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Thermal Chemistry of N_2, CO_2, and CH_4 on Cesiated Pt(111)
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— Promoting transition metal surfaces with alkali metals is known to drastically reduce the surface work function. We have investigated the effect of Cs promotion on the thermal chemistry of CH_4, N_2 and CO_2 using temperature programmed desorption (TPD). At low Cs coverage the CH_4TPD peak broadens and shifts to higher temperature. As the Cs coverage increases further three CH_4 peaks develop: one at higher temperature than on a bare Pt surface, and two at lower temperatures. With Cs coverage of one saturation monolayer (θ_{sat} = 0.41 ML) or more only the lowest temperature peak remains. CH_4 sticking also varies as a function of Cs coverage. N_2 displays similar behavior to CH_4 in response to coadsorption of Cs, but does not stick to Cs multilayers. CO_2 exhibits very unusual behavior as a function of Cs coverage. At low Cs coverage the physisorbed CO_2 peak broadens, then splits into a doublet, with one peak at higher temperature than the "normal" CO_2 peak, and the other at lower temperature. With increasing Cs coverage CO_2 begins to dissociate, evidenced by high temperature recombinative desorption and the presence of chemisorbed CO. As the Cs coverage approaches θ_{sat} the physisorbed peak disappears entirely, and only dissociative chemisorption is seen.

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