

The Mechanism of Higher Oxygenate Synthesis over Supported Rh Catalysts

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Extensive mechanistic studies have shown that higher oxygenates are formed from the insertion of CO into adsorbed alkyl species that is generated from CO dissociation and partial hydrogenation. The reduced Rh surface is known to be responsible for the formation of alkyl species. However, little is known about the nature of the active sites for CO insertion on various promoted Rh catalysts that are active for higher oxygenate synthesis. *In situ* infrared spectroscopy reveals linear CO on the single reduced Rh site as the most active adsorbed CO species for CO insertion on Rh/SiO₂ and Cu-, Ag-, Ce-, and Mn-promoted Rh/SiO₂ catalysts. Tilted CO exhibiting a band below 1700 cm⁻¹ is identified as a spectator that does not participate in CO insertion. Increasing reaction pressure causes an increase in the residence time of alkyl intermediate allowing CO insertion to occur. The selectivity toward higher oxygenates can be improved by increasing the relative concentration of linear CO sites and by increasing reaction pressure.

INTRODUCTION

The catalytic synthesis of oxygenates from synthesis gas, i.e., CO/H₂, is an important route to the production of clean fuels and chemical feedstocks from indirect coal liquefaction (1-12). There are a considerable number of experimental studies on the mechanism of higher oxygenate synthesis on Rh/SiO₂ and Cs-Cu-ZnO catalysts. Mechanistic study on Cs-Cu-ZnO reveals that Cs promotes β addition between surface species resulting in an increase in selectivity toward 1-propanol and 2-methyl-1-propanol, the principal higher alcohol products (6,7). The Cs-Cu-ZnO catalyst is more active and selective toward methanol than higher alcohols (7). Promoted Rh catalysts have been found to exhibit selectivity up to 75% for the formation of C₂₊ oxygenates in the conditions ranging from 0.07 MPa to 10 MPa and 473-573 K (13). Although the reaction pathway and the nature of active sites for higher oxygenate formation on Rh/SiO₂ catalysts have been identified (13-16), the effect of promoter and support on the nature of active sites remains unclear.

At present, there is no satisfactory single step synthesis that permits economic production of higher oxygenates (17). An in-depth understanding of the mechanism is a key step toward rational design of selective catalysts for higher oxygenate synthesis and the development of a more selective route to higher oxygenates.

This paper reports the use of *in situ* infrared (IR) spectroscopy to investigate the nature of CO insertion sites and the residence time of intermediates involved for CO insertion on Cu-, Ag-, Ce-, and Mn-promoted Rh/SiO₂ catalysts. *In situ* characterization of reaction intermediates is essential for the development of a fundamental understanding of catalytic processes (18-20). *In situ* infrared spectroscopy has been one of the most important tools for studying the nature and structure of adsorbed species and its coverage on supported catalysts under reaction conditions (16,21-26). The structure of adsorbed species is closely related to the nature of the sites.

Investigation of the nature and reactivity of adsorbed species will provide information on the activity of sites to which the adsorbed species bonds.

EXPERIMENTAL

A 0.5 wt% Rh/SiO₂ was prepared by impregnation of SiO₂ (Strem, 350 m²/gm) with an aqueous solution of rhodium chloride. Cu-Rh/SiO₂ catalyst with 3 wt% Rh loading was prepared by coimpregnation of aqueous solutions of copper and rhodium nitrates with Cu to Rh molar ratio of 1.0. Ag-Rh/SiO₂ with Rh loading of 3 wt% was prepared by the coimpregnation of aqueous solutions of silver and rhodium nitrates with Ag to Rh molar ratio of 1.0. A Ce-Rh/SiO₂ catalyst with 5 wt% Rh loading and Ce to Rh molar ratio of 0.74 was prepared by coimpregnating the silica support with a mixture of rhodium chloride and cerium nitrate solutions. Mn-Rh/SiO₂ catalyst with 4 wt% Rh loading and Mn to Rh molar ratio of 0.1 was prepared by sequential impregnation of manganese nitrate and rhodium chloride solutions. The ratio of solution to the support material used was 1 ml to 1 gm. After impregnation the catalyst samples were dried in air at 303 K and then reduced in flowing hydrogen at 673 K for 16 hr. The reduced catalysts were pressed into a self-supporting disk and then placed in the IR cell for *in situ* studies.

CO adsorption and the reaction of preadsorbed CO with C₂H₄ and H₂ were carried out in an infrared (IR) reactor cell. The IR cell can be operated at temperatures up to 723 K and at a pressure of 6.0 MPa (16). Infrared spectra were measured by a FTIR spectrometer with a DTGS detector at a resolution of 4 cm⁻¹. CO adsorption was conducted by exposing the catalyst to 0.1 MPa of CO at 303 K. Gaseous CO was removed by flowing helium. The infrared spectra of adsorbed CO were recorded at 0.1 MPa of CO or He. The reactivity of the adsorbed CO for CO insertion was investigated by introducing C₂H₄/H₂ (molar ratio of C₂H₄:H₂ = 1:1) to the adsorbed CO in the IR cell that served as a batch reactor. The infrared spectra of adsorbed CO and intermediates during the reaction were measured as a function of reaction time.

RESULTS AND DISCUSSION

It has been proposed that the formation of C₂₊ oxygenates over Rh-based and IFP catalysts involves the insertion of CO into adsorbed C_nH_x that is produced from CO dissociation and hydrogenation as shown in Fig. 1 (12-16,27-29). Higher alcohols such as ethanol can be produced from either the hydrogenation of acetaldehyde or direct hydrogenation of acyl species. A high selectivity (up to 75% carbon efficiency) has been achieved on promoted Rh catalysts at 573 K and 10 MPa (3,29). The selectivity can be compared to the maximum selectivity of 25% for C₂ products predicted by Anderson-Schulz-Flory distribution (29). The reaction pathway in Fig. 1 also suggests that CH₄ and C₂₊ oxygenates are produced from the same C₁ precursor, i.e., CH_x. Thus, it has been suggested that C₂₊ oxygenates should be viewed as C₁ compounds in Anderson-Schulz-Flory distribution that could, in principle, be produced with 100% selectivity (29). However, high hydrogenation activity of Rh catalyst and thermodynamically favorable formation of CH₄ usually lead to a substantial yield of CH₄. The challenge is how to suppress hydrogenation and enhance CO insertion in higher oxygenate synthesis.

The nature of active sites for CO hydrogenation has been a subject of extensive studies (13-16,27-29). It is generally agreed that CH_x is formed from CO dissociation followed by hydrogenation on the reduced Rh sites. However, the number of surface atoms (i.e., the size of ensemble) required for CO dissociation remains unclear.

Much controversy has existed on the nature of the active site for CO insertion on Rh catalysts for more than a decade (16). Since CO insertion is a key step toward the formation of

higher oxygenates, clarification of CO insertion sites is essential for the development of a comprehensive mechanism for C_2 oxygenates synthesis. Recently, we have employed ethylene hydroformylation as a probe reaction to determine the nature of active sites for CO insertion on the Rh catalysts. In ethylene hydroformylation, ethylene is hydrogenated to adsorbed ethyl species that may undergo CO insertion leading to the formation of propionaldehyde; adsorbed ethyl species can also be hydrogenated to ethane as shown in Fig. 2 (16,27). CO insertion into adsorbed ethyl species is analogous to CO insertion into CH_x species. Investigation of CO insertion into adsorbed ethyl species produced from C_2H_4 and H_2 provides direct information for elucidation of CO insertion sites without the complication resulting from CO dissociation and hydrogenation.

Our previous study on the reactivity of adsorbed CO on a reduced 3 wt% Rh/SiO₂ reveals that the linear CO adsorbed on a single Rh site is involved in CO insertion leading to the formation of propionaldehyde (16). Bridged CO and gem-dicarbonyl CO exhibit little reactivity towards CO insertion. Similar studies were conducted on the oxidized Rh/SiO₂ catalysts and showed that single Rh⁺ sites are more active for CO insertion than the single Rh⁰ sites (16). However, Rh⁺ sites are not able to withstand the reducing atmosphere of CO/H₂ above 393 K.

The high activity of linear CO sites and the lack of activity of bridged CO sites has led to preparation of supported Rh catalysts containing primarily linear CO sites. Adsorbed sulfur blocked the bridged CO sites, increasing the concentration of linear CO sites resulting in an increase in CO insertion selectivity and activity. Low-loading supported Rh catalyst contains highly dispersed Rh crystallite. Highly dispersed Rh which contains primarily single Rh sites may chemisorb linear CO. In contrast, CO adsorption on the 0.5 wt% Rh/SiO₂ produced bands at 2027 and 2004 cm⁻¹ that can be assigned to weakly adsorbed Rh(CO)₄ as shown in Fig. 3 (30). The intensity of the bands decreased in flowing helium suggesting that the species was weakly adsorbed. The exposure of this adsorbed CO to ethylene and hydrogen did not result in any reaction at 303 K. CO adsorption at 323 K also produced weakly adsorbed Rh(CO)₄ bands at 2027 and 2004 cm⁻¹ similar to those observed at 303 K. Exposure of adsorbed CO to ethylene and hydrogen at 323 K produced a propionaldehyde band at 1708 cm⁻¹ after approximately 20 min of reaction. An increase in the amount of propionaldehyde formed is shown by the increase in the intensity of the adsorbed band with time as observed in Fig. 3. An increase in the hydrocarbon band near 2983 cm⁻¹ is also observed with reaction time. The simultaneous formation of propionaldehyde and ethane indicates that CO insertion into adsorbed ethyl species competes with ethylene hydrogenation.

CO adsorption on a Cu-Rh/SiO₂ catalyst produced a linear CO band at 2058 cm⁻¹, a bridged CO band at 1875 cm⁻¹, and gem-dicarbonyl bands at 2091 and 2027 cm⁻¹ as shown in Fig. 4. A band at 2127 cm⁻¹ assigned to CO adsorbed on Cu is also observed. Reaction of C_2H_4 and H_2 with adsorbed CO on Cu-Rh/SiO₂ catalyst shows the formation of propionaldehyde 1 min after addition of the reactants. A decrease in the bands at 2127 cm⁻¹ and 2058 cm⁻¹ and the formation of propionaldehyde indicates that the linear CO on Rh and CO adsorbed on Cu participate in CO insertion into the adsorbed ethylene. The rate of propionaldehyde formation is much faster on the Cu-Rh/SiO₂ catalyst in comparison to the highly dispersed Rh/SiO₂ catalyst. A decrease in intensity was observed in the gem-dicarbonyl bands after approximately 10 min of reaction with the simultaneous formation of ethane at 2983 cm⁻¹ and a small amount of CO₂ at 2341 cm⁻¹. Thus, the addition of Cu appears to increase the rate of CO insertion as indicated by the higher rate of formation of propionaldehyde on the Cu-Rh/SiO₂ catalyst as compared to the dispersed Rh/SiO₂ catalyst.

CO adsorption on Ce-Rh/SiO₂ produced linear CO band at 2048 cm⁻¹, bridged CO band at 1857 cm⁻¹, gem-dicarbonyl bands at 2090 and 2027 cm⁻¹, and a tilted CO at 1766 cm⁻¹. CO

adsorption on Mn-Rh/SiO₂ produced linear CO band at 2040 cm⁻¹, bridged CO at 1835 cm⁻¹, weakly adsorbed gem-dicarbonyl band at 2090 cm⁻¹, and a tilted CO band at 1670 cm⁻¹. CO adsorption on Ag-Rh/SiO₂ produced linear CO band at 2072 cm⁻¹, a weak bridged CO band at 1879 cm⁻¹, and gem-dicarbonyl bands at 2095 and 2030 cm⁻¹.

The linear CO was found to be active for CO insertion. There is no obvious correlation between the wavenumber of linear CO and its CO insertion reactivity. The tilted CO that has been suggested to be highly active for CO insertion is in fact a spectator that does not participate in the reaction.

In conclusion, linear CO site is active for CO insertion. The selectivity toward higher oxygenates can be improved by increasing the relative concentration of linear CO sites and increasing reaction pressure.

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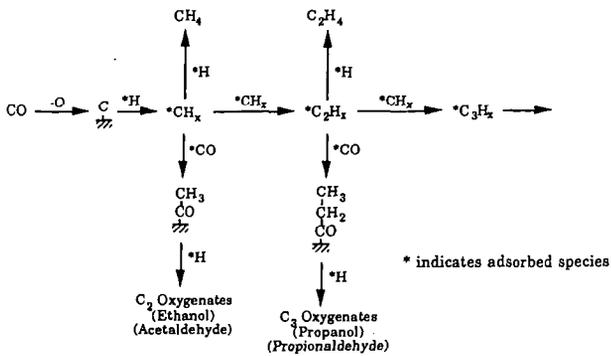


Figure 1. Reaction pathway for higher oxygenates synthesis on Rh- and IFP-based catalysts.

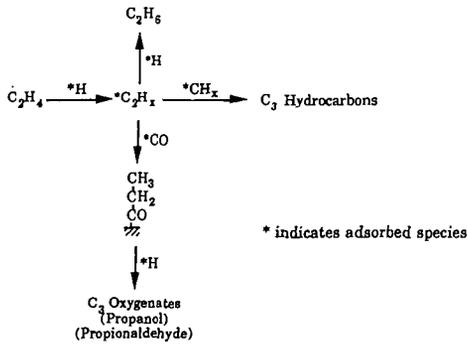


Figure 2. Reaction pathway for ethylene hydroformylation.

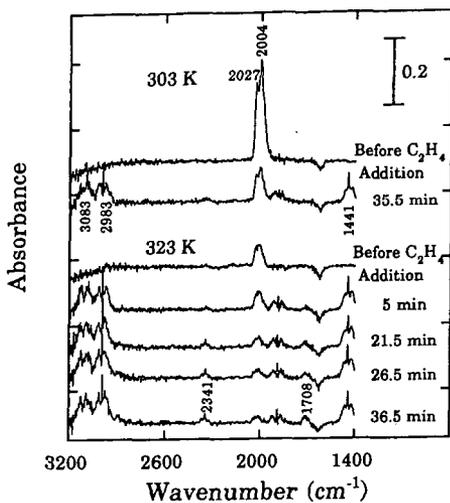


Figure 3. C₂H₄/H₂ addition to CO (ads.) on 0.5% Rh/SiO₂

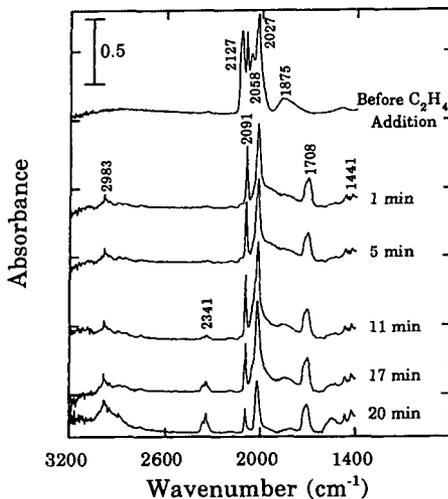


Figure 4. C₂H₄/H₂ addition to CO (ads.) on Cu-Rh(1:1)/SiO₂