measurements.

\[
\frac{d\theta_{\text{CO}}}{dt} = k_{\text{ap}} \cdot \theta_{\text{CO}} \quad (1), \quad \text{where} \quad k_{\text{ap}} = k_{1} \cdot P_{\text{H}_2}^{n_{\text{H}_2}} \quad (2)
\]

In Eq.1, a first order on ϵ₃ has been assumed and k₁ in Eq.2 represents the rate constant for the first H* addition to the adsorbed CO* (CO* + H* → HCO* + *) after quasi-equilibrated CO and H₂ adsorptions. The value of k1 fairly close to 0.5 indicates that the step of HCO* formation controls the rate at which the CO* is consumed over the Rh surface in absence of CO in the gas phase. It is also confirms that the CO and H₂ adsorptions are quasi-equilibrated steps, as proposed from steady-state kinetic study at similar reaction conditions.

![Figure 1. In-situ FTIR data for dynamic CO hydrogenation on Rh/Al₂O₃ at 220°C, Pₗ₂ (0–40kPa).](image)

Significance

The work addresses the mechanism for CO methanation reaction on Rh/Al₂O₃ through the infrared screening of catalyst surface at reaction conditions. This information could be valuable for reactor design and operation.

References