

there is an enormous variation in rate.

We have attempted to model the variations. The model is based on the previous work of Woodward and Hoffmann,⁵ who showed that one can identify especially active reaction pathways in reactions of organic and simple inorganic molecules by examining the symmetry of the orbitals available for reaction. In general, it has been found that a reaction is fast, if the orbitals of the right symmetry are present, while it is slow if they are absent.

Banholzer *et al.*³ examined the reaction $\text{NO}_{(\text{ad})} \rightarrow \text{N}_{(\text{ad})} + \text{O}_{(\text{ad})}$ in detail and noted that the availability of the antibonding orbitals needed to break the π bond in the NO varies significantly from face to face. Figure 1 also shows the site average orbital availability calculated as a function of crystal face. One observes that on Pt(111) there are no orbitals of the right symmetry available for reaction while on Pt(410) all the necessary orbitals are present. There is a continuous variation in the orbital availability for faces in between.

A comparison of the data and the calculations shows that the orbital availability is a good indicator of the catalytic activity. The rate is low when the orbital availability is low and high when the orbital availability is high. The magnitude of the effect is enormous. The changes in orbital avail-

ability explain why Pt(210) is less active than Pt(410) and why Pt(511) is less active than Pt(100). Neither of these observations is easily explained by previous models. Clearly, the orbital availability is not the only effect; Pt(210), for instance, is slightly more active than Pt(100) even though the orbital availabilities of the two faces are the same. However, the effects of changes in the orbital availability explains much of the data. These effects need to be more extensively explored.

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Summary Abstract: Comparative studies of alkane activation by low-index surfaces of iridium and platinum^{a)}

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The interaction of alkanes with low-index surfaces of iridium at low temperatures and pressures has been studied in our laboratory by thermal desorption mass spectrometry and low-energy electron diffraction.^{1,2} While the reconstructed (110)-(1×2) surface of iridium initiates dissociative chemisorption of ethane and all higher alkanes at 125 K in the low coverage limit, similar reactions with the close-packed (111) surface occur readily only at defect sites.¹ Thus, surface geometry influences strongly the activation barriers to C-H bond scission in alkanes on iridium surfaces.

Likewise on the Pt(111) surface, normal alkanes which desorb molecularly below 250 K do not adsorb dissociatively under similar conditions.³ On the other hand, both *n*-butane and *n*-pentane are observed to adsorb dissociatively on the Pt(110)-(1×2) surface. This demonstrates that the surface structure sensitivity of alkane activation, which was observed on iridium surfaces, occurs also on platinum surfaces.

Low exposures (< 0.5 L) of *n*-butane and *n*-pentane adsorb dissociatively on Pt(110)-(1×2) with a threshold temperature of approximately 200 K. The hydrocarbon fragments which form evolve hydrogen which is manifest as thermal desorption features at approximately 300, 400, and 550 K. At higher exposures, molecular desorption of the

parent alkanes is observed at 200 K for *n*-butane and 230 K for *n*-pentane. No hydrocarbons other than the parent alkane which was adsorbed are observed in the thermal desorption spectra. The hydrogen feature at 300 K appears to arise from the desorption of hydrogen bound to the platinum surface, while the features at approximately 400 and 550 K are a consequence of the decomposition of hydrocarbon fragments adsorbed on the surface. Saturation coverages of the dissociatively adsorbed alkanes, after adsorption at 150 K, in units of 10^{13} molecules cm^{-2} , are 4.0 ± 0.4 for *n*-butane and 5.0 ± 0.5 for *n*-pentane, based on the known coverage of hydrogen at saturation reported by Jackman *et al.*,⁴ namely 1.1×10^{15} atoms cm^{-2} . During these thermal desorption measurements, no loss of intensity of the half-order LEED beams is observed, demonstrating that the reconstruction of Pt(110) is not relaxed by alkane adsorption.

The dissociative adsorption of *n*-butane can be inhibited by preadsorption of hydrogen. The extent of inhibition is linear in precoverage of hydrogen, and is complete after a preexposure of 0.5 L of hydrogen. Furthermore, if 0.5 L of hydrogen is exposed to the surface after the adsorption of *n*-butane at 150 K, then the dissociative adsorption of the *n*-butane is inhibited completely. However, if the adlayer of *n*-

butane is annealed to 200 K, then exposure of hydrogen has no inhibiting effect on dissociative adsorption. This threshold temperature for dissociative adsorption of 200 K implies an activation energy of approximately 12 kcal/mol. This is consistent with the observed absence of dissociative adsorption for propane, for which only molecular desorption is observed at 170 K.

The Pt(110)-(1×2) surface activates alkanes at low temperatures (~200 K) and pressures, although this activation is not so effective as that observed on the same surface of iridium. On iridium the threshold temperature for dissociative adsorption is only 125 K, and somewhat higher saturation coverages of dissociatively adsorbed overlayers are observed. While differences in the details of the reaction chemistry are manifestations of electronic structural differ-

ences between the metals, for both metals the availability of high coordination adsites appears to lower the kinetic barriers that must be overcome to activate carbon-hydrogen bonds in alkanes.

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Summary Abstract: A molecular beam study of the dissociative adsorption of CO₂ on Ni(100)

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A supersonic molecular beam system was used to study the dynamical characteristics of the dissociative adsorption of CO₂ on Ni(100). CO₂ dissociated into adsorbed CO and O. The dissociative sticking probability s_0 was increased by two orders of magnitude by increasing the translational kinetic energy of the CO₂ by a factor of slightly more than 12. The addition of vibrational energy also increased s_0 . Small amounts of oxygen completely poisoned the dissociation. The results also indicated that in addition to a direct activated route CO₂ could dissociate through a molecularly adsorbed state.

A brief description of the reactive scattering apparatus will be given; for a more detailed description see Ref. 1. The reactive scattering apparatus was equipped with low energy electron diffraction (LEED)/Auger electron spectroscopy

(AES) optics, an ion gun for Ar sputtering, and two mass spectrometers. The mass spectrometers were used to determine beam energies and fluxes and for temperature programmed desorption (TPD) studies. The scattering chamber was pumped by a 1500 l/s turbomolecular pump, a 220 l/s vac-ion pump, and a titanium sublimation pump.

The supersonic molecular beam source could deliver up to 10^{15} molecules/cm²/s to the sample. The duration of the beam dose was controlled by an electronically operated shutter, which intercepted the beam outside the scattering chamber. The kinetic energies of the CO₂ beam ranged from 1.8 to 30 kcal/mol. The beam energies were obtained by varying the temperature of the nozzle and by seeding He and H₂ beams with CO₂ (the lighter molecules accelerate the heavier CO₂ molecules).²

Subsequent to exposure of the surface to CO₂ at a surface temperature of 400 K, CO was desorbed by TPD in the range of 450 to 470 K ($\theta_{\text{CO}} < 0.03$ monolayer) and oxygen remained on the surface as determined by AES. This allowed the use of CO TPD to measure the number of CO₂ molecules dissociating. TPD data were calibrated with a saturation dose of CO at room temperature ($\theta_{\text{sat}} = 0.55$ monolayer).³ To test this procedure the initial sticking probability of CO on Ni(100) was determined to be approximately 0.9 at two kinetic energies. The value is in good agreement with a previous determination of approximately unity.⁴

The data (Fig. 1) for the room temperature nozzle showed a 300-fold increase in s_0 with the CO₂ beam energy. At low beam energies s_0 was 10^{-4} , it then increased slowly to 0.02 at a beam energy of ≈ 9 kcal/mol and finally rose moderately to 0.13 at 25 kcal/mol. In the energy range studies here s_0 did not appear to saturate with increasing incident energy.

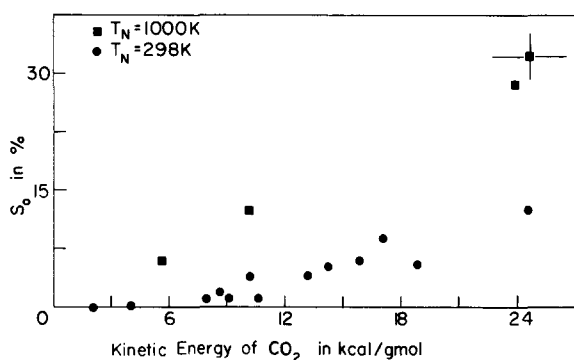


FIG. 1. The initial dissociative sticking probability for CO₂ on Ni(100) as a function of the CO₂ translational kinetic energy for nozzle temperatures of 298 K (circles) and 1000 K (squares).