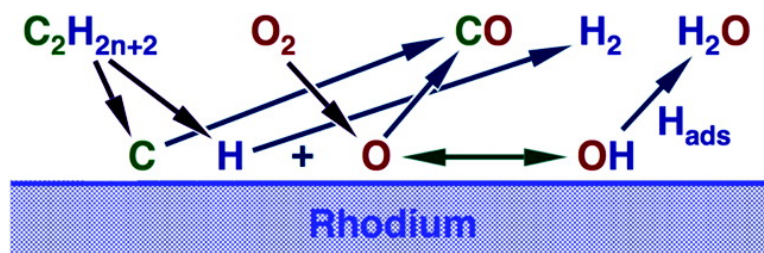# J|A|C|S
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Kinetics and Mechanism of Catalytic Partial Oxidation Reactions of Alkanes on Rhodium Surfaces

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Typically, the oxidation of alkanes leads to the production of carbon dioxide and water, the most thermodynamically favored products. Nevertheless, it has been shown that, by using a metal catalysts and relatively high (~1000 K) temperatures, it may be possible to control that oxidation to produce a more desirable carbon monoxide + hydrogen (syngas) mixture.[1−3] In fact, processes with short contact times between the catalyst and the reaction mixture, which may be achieved by using high space velocities, short catalyst beds, and/or new reactor designs, have been shown to enhance hydrogen production.[3−9] However, optimization of the selectivity of these processes has been hampered by the limited understanding presently available on the kinetics of the reactions involved. Two main mechanisms have been proposed, a direct partial oxidation to H_2 and CO and the total combustion to H_2O and CO_2 followed by reforming back to the desired syngas,[10−15] and the resolution between the two is still ongoing. The fact that oxidations are fast exothermic reactions, together with heat and mass transport issues, has hindered the extraction of elementary step information from experiments.[15,16] Here we report on studies using molecular beams on single crystals aimed at obtaining direct information on the kinetics of these surface reactions. Interestingly, both hydrogen and water (but not carbon dioxide) were found to be products of primary reactions on rhodium substrates. The selectivity between the two was found to depend on the conditions used to carry out the reaction.

The experiments reported herein were carried out in an ultrahigh vacuum (UHV) apparatus described previously.[17−20] A Rh(111) single crystal was mounted on a manipulator capable of liquid-nitrogen cooling and resistive heating to any temperature between 100 and 1200 K, as set by a homemade temperature controller and monitored by a chromel-alumel thermocouple spot-welded to the back side of the crystal. The surface was cleaned before each experiment by sequential Ar^+ sputtering, heating in 1×10^{-7} Torr of O_2, and annealing at 1200 K. The kinetic experiments were carried out by following a variation of the so-called King and Wells method where the front surface of the crystal is exposed to an effusive molecular beam of the desired premixed alkane + oxygen gas generated by a multichannel microcapillary array doser.[18,19] The rates of evolution of all reactants and products are followed versus time by mass spectrometry while maintaining the crystal at the desired temperature. Conversion of the raw signals to rates is carried out by following established procedures.[17,20] The gases, Ar (Liquid Carbonic 99.999%), O_2 (Nellcor Purtain Bernett, 99.5%), and i-C_4H_{10} (Matheson, >99.9%), were all used as provided.

Figure 1 displays typical results from these studies, in this case for a 2:1 i-C_4H_{10}/O_2 mixture impinging on the Rh(111) surface while holding its temperature constant at 940 K (total gas flux = 1.2 ML s^{-1}). A number of observations derive from these data, in particular: (1) the production of H_2, H_2O, and CO, but not of CO_2; (2) a sharp transient within the first 2−3 s of reaction characterized by an excess uptake of O_2 and a spike in the production of H_2; and (3) a fast attainment of a steady-state condition by all compounds but water,
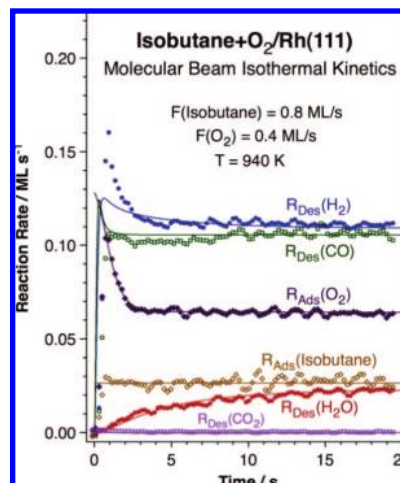

Figure 1. Kinetic data for the conversion of a 2:1 isobutane/oxygen mixture on a Rh(111) surface at 940 K. Shown are the rates for the uptake of both oxygen and the alkane as well as for the production of hydrogen, water, carbon monoxide, and carbon dioxide, both the experimental data (dots) and the results from kinetic modeling (solid lines). All but CO_2 are produced in this process, even if the evolution of water reaches its final steady-state rate slowly over time.

the rate of which raises more slowly, over a period of ~20 s. It should be emphasized that since these experiments were carried out under vacuum and by using a low-surface-area single-crystal sample, they are void of any mass or heat transfer problems and directly reflect the kinetics of the reactions occurring upon a single collision of the reactants with the surface.

A simple mechanism was used to help interpret the kinetic data involving the rapid dissociative adsorption of both O_2 and the alkane, the reversible recombination of surface atomic oxygen back to the gas phase, the rapid recombination of surface carbon with oxygen to produce CO, and the stepwise formation of H_2O via a hydroxo surface intermediate. The results from this modeling are reported as solid lines in Figure 1, with more details provided in the Supporting Information. This model is quite simplistic and cannot reproduce all the data, in particular some of the transient behavior, but does highlight a few of the key features of the alkane partial oxidation reaction. For one, it explains the sharp transient in the uptake of O_2 as the consequence of a buildup of a steady-state concentration of atomic oxygen on the surface before reaching equilibrium with the reverse oxygen recombination. In fact, a similar spike is seen in kinetic studies with O_2 beams alone (data not shown). This uptake has already been well documented.[21,22]

Our kinetic mechanism also explains the slow initial production of water. That is simply the reflection of the kinetics of formation and subsequent conversion of hydroxo intermediates on the surface. In this model, the rate of OH(ads) formation from recombination of oxygen and hydrogen surface atoms defines the ultimate yield
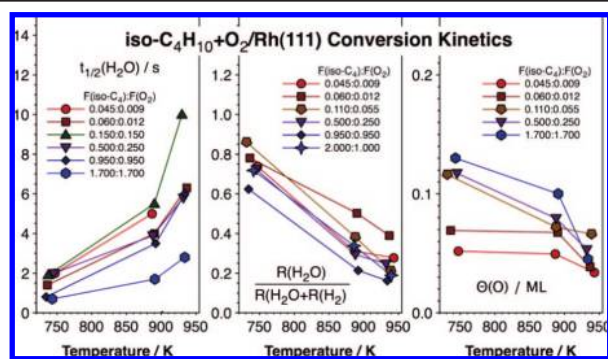
Figure 2. Half-life time for water to reach its steady state ($t_{1/2}(H_2O)$, left), fraction of water produced ($S(H_2O)=R(H_2O)/[R(H_2O)+R(H_2)]$, center), and steady-state oxygen surface coverage ($\Theta(O)$, right), all estimated from isothermal kinetic experiments such as that in Figure 1 carried out at different temperatures and gas compositions. A general increase in $t_{1/2}(H_2O)$ and decreases in $S(H_2O)$ and $\Theta(O)$ are seen as the reaction temperature is increased. The changes induced by variations in the gas composition are subtler, but a clear proportionality is seen between the $\Theta(O)$ and the flux of O_2 at low temperatures.

of water, whereas the rate of reaction of those OH intermediates with additional hydrogen controls the time it takes for water production to reach its steady state. In the simulations the rates of both steps are typically comparable in magnitude, so a significant ($\sim$0.1 ML) coverage of OH(ads) builds up on the surface. The role of OH surface groups has certainly been discussed in the past,[23,24] but our results highlight the fact that they are intermediates in the network of the primary reactions that take place after adsorption of O_2 and the alkane.

Further details of the kinetics of these alkane partial oxidation reactions were obtained by carrying out experiments at different surface temperatures and with various gas compositions and fluxes. Some of the resulting data, specifically the half-life time for water production to reach its steady state ($t_{1/2}(H_2O)$), the selectivity for water production over hydrogen ($S(H_2O)$), and the steady-state coverage of atomic oxygen on the surface (Θ_O), are summarized in Figure 2. Although Θ_O, estimated by integration of the initial spike in the uptake of O_2, clearly scales with the flux of oxygen in the beam, especially at the lower temperatures, the other two parameters do not exhibit a strong dependence on gas composition or total flux. The main effects are seen as a function of reaction temperature. It is seen that the steady-state coverage of oxygen decreases with temperature, a straight consequence of the fact that atomic oxygen recombination to O_2 is activated whereas the reverse dissociative adsorption of O_2 is not. The selectivity for water production also decreases with increasing temperature, suggesting that the activation energy for hydrogen recombination to H_2 may be larger than that for OH(ads) formation. Perhaps more surprising is the increase in $t_{1/2}(H_2O)$ with temperature. This points to a more significant contribution of the reverse OH(ads) dissociation step in the overall kinetics at higher temperatures, an effect not included in our model. Also missing from our model is an explanation for the spikes in hydrogen production seen within the first couple of seconds of the reaction (see above), which may be due to an effect exerted by coadsorbed oxygen on the rate of hydrogen recombination.

In summary, our results demonstrate the primary nature of the steps responsible for the formation of both H_2 and H_2O in the partial oxidation of alkanes on rhodium surfaces. Here we report on results for isobutane, but similar qualitative behavior has also been seen in preliminary experiments with methane, propane, n-butane, and n-hexane. It was found that although water production stems directly from the conversion of the alkane with oxygen on the rhodium surface, it proceeds via the formation of a hydroxo surface intermediate and can be minimized at higher temperatures. It was also noted that under no circumstances carbon dioxide production was detected in these molecular beam experiments. This is due to the fact that carbon monoxide desorbs rapidly after formation, before it has time to react with surface oxygen; that behavior has already been shown in molecular beam experiments on clean and oxygen-precovered Rh(111) surfaces.[19,25] CO_2 formation has been seen on Pt(111) under similar molecular-beam conditions,[26] suggesting that it could also occur in catalytic alkane oxidation processes with real catalysts containing that metal. It is hoped that the insight into the kinetics of partial oxidation reactions reported here will be incorporated into more complete mechanistic models to settle the questions remaining on these systems and to be able to design better processes for the direct production of hydrogen from natural gas and other hydrocarbon sources.

Supporting Information Available: Details of the mechanism used to simulate the kinetic data in Figure 1 and kinetic parameters from simulations of the runs in Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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