

DISSOCIATIVE CHEMISORPTION OF METHANE ON Pt(111)

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Dissociative chemisorption of methane on clean Pt(111) was studied with a supersonic molecular beam. Initial dissociative sticking probabilities from 0.01 to 0.19 were measured directly with incident total beam energies from 68 to 95 kJ/mol, surface temperatures from 500 to 1250 K, and angles of incidence from 0° to 45° measured from the surface normal. The nozzle temperature and stagnation pressure were both fixed so that the effect of translational energy at a fixed incident vibrational energy could be probed. The initial dissociative sticking probability of methane on clean Pt(111) equaled 0.06 ± 0.02 and was independent of surface temperature between 500 and 1250 K for a fixed normal incident kinetic energy of 68 kJ/mol, implying that dissociation proceeded via direct collisional activation rather than via trapping or precursor-mediated processes in this energy range. The initial dissociative sticking probability of methane on clean Pt(111) increased exponentially with increasing normal kinetic energy. The barrier height for C-H bond rupture by kinetic energy is 121 kJ/mol. The exponential dependence is consistent with a model for dissociative methane adsorption that involves quantum mechanical tunneling of a hydrogen atom through a one-dimensional, parabolic barrier of this height with a thickness at half height of 0.13 ± 0.01 Å. Differences in the initial dissociative sticking probabilities observed on Pt(111) versus Ni(111) and W(110) in studies from different laboratories can be reconciled on the basis of the different vibrational energies employed, but this explanation does not account for the high reactivity on Ir(110)-(1 × 2). The activation barriers predicted by the bond order conservation theory of Shustorovich agree closely with the barrier heights estimated from the tunneling model for Pt(111), W(110), and Ir(110) if no correction for energy dissipation to the lattice is made. The activation barriers predicted by the molecular orbital analysis of Anderson and Maloney are much lower than the barrier heights estimated from the tunneling model. The barrier thicknesses show qualitative agreement with the C-H bond elongations in the transition state predicted by their molecular orbital theory, but do not correlate with the crystalline radii of the metal atoms or the stiffness of the metal lattices. Furthermore, the values of the tunneling parameters may be dependent on the vibrational and translational energies employed in the studies.