

# Activation of small molecules on oxides and at metal-oxide interfaces

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The catalytic activation of small molecules, like CO, H<sub>2</sub>O and H<sub>2</sub> is of importance in different processes, such as hydrogenation of CO and water gas shift reaction, for which metal oxide supported rhodium catalysts can be applied [1]. The critical role of metal-oxide interface in activating small molecules was established under high pressure conditions [2], but has rarely been addressed by UHV model studies. We have investigated the effect of rhodium-titania and Rh-molybdenum oxide interfaces on the surface reactions of CO and H<sub>2</sub>O by AES, ISS, STM, XPS, TPD and sensitive temperature-programmed work function (WF) measurements.

The TiO<sub>x</sub> overlayers were formed by annealing the TiO<sub>2</sub>(110) supported rhodium particles, while molybdenum oxide supports and films were produced by the oxidation of Mo deposits. Both TiO<sub>x</sub> and MoO<sub>x</sub> overlayers exerted inhibition effect on the molecular bonding of CO to rhodium, accompanied by considerable promotion of CO dissociation maximized at 0.2-0.3 ML oxide coverages. The MoO<sub>x</sub> overlayer, having lower surface free energy than the atomically thin TiO<sub>x</sub> film, completely covered the molybdena supported Rh particles by annealing to 650 K and eliminated the CO adsorption capability of the surface. On the contrary, the titania supported Rh clusters showed maximum CO dissociation propensity after annealing to 700 K. The maximization of CO decomposition is straightforwardly associated with the active role of Rh-metal oxide interfaces. The desorption peak temperature for the associative CO desorption on the MoO<sub>x</sub> modified rhodium (T<sub>p</sub>=700 K) suggests a lower activation energy in the recombination reaction of O<sub>a</sub> and C<sub>a</sub> atoms than that for the TiO<sub>x</sub> covered Rh surfaces (T<sub>p</sub>=800 K), which allows higher reaction rates for these intermediates on the MoO<sub>x</sub> containing catalysts. Our UHV study is in harmony with the results of high pressure experiments, concerning the formation of carbon intermediate from CO dissociation during CO methanation [3]. The reactions of water showed variety with the extent of reduction of titania support. Strongly reduced surfaces produced H<sub>2</sub>O and H<sub>2</sub> desorption states with T<sub>p</sub>=370 and 470 K, corresponding to recombinative and dissociative reaction paths of the surface OH moieties. The interaction of water with the Rh-TiO<sub>x</sub> interface was characterized with H<sub>2</sub> desorption peaked at 580 K, arising from OH groups which exhibited maximal population at intermediate TiO<sub>x</sub> coverages. The concomitant inhibition and promotion effects of metal oxide overlayers on the adsorption properties of a metal is rationalized within the frame of an island model.

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