

Mechanistic study of ethylene hydroformylation over Rh/Al₂O₃ under reaction conditions by time resolved FTIR spectroscopy

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Introduction

Hydroformylation or oxo synthesis is an important industrial process in which an alkene reacts with CO in the presence of hydrogen to produce aldehydes [1-3]. Development of a viable heterogeneous catalytic path for hydroformylation remains a critical challenge. The understanding of the kinetics and mechanism of hydroformylation is of paramount interest to attain high product selectivity as well as to design efficient catalysts [2-3]. However, there are currently no reports on the observation of transient reaction intermediates of heterogeneous hydroformylation under reaction conditions. Time resolved FTIR spectroscopic technique in the millisecond regime has been successfully used to detect kinetically relevant transient species in important heterogeneous catalytic reactions such as hydrogenation of CO, ethylene and propylene in our group [4]. We report here millisecond FTIR spectroscopic investigation of ethylene hydroformylation over Rh/Al₂O₃ catalyst at 443 K, resulting in the direct observation of growth and reaction of surface propionyl intermediate for the first time.

Materials and Methods

Time resolved spectroscopic (TRS) studies of heterogeneous ethylene hydroformylation were conducted in a Bruker IFS 88 FTIR spectrometer containing a stainless steel catalytic reactor cell fitted with CaF₂ windows. The ambient pressure-continuous-flow reactor could be operated between 298-823 K. The Rh/Al₂O₃ catalyst (Alfa Aesar, 5 wt% Rh) was mounted at the center of the reactor cell in the form of a self supporting pellet for transmission infrared spectroscopy. In the present studies, Time-resolved FTIR spectroscopy at millisecond resolution by rapid-scan technique was achieved using a continuous flow of an H₂/N₂ mixture (4.8 L/min, ratio 0.067) over Rh/Al₂O₃ catalyst while injecting 250 ms pulses of CO or C₂H₄ or CO+C₂H₄ or ¹³CO+C₂H₄ through a fast mechanical valve (Iota one valve). The reactant pulses were synchronized with the recording of rapid-scan FTIR spectra by utilizing forward motion of the interferometer mirror signal [5].

Results and Discussion

The ethylene hydroformylation reaction with CO over alumina-supported Rhodium catalyst (Rh/Al₂O₃) has been studied by *in-situ* FTIR time resolved spectroscopy (TRS) on the millisecond time-scale (128-12032 ms) at 443 K. In order to understand the mechanism of hydroformylation, prior to the initiation of CO+C₂H₄ reaction, the hydrogenation reactions of CO and C₂H₄ were also conducted separately. The single component reaction of CO in the presence of H₂ over Rh/Al₂O₃ catalyst lead to linearly adsorbed CO (2067 cm⁻¹), bridge-bonded CO (1864 cm⁻¹) and trace amounts of carbonates (1655, 1420, 1356 and 1229 cm⁻¹) at t=128 ms while formate (1608 and 1378 cm⁻¹), bicarbonate (1483 cm⁻¹) methoxy/methanol (2953, 2898, 2846, 2819, 1092 cm⁻¹) species were also observed after 832 ms. Similarly, the single

component reaction of C₂H₄ mainly showed the formation of ethane (2893 and 2878 cm⁻¹) and small amounts of surface ethylidyne (Rh₃CCH₃; 2878 and 1337 cm⁻¹) species at t=128 ms.

The time-resolved infrared spectra of CO+C₂H₄ hydroformylation reaction over Rh/Al₂O₃ at 443 K revealed primarily the appearance of a band in the t=384 ms spectra at 1675 cm⁻¹ assigned to surface propionyl (Rh-CO-C₂H₅) species. The intensity of propionyl band at 1675 cm⁻¹ increased to maximum at t=3072 ms and decreased subsequently with the formation of propionaldehyde (1737 and 2718 cm⁻¹) by hydrogenation. The formation of propionyl species and propionaldehyde was further confirmed by ¹³CO+C₂H₄ studies in which 1675 and 1737 cm⁻¹ bands appropriately shifted to 1636 and 1696 cm⁻¹, respectively. In the CO+C₂H₄ reaction at 443 K, no ethane product was observed, in contrast to the single component reaction of C₂H₄ with H₂ over Rh/Al₂O₃. Clearly, hydroformylation overwhelms ethane formation in the presence of CO. On the other hand, transient spectra of the hydroformylation reaction showed the emergence of new bands corresponding to surface ethyl species (at 2876, 2855 and 1182 cm⁻¹) at t=128 ms, which disappeared by 3072 ms. Furthermore, data show that the formation of surface propionyl intermediate (Rh-COC₂H₅) might be due to the direct interaction of the surface ethyl group with the neighboring adsorbed carbon monoxide. The rate of formation of propionyl intermediates is very likely limited by the formation of surface ethyl species as indicated by the fact that the intensity of the 1675 cm⁻¹ band started to decrease only when there was no surface ethyl intermediate present. As expected, the disappearance of the propionyl species was found to be correlated to the appearance of the propionaldehyde product.

Significance

Hydroformylation of alkenes by CO has wide-ranging applications in industrial processes to prepare linear, branched and chiral aldehydes and their subsequent hydrogenation to alcohols. Yet, the use of heterogeneous catalysis for these processes has remained limited. The study of the kinetics and mechanism of the hydroformylation process over supported metal catalyst is the key for understanding the specific reaction steps. In particular, it sheds light on the product branching between complete hydrogenation of the alkene to alkane versus CO insertion into surface alkyl intermediates. We find that in the case of the system studied here that hydroformylation quantitatively replaces hydrogenation over supported Rh catalyst. Furthermore, by temporally resolving both growth and reaction of the surface propionyl intermediate, kinetic insight into the rate limiting aldehyde formation step as well as the preceding fast reaction step is achieved. Expanding the time resolution to the microsecond regime will open up more detailed insight into the mechanism of the CO addition step.

References

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