Direct observation of surface ethyl growth kinetics upon hydrogenation of C_2H_4 on Rh/Al_2O_3 by step-scan FT-IR spectroscopy

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Introduction and Objectives

Time resolved FT-IR spectroscopy has recently allowed the detection and kinetic study of reaction intermediates of heterogeneous catalysis under reaction conditions. Specifically, monitoring of transient ethyl and propionyl species upon ethylene hydroformylation over supported Rh nanocatalyst surfaces [1], or of C_2H_5-Pt during ethylene hydrogenation over mesoporous silica supported Pt nanoparticles [2] have provided the first insights into the dynamics of elementary steps by a structure specific, vibrational spectroscopy. The millisecond temporal resolution of the rapid scan method is adequate for observing the kinetics of key reaction steps, yet important elementary processes such as the hydrogenation of surface ethylene (π-C_2H_4) to ethyl are too fast for this method. Here, the step-scan technique which allows time resolution from milliseconds to nanoseconds is required. The goal of the present work is to kinetically resolve the rise of surface ethyl intermediate over supported Rh nanocatalyst and, more generally, expand *in-situ* FT-IR spectroscopic methods for monitoring heterogeneous catalysis to microsecond regime.

Results and Discussion

A 20 ms ethylene gas pulse (20 psi back pressure) was released into a continuous gas flow of H_2 (300 mL/min) and N_2 (4.5 L/min, 1 atm). The Rh/Al_2O_3 catalyst was held at 295 K. Acquisition of step-scan data was initiated at the end of the 20 ms gas pulse, and 700 time slices at 100 microsecond intervals were collected. The results of up to 60 such experiments were averaged for S/N improvement. Using under-sampling in order to hold the interferogram measurement time in practical limits, spectra were collected in 1400-1100 cm^{-1} region where the intense wagging mode of surface ethyl species is known to absorb (in rapid scan experiments, a broad band in the range 1240 cm^{-1}-

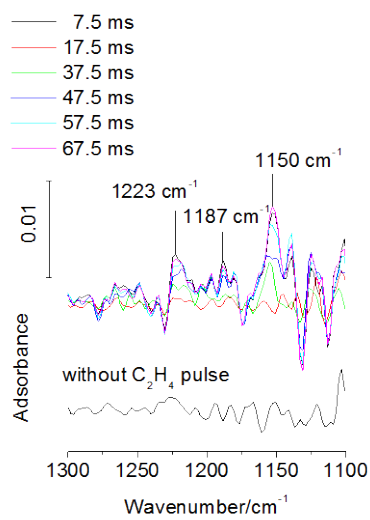

Figure 1. The Step-Scan FTIR spectra in 1300-1100 cm^{-1} region observed following the initiation of C_2H_4 + H_2 catalysis at 298 K. The bottom trace shows a time slice of a control experiment without C_2H_4 gas pulse.

1160 cm^{-1} is observed [1]). As shown in the spectral time slices of Figure 1, three peaks, 1223 cm^{-1}, 1187 cm^{-1} and 1150 cm^{-1} grow in this region. We attribute these bands to surface ethyl groups, C_2H_5Rh, in different local environments. The growth of the 1223 cm^{-1} site is shown in Figure 2. A first order fit indicates a rise time of 64 ms. The growth kinetics varies appreciable for the three sites: A rise time of 38 ms was determined for the 1187 cm^{-1} band, while the 1150 cm^{-1} peak showed a rise time of 58 ms. The spread of the growth kinetics is consistent with the assignment of the sites to different local environments in terms of surface H and ethylene species.

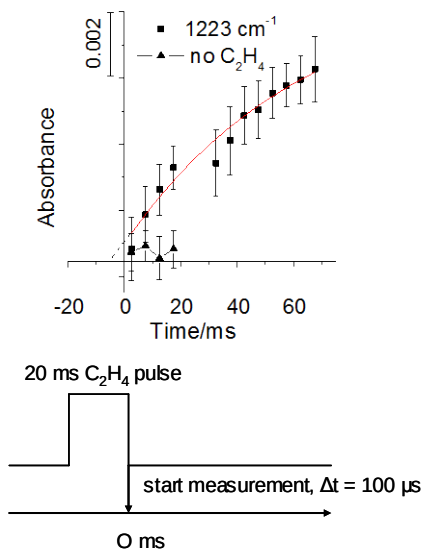

Figure 2. Growth kinetics of the surface C_2H_5-Rh site at 1223 cm^{-1}.

In order to monitor elementary steps of heterogeneous catalysis on the early microsecond time scale, we are developing a method that initiates catalysis with a nanosecond laser pulse for heating of the metal nanoparticle catalyst coupled with step-scan FT-IR monitoring. The laser heating pulse generates hot electrons and lattice vibrations that may activate adsorbed reactants or intermediates. In order to maximize reactant surface coverage prior to arrival of the laser heating pulse, the latter is preceded by a gas pulse from a fast valve for reactant loading (two pulse method). Recent results with this method using hydrogenation of ethylene over supported Rh/Al_2O_3 nanoparticles will be presented.

Summary

In summary, we used step-scan FT-IR spectroscopy to monitor the growth kinetics of the initial elementary step of ethylene hydrogenation over a metal nanoparticle catalyst for the first time. Distinct sites of surface ethyl were observed, each exhibiting different kinetics consistent with variations in the local surface environment. Experiments are in progress to exploit laser pulse heating of metal nanoparticles coupled with step-scan monitoring for resolving heterogeneous catalytic processes on the early microsecond time scale.

References

[1] N. Sivasankar and H. Frei. *J. Phys. Chem. C* **115**, 7545-7553 (2011).

[2] W. Wasylenko and H. Frei. *J. Phys. Chem. B* **109**, 16873-16878 (2005).