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Water-gas shift Reaction on K/Cu(111) and Cu/K/TiO₂(110) Surfaces: Alkali Promotion of Water Dissociation and the Production of H₂

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Abstract

The addition of potassium atoms to Cu(111) and Cu/TiO₂(110) surfaces substantially enhances the rate for water dissociation and the production of hydrogen through the water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$). In the range of temperatures investigated, 550-625 K, Cu/K/TiO₂(110) exhibits a WGS activity substantially higher than those of K/Cu(111), Cu(111) and a Cu/ZnO(000 $\bar{1}$) system used to model an industrial Cu/ZnO catalyst. The apparent activation energy for the WGS drops from 18 Kcal/mol on Cu(111) to 12 Kcal/mol on K/Cu(111) and 6 Kcal/mol on Cu/K/TiO₂(110). The results of density functional calculations show that K adatoms favor the thermochemistry for water dissociation on Cu(111) and Cu/TiO₂(110) with the cleavage of an O-H bond occurring at room temperature. Furthermore, at the Cu-K/TiO₂ interface, there is a synergy, and this system has a unique ability to dissociate the water molecule and catalyze hydrogen production through the WGS process. Therefore, when optimizing a regular catalyst, it is essential to consider mainly the effects of an alkali promoter on the metal-oxide interface.

Keywords: Water-gas shift reaction, Cu(111), Cu/K/TiO₂(110), alkali promoters, water dissociation

Introduction

The activity and selectivity of a heterogeneous catalysts can be substantially affected by the addition of an alkali metal.^{1,2} Experimental and theoretical studies have shown that an alkali can affect the chemical properties and catalytic performance of metals, oxides and sulfides.^{3,4,5,6,7,8} Alkali metals are used as promoters in key processes of the chemical industry (ammonia synthesis, the production of alcohols from the hydrogenation of CO or CO₂, the forward and reverse water-gas shift reaction, olefin epoxidation, Fischer-Tropsch synthesis, etc). Different mechanisms have been invoked to explain the promotional effect of an alkali on a catalytic process. In principle, an alkali can be involved directly in a surface reaction or it can change the chemical properties of the catalyst components.^{9,10} Most catalysts used in the chemical industry combine metals and oxides. On these complex systems, the alkali can modify the properties of the metal, the oxide or the metal-oxide interface.^{11,12,13,14,15}

In the industry, the water-gas shift reaction (WGS, $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$) is widely utilized for generating the hydrogen necessary for many chemical transformations,¹⁶ and for removing the CO present in feed streams employed for ammonia synthesis and energy generation through fuel cells.¹⁷ A catalyst involving a mixture of Cu/ZnO/Al₂O₃ is commercially used for the low-temperature WGS reaction.^{17,18} The active phase of the system involves Cu/ZnO and it has problems of activity and stability. There is a continuous search for new and more efficient WGS catalysts^{18,19} The addition of Cs to a Cu/ZnO powder²⁰ or a well-defined Cu(110) surface²¹ leads to a significant increase in catalytic activity. This effect was attributed to a lower energy barrier for O-H bond cleavage in the rate-determining step (i.e. the dissociative adsorption of water)²¹ A hypothesis that agrees well with the results of theoretical calculations for the dissociation of water

on clean and K-modified Cu(111) and Cu(110) surfaces.¹⁴ Alkali adatoms can affect the bonding of the two WGS reactants, H₂O and CO, to pure metal surfaces.^{7,9,14,15} One can have direct alkali $\leftrightarrow$ H₂O and alkali $\leftrightarrow$ CO interactions or the alkali can modify the electronic and chemical properties of the underlying metal by an alkali $\rightarrow$ metal charge transfer.^{7,9,15} The magnitude depends strongly on the alkali coverage and the ionicity of the alkali-metal bond changes from highly ionic at low coverages ($\Theta_{\text{alkali}} < 0.25$ monolayer) to mostly metallic at high coverage ($\Theta_{\text{alkali}} > 0.35$ ML).^{7,9,15} Furthermore, recent studies have shown that the addition of potassium or sodium to WGS powder catalysts which contain gold or platinum leads to a substantial increase in catalytic activity by inducing the formation of single-site (Pt or Au)-O(OH)_x-(Na or K) species.^{22,23,24} Active sites which contain only a metal center are formed as a consequence of interactions of the metal with (OH)_x-(Na or K) groups. It is not clear how these groups are formed by the interaction of the alkali with water molecules. Also, in these systems,^{22,23,24} one can see a [metal-alkali-oxide] unit and the relative importance of the alkali effects upon the metal and the metal-oxide interface is unknown.

In this work, we investigate the effects of K on the ability of Cu(111) and Cu/TiO₂(110) surfaces to cleavage O-H bonds in water and catalyze the WGS process. Cu(111) is a typical benchmark for fundamental studies of the WGS.^{14,21,25,26} The low reactivity of Cu(111) towards water^{25,26} disappears upon the addition of K but the major effect of the alkali is on the Cu/TiO₂ interface. The Cu/K/TiO₂ system displays a better performance than a commercial Cu/ZnO catalyst. Its excellent WGS activity is a consequence of a synergy at the Cu-K/TiO₂ interface which significantly facilitates water dissociation.

Experimental and theoretical methods

Photoemission and catalytic studies

The experiments of photoemission and the catalytic studies were carried out in a system which combines an ultrahigh-vacuum (UHV) chamber (base pressure $\sim 5 \times 10^{-10}$ Torr) and a batch micro-reactor.^{27,28} The sample could be transferred between the reactor and UHV chamber without exposure to air. The UHV chamber was equipped with instrumentation for X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), ion scattering spectroscopy (ISS), and temperature-programmed desorption (TPD). The experiments were done using Cu(111) or rutile TiO₂(110) single crystals cleaned following standard procedures used in our previous studies for the water-gas shift.^{25,26} Potassium was deposited from a getter source whose evaporation rate on Cu(111) was calibrated by a combination of LEED and XPS.²⁹ The same fluxes were then used in the studies on the TiO₂(110) substrate. An Oxford evaporator was also used to vapor deposit Cu on K/TiO₂(110) at 300 K.³⁰

In the kinetic measurements the sample was transferred to the batch reactor at ~ 300 K, then the reactant gases were introduced (20 Torr of CO and 10 Torr of H₂O) and the sample was rapidly heated to the reaction temperature (550-625 K).^{25,26,30} The amount of molecules produced was normalized by the active area exposed by the sample.^{25,26,30} In our reactor a steady-state regime for the production of H₂ and CO₂ was reached after 2-3 minutes of reaction time.

Density functional calculations

All periodic DFT calculations examining the bonding of the alkali metals and dissociation of water were performed by means of the VASP code,^{31,32} using plane-waves as basis set together with the GGA exchange correlation functional proposed by Perdew,

Burke, and Ernzerhof (PBE).³³ The energy cutoff for the plane-waves was set to 400 eV. We treated the Cu (3d 4s), Ti (3d, 4s), K (3s, 3p, 4s) and O (2s, 2p) electrons as valence states, while the remaining electrons were kept frozen and taken into account using the projector augmented wave (PAW).^{34,35} For copper surface models, the Brillouin zone was sampled using a (6x6x1) gamma-centered mesh of k-points. For TiO₂ based models the energy was estimated at the gamma point. In order to represent adequately the electronic structure of reduced titania, a Hubbard-like U term was added to Ti 3d levels using the rotationally invariant approach proposed by Dudarev *et al.*,³⁶ in which the Coulomb U and exchange J parameters are combined into a single parameter $U_{eff} = U - J$. The U_{eff} value for Ti 3d states was of 4.5 eV.³⁷ To obtain faster convergence, thermal smearing of one-electron states was allowed using the Gaussian smearing method, with $\sigma = 0.01$ eV, and the total energies were taken after extrapolation to 0K. Finally, although dispersion corrections increase total energies, it has been reported that relative energies and energy reactions are not significantly affected by Van der Waals corrections in similar systems, and therefore have not been included.³⁸ As we will see below, K binds strongly to Cu(111) and TiO₂(110) and our calculated adsorption energies for water are comparable to those found in previous theoretical studies. Our main objective here is to see how the presence of the alkali affects trends for the binding and dissociation of water.

Copper surface was represented through (2x2) and (4x4) supercells, 4 atomic layers thick, that are repeated into the three directions. A vacuum of 15 Å was allowed between the slabs. We used the lattice parameter optimized for the bulk, $a = 3.64$ Å. In structural optimizations the two lowest Cu layers were kept frozen while the rest of the atoms were allowed to fully relax their atomic positions. The rutile TiO₂(110) surface was represented

using (6x2) supercells, 12 atomic layers thick (or four TiO₂-trilayers) that were built using the optimized lattice parameters for the bulk, $a = 4.669 \text{ \AA}$, $c = 3.025 \text{ \AA}$. A vacuum of 15 Å was also added to the supercells. In structural optimizations the two lowest TiO₂ trilayers were kept frozen while the rest of the atoms were allowed to fully relax their atomic positions. Geometry optimizations were performed using a conjugated gradient algorithm and stopped when forces acting on atoms were below 0.01 eV Å⁻¹. Transition states were located by using the climbing image version of the nudged elastic band (NEB) algorithm,³⁹ using three images in the search. To fully characterize the nature of these stationary states, a vibrational analysis was performed in all cases and only one imaginary frequency was obtained for these structures.

Results and Discussion

Adsorption and reaction of water on K/Cu(111) and Cu/K/TiO₂(110): Photoemission and kinetic studies

Previous experimental and theoretical studies indicate that the slow step of the WGS reaction on Cu-based catalysts is the dissociation of water.^{14,21,25,26,40} Thus, it is important to study the ability of the K-modified surfaces to break O-H bonds. Water interacts weakly with Cu(111).⁴¹ At 100 K, the molecule adsorbs without dissociation and desorbs intact at temperatures below 200 K. Theoretical calculations predict that K adatoms should enhance the dissociation of water on Cu(111).¹⁴ Experimental studies for the adsorption of K on Cu(111) show a large decrease of the surface work function as a consequence of a K→metal charge transfer.²⁹ The ionicity of the K-Cu bond decreases with alkali coverage. A clear LEED (2x2) pattern is seen at a K coverage of 0.25 ML.²⁹

Figure 1 displays O 1s XPS spectra collected after exposing clean Cu(111) and a copper surface precovered with 0.2 ML of potassium to 1 Torr of water at 300 K. On Cu(111), there was no adsorption of water, in good agreement with previous studies.⁴¹ In contrast, on the K/Cu(111) surface, there is a clear peak around 531.1 eV that denotes the presence of adsorbed OH groups^{41,42} produced by the dissociation of water. In the K 2p XPS region, Figure 2, we saw a negative binding energy shift of ~ 0.6 eV which is consistent with the formation of small amounts of a KOH_x species.^{42,43} Heating from 300 to 400 K induced desorption of water and produced a partial $\text{KOH}_x \rightarrow \text{KO}_y$ transformation. We found that the $\text{KO}_y/\text{Cu}(111)$ surface was still able to adsorb water (top curve in Figure 1A). The K/Cu(111) and $\text{KO}_y/\text{Cu}(111)$ surfaces displayed a much higher reactivity towards O-H bond cleavage than that found for clean Cu(111) (Figure 1B). After varying the coverage of K on Cu(111), we saw a continuous increase in the amount of water dissociated on the surface when the alkali coverage was increased. For submonolayer and multilayer coverages of K, we detected the formation of KOH_x species in the system.

In a previous study, it has been found the K also enhances the interaction of Cu(111) with CO, the second reactant of the WGS reaction.²⁹ At alkali coverages of 0.1-0.2 ML, there is an increase of 100-150 K in the CO desorption temperature from Cu(111).²⁹ This effect is probably a consequence of a $\text{K} \rightarrow \text{Cu}$ charge transfer which enhances the bonding interactions between the noble metal and the LUMO of the CO molecule.^{5,7,9,29} It was found that a direct reaction of CO with K can lead to dissociation of the adsorbed molecule with formation of CO_2 or CO_3 species on the surface.²⁹

Figure 3 displays data for the generation of H_2 through the WGS reaction on a series of K/Cu(111) surfaces with different coverages of potassium. The addition of K continuously

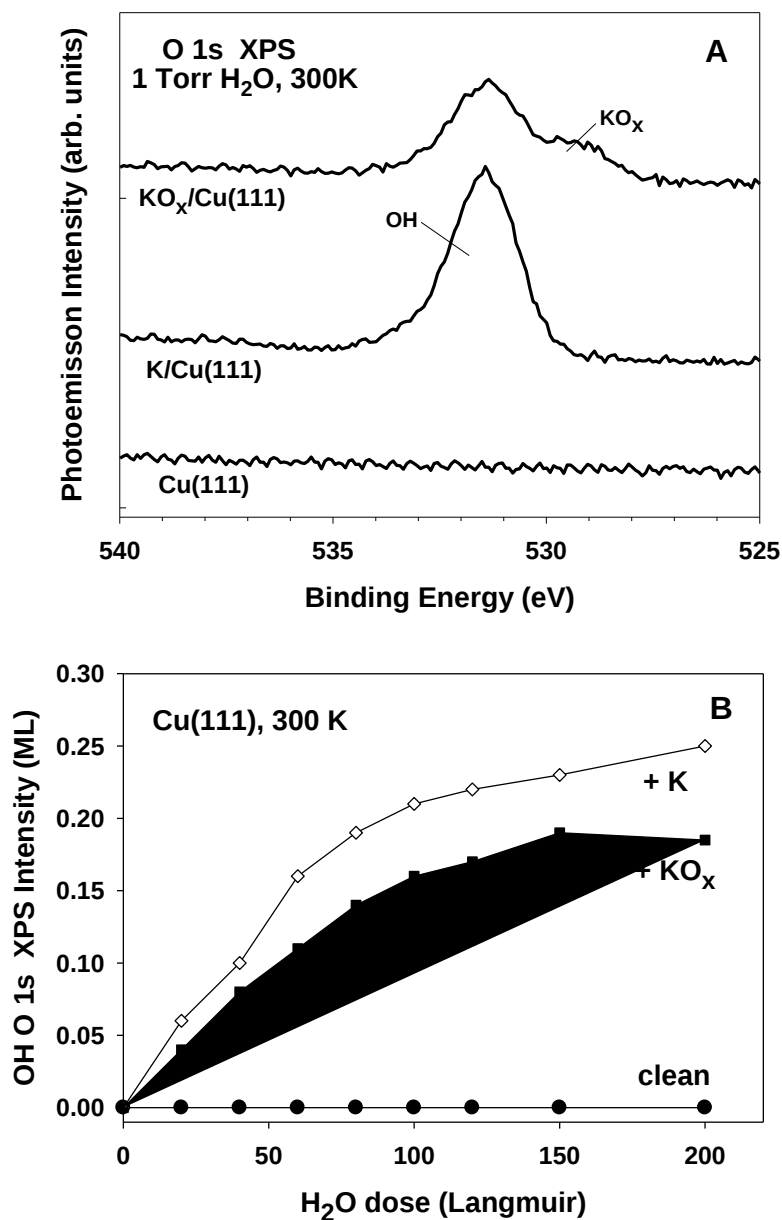


Figure 1. Part A: O 1s XPS spectra collected after dosing water to Cu(111), K/Cu(111) and KO_x/Cu(111) surfaces at 300 K. The surfaces were exposed to 1 Torr of water at 300 K for five minutes. The coverage of K in the K/Cu(111) and KO_x/Cu(111) systems was ~ 0.15 ML. Part B: Amounts of OH produced after several doses of water to Cu(111). K/Cu(111) and KO_x/Cu(111) surfaces at 300 K.

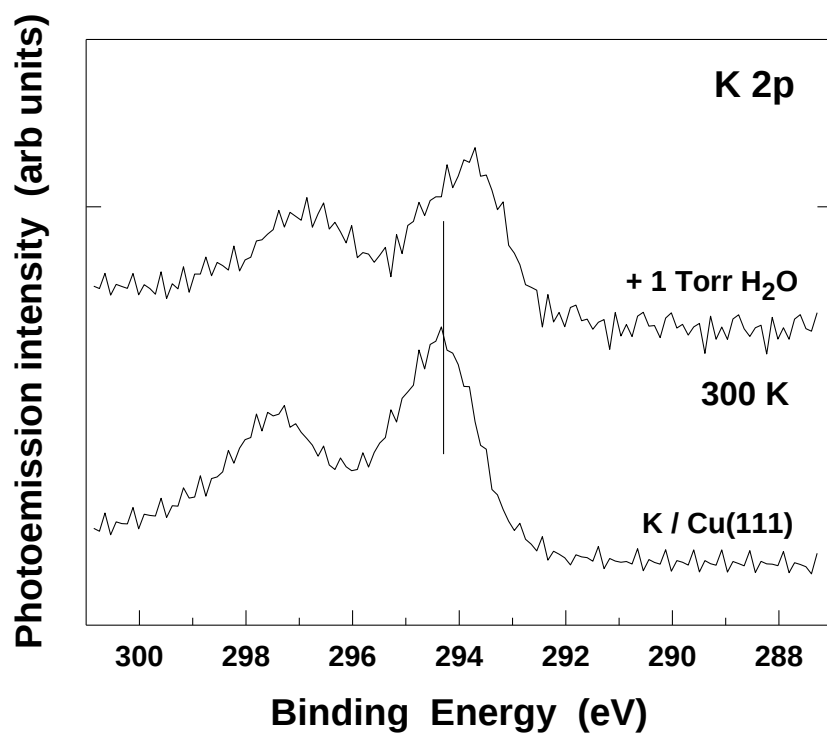


Figure 2. K 2p XPS spectra recorded before and after exposing a K/Cu(111) surface to to 1 Torr of water at 300 K for five minutes. The coverage of K in the K/Cu(111) system was ~ 0.15 ML.

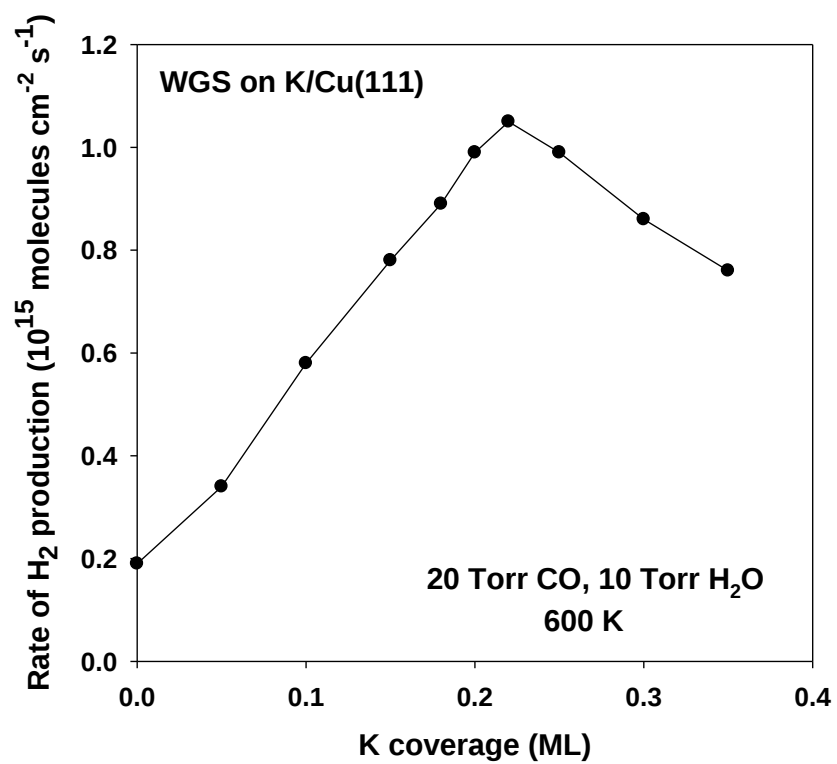


Figure 3. Rate of H₂ production for the water-gas shift reaction on a series of K/Cu(111) surfaces as a function of alkali coverage. Reaction conditions: 600 K. 20 Torr of CO. 10 Torr of water.

increases the rate of H₂ production until a maximum is reached for an alkali coverage of ~ 0.25 ML. At this point a (2x2) pattern is observed for the K/Cu(111) surface and the K-Cu adsorption bond is highly ionic.²⁹ At higher coverages of K the ionicity of the K-Cu decreases and the alkali overlayer becomes disordered. We found that at alkali coverages above 0.25 ML the K/Cu(111) surfaces formed significant amount of carbonates after being exposed to mixtures of CO/H₂O. Figure 4 shows K 2p and C 1s XPS spectra collected after performing the WGS reaction on surfaces pre-covered with 0.15 and 0.35 ML of potassium. The position observed for K 2p features is not the same seen after the formation of K-OH species in Figure 2 probably as a consequence of an interaction between the alkali and a CO_x species. In the C 1s region of the spectrum for the surface with 0.15 ML, one can see a weak peak at ~ 289.5 eV which can be assigned to a carbonate-like species.^{12,15,44} The intensity of this peak substantially grows when the alkali coverage is increased from 0.15 to 0.35 ML, bottom panel in Figure 4. For the surface with 0.35 ML of potassium, one also finds a feature around 284 eV which can be assigned to C.¹² In test experiments, we found that the surface with only 0.15 ML of K and a low coverage of C-containing species was more reactive for the dissociation of water than the surface with 0.35 ML of K and substantial amounts of CO_x and C. Thus, the two extremes in the curve of Figure 3 can be explained in the following way. At K coverages below 0.2 ML, the production of H₂ is fast thanks to the rapid dissociation of water (Figure 1). On the other hand, at K coverages above 0.25 ML, the deposition of CO_x and C on the catalyst surface slows down the dissociation of water and H₂ production by the WGS. Similar trends have been observed previously for the WGS reaction on Cs/Cu(110).^{15,21} At small coverages of K, when the alkali is in a highly ionic state,²⁹ the potassium binds mainly to the copper substrate and

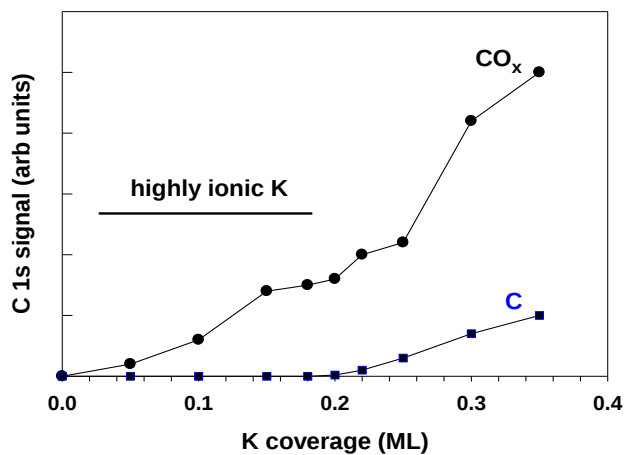
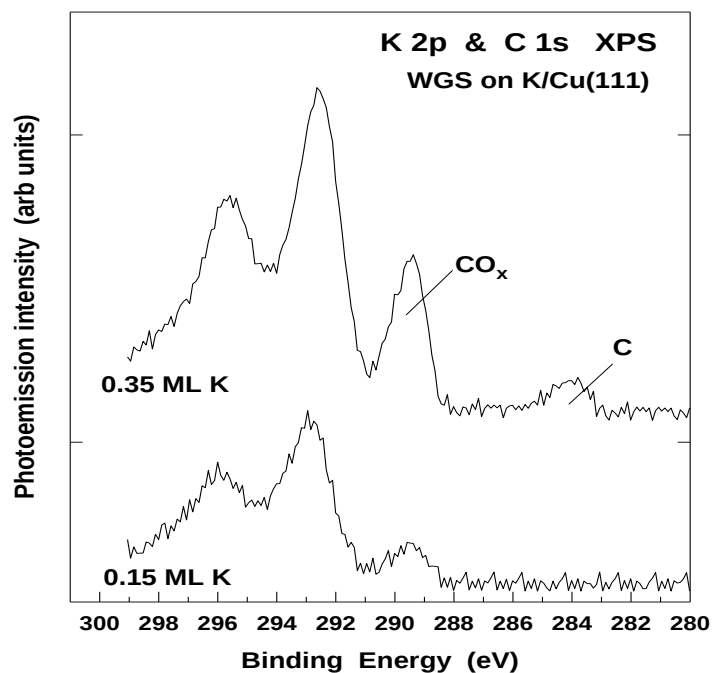


Figure 4. Top: K 2p and C 1s spectra collected after performing the water-gas shift reaction on Cu(111) surfaces pre-covered with 0.15 and 0.35 ML of potassium. Reaction conditions: 600 K. 20 Torr of CO. 10 Torr of water. Bottom: Amount of CO_x and C measured after the WGS reaction on a series of K/Cu(111) surfaces.

the $\text{K} \leftrightarrow \text{CO}$ and $\text{K} \leftrightarrow \text{CO}_2$ interactions are not strong enough to induce the deposition of significant amounts of CO_x and C on the surface, bottom panel in Figure 4. A metallization of the alkali occurs at high coverages of K,²⁹ and the weakening of the bonding with the copper facilitates interactions with gas molecules and the deposition of CO_x and C poisons on the surface.

Figure 5 shows an Arrhenius plot collected by performing the WGS reaction on a Cu(111) surface pre-covered with ~ 0.2 ML of potassium. When compared to plain Cu(111), the K/Cu(111) system always displays higher catalytic activity at temperatures between 550 and 625 K. The apparent activation energy for the WGS reaction decreased from 18 kcal/mol on Cu(111) to 12 kcal/mol on K/Cu(111). The improvement in catalytic activity was significant but not as large as that found after depositing Cu nanoparticles on a $\text{TiO}_2(110)$ surface.³⁰ Thus, we decided to investigate water dissociation and the WGS reaction on Cu/K/ $\text{TiO}_2(110)$ surfaces.

Clean $\text{TiO}_2(110)$ is not very good at dissociating water at 300 K.^{30,43,45} As a consequence of interactions with O vacancies and defect sites, a small amount of water molecules dissociate to form a few OH groups on the oxide surface (Figure 6). The reactivity of the surface towards water increases after adding Cu (~ 0.3 ML) and K (~ 0.15 ML) to $\text{TiO}_2(110)$. K/ $\text{TiO}_2(110)$ alone has a negligible activity for the WGS. Results of scanning tunneling microscopy (STM) has revealed that potassium has a high mobility on $\text{TiO}_2(110)$ being anchored to the oxide surface by OH groups.⁴³ Then, this K-OH units can act as anchor sites for metal particles.^{12,43} STM images for Cu/K/ $\text{TiO}_2(110)$ show K atoms, Cu particles and Cu-K interfaces on top of titania. In principle, only a fraction of the admetal (30-40%) may be close to the alkali, but K has a high mobility on titania and

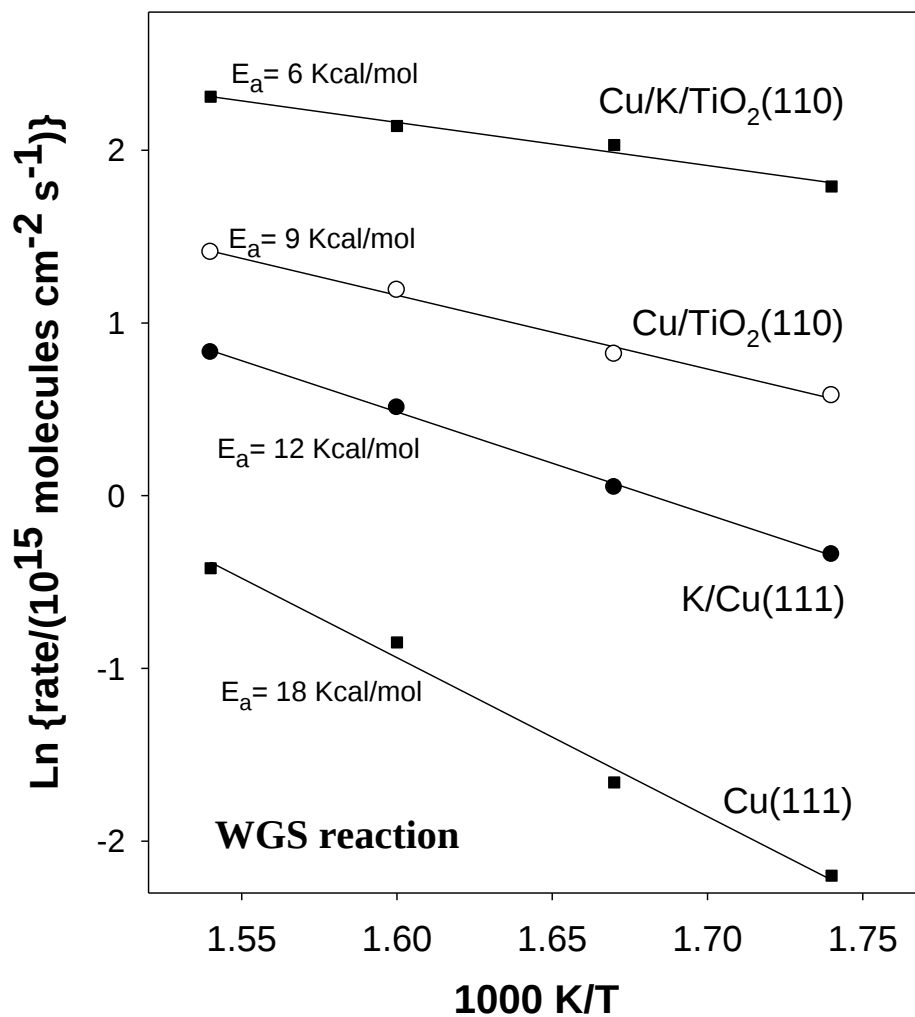


Figure 5. Arrhenius plots for the water-gas shift on Cu(111), K/Cu(111) ($\Theta_K \sim 0.2 \text{ ML}$), Cu/TiO₂(110) ($\Theta_{Cu} \sim 0.3 \text{ ML}$), and Cu/K/TiO₂(110) ($\Theta_{Cu} \sim 0.3 \text{ ML}$; $\Theta_K \sim 0.15 \text{ ML}$). Reaction conditions: 20 Torr of CO. 10 Torr of water.

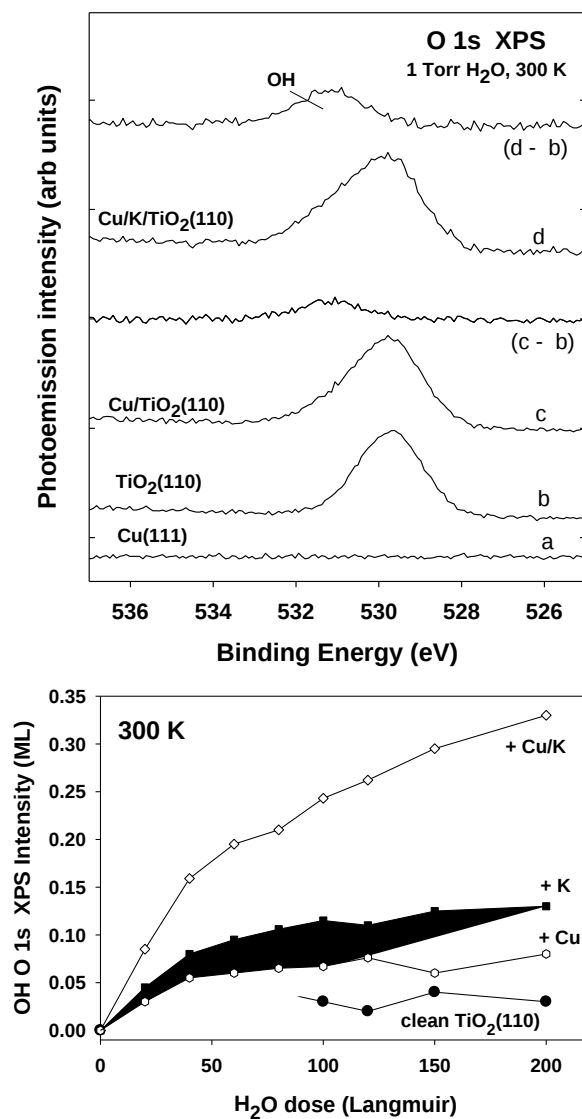


Figure 6. Formation of adsorbed OH by water dissociation at 300 K on Cu(111), TiO₂(110), K/TiO₂(110) ($\Theta_K \sim 0.15$ ML), Cu/TiO₂(110) ($\Theta_{Cu} \sim 0.3$ ML), and Cu/K/TiO₂(110) ($\Theta_{Cu} \sim 0.3$ ML; $\Theta_K \sim 0.15$ ML). The surfaces were exposed to water under UHV conditions, bottom panel, or to 1 Torr of water for five minutes in a batch reactor, top panel.

additional admetal-K interfaces can form after exposure to gases.^{12,41} In Figure 6, the Cu/K/TiO₂(110) system exhibits by far the highest reactivity towards water dissociation. Its chemical activity is larger than those of K/TiO₂(110), Cu/TiO₂(110) and K/Cu(111). Among the components of the Cu-KTiO₂ interface, there is a synergy, and this system has a unique ability to dissociate the water molecule. As we will see in the next section describing DFT studies, the calculated dissociation energy for water on Cu/K/TiO₂(110) is substantially more exothermic than those calculated on K/Cu(111) or pure copper systems. On the Cu/K/TiO₂(110) surface, one can imagine a situation where H₂O dissociates on the Cu-KTiO₂ interface and then OH migrates to the Cu component where the final steps of the WGS process take place. This is probably the case for the experiment depicted at the top of Figure 6.

Activity data for the WGS on Cu/K/TiO₂(110) surfaces as a function of Cu and K is shown in Figure 7. In our previous study for the WGS on Cu/TiO₂(110),³⁰ we found that the highest activity occurred at small coverages of copper when the average metal particle size was below 3 nm. At large coverages of Cu, the average metal particle size increased and the overall activity decreased. Something similar is probably occurring for the WGS on the Cu/K/TiO₂(110) surfaces. In Figure 7, one can see an increase in WGS activity after adding K to the oxide surface. The optimal performance is found for catalysts which contained a potassium coverage of ~ 0.15 ML, bottom panel in Figure 7. At higher alkali coverages, the formation of CO_x species and C led to deactivation as seen in the case of K/Cu(111), Figure 4, and Cs/Cu(110).¹⁵ This deactivation was gradual and surfaces with 0.2 and 0.25 ML of potassium still display in Figure 7 a WGS activity which is 2-3 times larger than that of Cu/TiO₂(110). XPS and Auger spectra collected after the WGS process

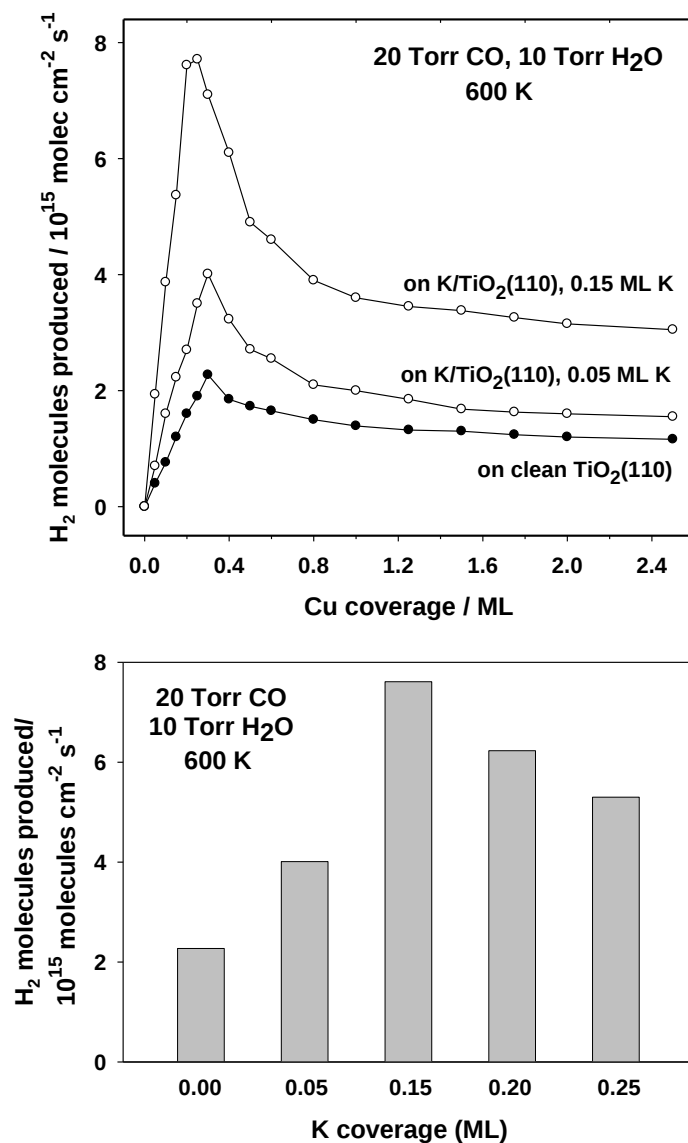


Figure 7. Production of H₂ through the water-gas shift on Cu/K/TiO₂(110) surfaces as a function of Cu coverage (top panel) and K coverage (bottom panel). In the experiments of the bottom panel, the Cu coverage was ~ 0.3 ML. In all cases, the reaction conditions were: 600 K, 20 Torr of CO, 10 Torr of water.

indicate that the copper particles present in the Cu/K/TiO₂(110) surfaces were not highly ionized ($\text{Cu}^{\delta+}$, $\delta < 1$). Most of the electronic charge transferred by the alkali landed on titania, OH or CO_x groups.

An Arrhenius plot for a Cu/K/TiO₂(110) ($\Theta_{\text{Cu}} \sim 0.3$ ML; $\Theta_{\text{K}} \sim 0.15$ ML) surface is shown in Figure 5. In the range of temperatures investigated, 550-625 K, Cu/K/TiO₂(110) exhibits a WGS activity substantially higher than those of Cu/TiO₂(110),³⁰ Cu/CeO₂(111)²⁸ and Cu/ZnO(0001̄).²⁸ Cu/ZnO catalysts are frequently used in industrial processes for the production of hydrogen through the WGS.^{17,20} In Figure 5, the apparent activation energy for the WGS drops from 18 Kcal/mol on Cu(111) to 9 Kcal/mol on Cu/TiO₂(110) and 6 Kcal/mol on Cu/K/TiO₂(110). In addition, we found a decrease of a factor of two in the pre-exponential factors. The kinetic parameters derived from the Arrhenius plots in Figure 5 are probably not associated with a single reaction step, but the substantial variations in these kinetic parameters point to drastic changes in key steps of the catalytic process as a consequence of K-promotion; changes which enhance the rate of hydrogen production by several orders of magnitude when going from a plain metal to an alkali-promoted metal-oxide interface. The K/TiO₂(110) system is efficient for the dissociation of water⁴³ but does not catalyze the WGS. Synergistic interactions make the Cu-K/TiO₂ interface highly active for water dissociation (Figure 6), and on the metal component of the interface, copper, the adsorption of CO and the WGS process could take place.³⁰

Interaction and conversion of water on K/Cu(111) and Cu/K/TiO₂(110) a: DFT studies

Previous theoretical studies have stressed the important role that water dissociation plays in the WGS process.^{14,25,25,28} An alkali can enhance the stability of OH groups and other oxygenates on copper surfaces but water dissociation is always an essential step.¹⁴ In the following sections, we will investigate in detail the cleavage of O-H bonds on metals {Cu(111), K/Cu(111)}, oxides {TiO₂(110), K/TiO₂(110)} and metal-oxide surfaces {Cu/TiO₂(110), Cu/K/TiO₂(110)}. Our aim is to explain the data displayed in Figures 1 and 6 which was obtained after dosing water to plain K/Cu(111) and Cu/K/TiO₂(110) surfaces. In K/Cu(111) and Cu/K/TiO₂(110), the K is in an ionic state and there are K-O bonds in the case of Cu/K/TiO₂(110). At a theoretical level a synergy for water dissociation is found on the Cu/K/TiO₂(110) system.

Adsorption of water on the Cu(111) surface

In our study, we start by choosing an initial state for water on Cu(111), that will act as reference to compare the extent of the effects induced by the presence of K. Interaction of water with transition metals, in particular Cu, has been theoretically analyzed a number of times.^{14, 25, 26, 38, 46} Focusing on the interaction of a single water molecule with the Cu(111) surface, effects due to the coverage, size and thickness of the slab models, functionals, etc. have been reported. There is agreement that at 25% coverage water molecule lies practically flat on the surface at a distance of 2.0-2.5 Å above the surface, the adsorption energy being of about -0.20 eV, while at lower coverage the interaction becomes larger.³⁸ As recently reported by Hao et al.³⁸ a strong coverage dependence of the adsorption energy and geometry of water on Cu(111) is found in the low regime. The adsorption energy increases for decreasing coverage.

In Table 1 we report adsorption energies and structural data calculated using differently sized supercells as well as selected values taken from the literature. Also, as we are interested in the reactivity, we include the dissociation energy of water and the activation energy for the dissociation. Our results agree with the trends reported in the literature, though it should be beard in mind than the calculations setup may differ in several aspects. However, some relevant conclusions may be drawn. First, the adsorption energy increases from -0.20, to -0.36 and finally to -0.57 eV for decreasing coverages of 25, 6.25 and 2.8 %, respectively, in agreement with the results of Hao et al.³⁸ The initial nearly flat orientation of the water molecule (flap angle of 3°) changes to an angle of 22-23°, these geometrical changes being in agreement with the results previously obtained from an MD simulations.⁴⁶ Accordingly the Cu-O distance decreases from 2.45 to 2.30 Å. On the other hand, this stronger interaction favors the dissociation of water making the process less endothermic passing from 0.47 eV at coverage of 25% to 0.12 eV at 2.8 %. Surprisingly, the activation energy for the dissociation of water is not affected by the coverage. In summary, we find out that lowering coverage increases the initially weak interaction of single water molecules with copper, thermodynamically favoring its adsorption and dissociation.

Table 1. Energetic and structural data for water adsorbed on the Cu(111) surface at different coverage computed using distinct models and computational setup. E_{ads} : adsorption energy, E_{dis} : dissociation energy, E_a : activation energy, α : tilt angle in degree, $d_{\text{Cu-O}}$: Cu-O distance in Å.

Reference	Slab width*	Slab model	DFT funct.	Coverage (%)	E_{ads} (eV)	E_{dis} (eV)	E_a (eV)	α (°)	$d_{\text{Cu-O}}$ (Å)
Gokhale <i>et al.</i> ²⁶	3 (3,0)	p(2x2)	PW91 ^{&}	25.0	-0.18	0.37	1.36	flat	2.81
Fajin <i>et al.</i> ²⁵	3 (3,0)	p(2x2)	PBE	25.0	-0.20	0.24	1.11	flat	2.54
Nadler <i>et al.</i> ⁴⁶	7 (6,1)	p(4x4)	PBE	25.0	-0.15	-	-	1.5	2.50
Wang <i>et al.</i> ¹⁴	4 (2,2)	p(3x3)	PW91 ^{&}	11.1	-0.20	0.20	1.37	flat	1.99
Hao <i>et al.</i> ³⁸	4 (3,1)	p(3x3)	PBE ^{&}	11.1	-0.56	0.23	1.43		2.45
		p(2x2)		25.0	-0.47	0.32	1.35		2.53
		p(2x1)		50.0	-0.48	0.78	1.47		2.84
This work	4 (2,2)	p(6x6)	PBE	2.8	-0.57	0.10	1.30	22.6	2.31
This work	4 (2,2)	p(4x4)	PBE	6.25	-0.36	0.12	1.21	22.2	2.32
This work	4 (2,2)	p(2x2)	PBE	25.0	-0.20	0.47	1.29	3.0	2.45

*Number of atomic layers (relaxed layers, fixed layers).

[&] Zero-point energy (ZPE) corrections are included.

Deposition of K atoms on the Cu (111) surface

Isolated K atoms were deposited on the bare surface at the low regime of coverage (<25%), when experiments show the strongest interactions of the alkali with Cu(111).²⁹ It is worth to note that, because of the size of K atoms, 25% is the maximum coverage reachable in a monolayer. Indeed, since the cross section of a sphere having radius of atomic K (2.3 Å) is 16.6 Å^2 , we need, at least, a p(2x2) surface unit cell (22.6 Å^2) to accommodate such a sphere (see Figure 8). The interaction of K atoms with the Cu(111) surface is characterized by some relevant facts. First, there is a large charge transfer from K atoms to the copper surface, as shown by Bader analysis that gives a value for the charge

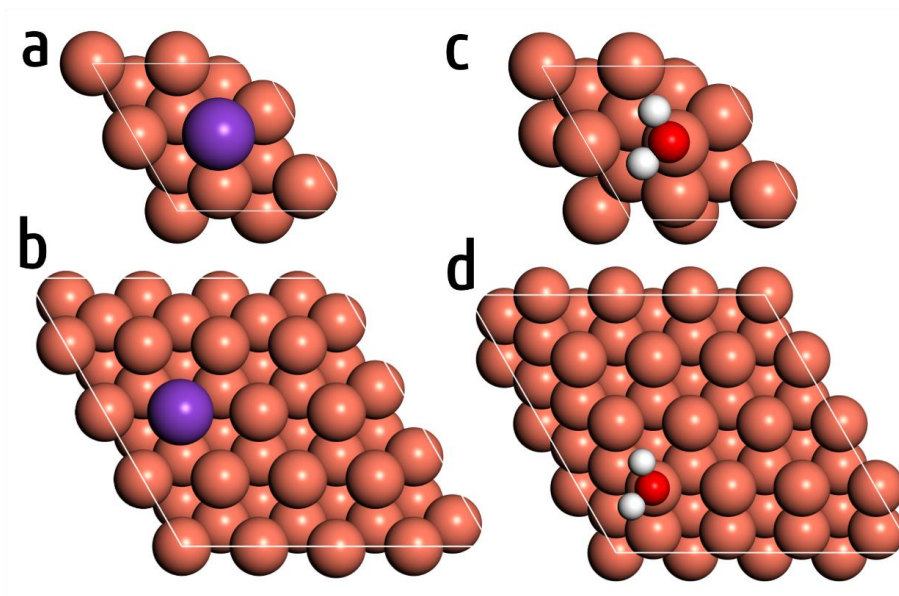


Figure 8. Top view of the models for adsorption of K (left images) and water molecule (right images) for different coverages 25% (top images) and 6.25% (bottom images), using respectively slab models of p(2x2) (top) and p(4x4) (bottom). Colors code: Cu (light brown), K (violet), O (red), H (white).

of $q_K = 0.82 |e|$ at 6.25% coverage, which is consistent with work function measurements.

²⁹ Notice on the other hand, that the amount of charge transfer lowers when coverage increases, the Bader charge being $q_K = 0.61 |e|$ at 25% coverage. Since at this coverage the K-K interatomic distance is 5.11 Å, *i.e.* almost twice the K ionic radius, the picture would be a Cu surface covered by a layer of K atoms, each one bearing 0.4 e instead of 1. Secondly the negative charge is accumulated almost exclusively on the nearest Cu atoms of the uppermost layer of the slab. Formally, copper reduction involves electron transfer to the Cu 4s band, which in principle is delocalized. However, due to the electrostatic attraction, the presence of the potassium positive charge polarizes the excess of electron density to its immediacy. Third, a strong interaction K-Cu takes place due to the subsequent favorable electrostatic interaction between the K^+ cation and the negatively charged surface layer. Finally, because the size of the K ions produced (radius falling somehow between the atomic 2.3 Å and the ionic 1.52 Å values⁴⁷) is larger than that of Cu atoms (1.35 Å),⁴⁸ there is almost no preference for a specific site of adsorption on the surface, as a single K atom is stepping several Cu atoms at the same time. The K-Cu bond should be seen as a kind of averaged interaction between a single formally K^+ ion and a portion of a Cu surface negatively charged.

With regard to the adsorption energy, we found out that the lower the coverage (in parenthesis), the higher the adsorption energy: -1.71 (25%), -2.29 (6.25 %), -2.35 (2.8 %) eV. This behavior reflects the increment of Coulomb repulsion between the K^+ species when K coverage grows. The K-K distances are 5.11, 10.22 and 15.34 Å for coverage 25%, 6.25% and 2.8%, respectively. In experiments, a large decrease (~ 700 K) in

desorption temperature from Cu(111) has been observed when the K coverage is increased from almost zero to a full monolayer.²⁹

Water adsorption on the K/Cu (111) surface

To analyze the effect of K deposition on the adsorption and dissociation of water two coverages were selected: 6.25 % (1 K atom every 16 surface Cu atoms) and 25% (1 K atom every 4 surface Cu atoms). Notice that this later coverage, which is the practical limit for full coverage as already commented, coincides with the value at which the highest catalytic activity is observed. For this optimal K coverage, we also considered the effect of the water coverage. Computed values for energies of adsorption, dissociation as well as dissociation barriers are reported in Table 2. Recent results reported by Wang *et al.* are also included.¹⁴

Table 2. Adsorption (E_{ads}) and dissociation (E_{dis}) energies and activation barriers for dissociation of water (E_{a}) at different coverages. All values in eV.

Coverage %		E_{ads}	E_{dis}	E_{a}
H_2O	K			
6.25	0.0	-0.36	0.12	1.21
6.25	6.25	-0.79	0.33	1.23
6.25	25.0	-0.90	-0.34	0.82
25.0	25.0	-0.71	0.17	0.87
11.1*	11.1	-0.60	0.37	1.08

* Wang *et al.*¹⁴

Let us first consider the interaction of a single water molecule (coverage 6.25%) with the p(4x4) surface model. As can be observed, the presence of K atoms on the surface dramatically increases the adsorption energy from -0.36 eV (no K) to -0.90 eV (25% K). An intermediate value of -0.79 eV is found for K coverage of 6.25%. For a fully covered surface, (25% H_2O ; 25% K) a slightly lower value (-0.71 eV) is estimated. With respect to water dissociation energies, which is the limiting step of the WGS reaction, we can see

that the presence of isolated adsorbed K ions (6.25% K) does not help to stabilize the hydroxyl species on the surface, at least compared with the strong stabilization featured by the water molecule. That is why the dissociation process is more endothermic in the presence of K atoms (0.33 eV) than on the bare surface (0.12 eV). The barrier for the dissociation does not change either. This behavior may be understood if we consider that at very low K coverage, K^+ ions are relatively separated from each other and perform as isolated centers that might stabilize either a water molecule or a hydroxyl species. In Figure 9, the structure of initial, transition and final states for the dissociation is shown. We can see that water binds the surface interacting with the K^+ ion, with hydrogen atoms pointing towards the surface. After dissociation, the hydroxyl group appears to bind both K^+ ion and a copper atom. These values are consistent with those reported in ref [14].

Things change when the surface is fully covered with K^+ ions (6.25% H_2O ; 25% K). Beyond the increment of the adsorption energy already commented, an outstanding change in the dissociation energy is observed, the process now being neatly exothermic by -0.34 eV. Also, of most relevance for the reactivity of the system, the barrier for the dissociation drops by 0.41 eV. This behavior might be understood analyzing the geometries of the initial, transition and final states reported in Figure 10. As can be seen, optimization of the initial state finds that adsorbed water coordinates to 2 K^+ ions, and is located just between them, thus shielding their electrostatic repulsion. Of course, this configuration is consistent with the high adsorption energy estimated from our DFT calculations. This special arrangement, in which the oxygen atom is located between two K^+ ions keeps all along the reaction pathway, finally leading to a hydroxyl anion bridging the two cations (Figure 10c). With respect to the hydrogen atom, it forms a H-Cu bond with a surface atom.

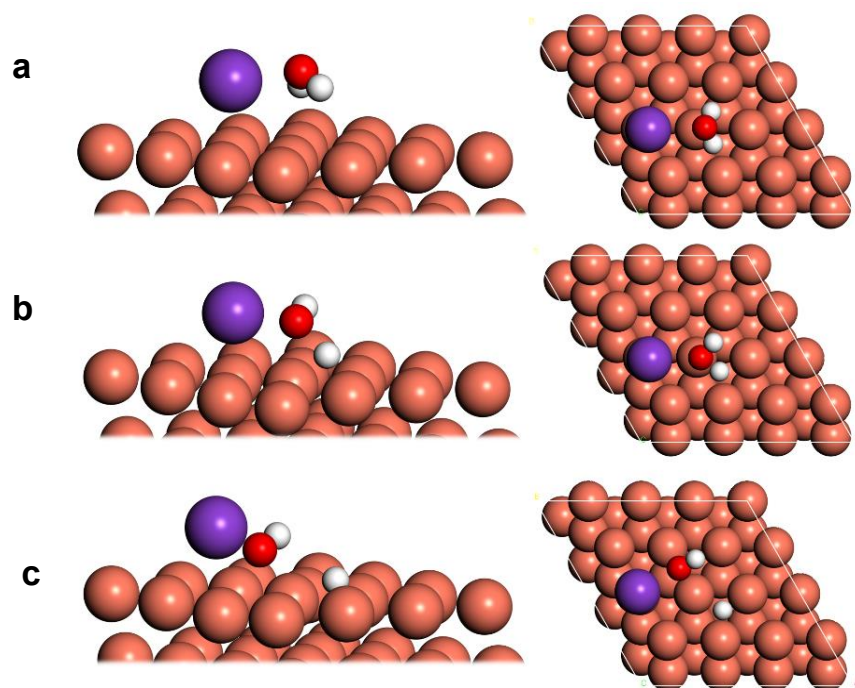


Figure 9. Initial (a), TS (b) and final geometries (c). Colors code: Cu (light brown), K (violet), O (red), H (white).

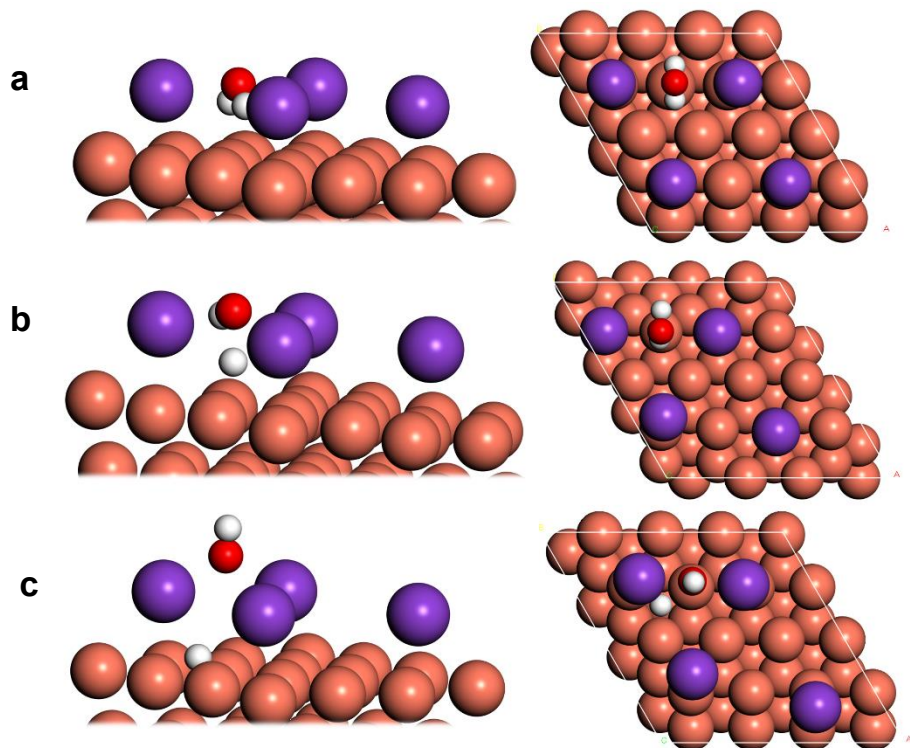


Figure 10. Initial (a), TS (b) and final geometries (c) for water dissociation on K(25%)/Cu(111). Colors code: Cu (light brown), K (violet), O (red), H (white).

Since surface Cu atoms close to K sites are negatively charged, the OH bond cleavage involved in this dissociation could be ascribed to the heterolytic type. We attribute to this special atomic arrangement the outstanding lowering of the activation energy computed for the water dissociation. In other words, for an efficient promoting effect, deposited K atoms must be located relatively close each other in order to allow the hydroxyl ions coming from water dissociation to be stabilized by bridging neighbors K^+ ions. Also, the presence of nearby K^+ ions ensures the existence of Cu^- centers needed to bind the proton resulting from the dissociation. This effect plays not only for the dissociation products but also for the activation barrier. That the promoting effect of K deposition is due to its arrangement on the surface is also consistent with the small influence played by water coverage, since as shown in the Table, increasing the water coverage to 25% only makes the reaction slightly endothermic while the activation barrier remains practically unchanged.

As aforementioned, due to simple geometrical considerations, the “theoretical” limit coverage for a K monolayer is 25%, which, on the other hand coincides with the maximum of activity experimentally observed. Let us now analyze, from a computational point of view, the effects of increasing K coverage beyond this limit. Our calculations show that increasing coverage beyond 25% leads to K atoms to arrange in a second layer. While the underlying K layer still are positively charged ($q_K = 0.63 |e|$), these extra K atoms are not oxidized ($q_K = \sim 0 |e|$). Their interaction with the underlying K/Cu surface also appears to be weaker, the adsorption energy being -0.87 eV (almost half of that found for 25%, -1.71 eV). This fact correlates very well with the observed evolution of the catalytic activity with K coverage that increases continuously from 0 to around 25%, decreasing beyond this

coverage. Assuming that the presence of K^+ and some Cu^- on the surface is needed, then, the activity increases as the coverage of K increases. However, beyond the 25% of K coverage, additional K atoms actually start covering the K/Cu surface, diminishing the availability of K^+ / Cu^- surface pairs, therefore hampering the reaction. Furthermore, the K atoms in a second adlayer will be more available to react with CO and form carbonate species, which eventually will kill the WGS reaction.^{15,44}

Water adsorption on the Cu/K/TiO₂(110) surface

Finally, the interaction of water with the three-component system containing K atoms and Cu NPs deposited on the TiO₂(110) surface was considered. To model the copper-oxide interface we used a Cu₈ nanocluster deposited near a row of bridging oxygens of the TiO₂(110) surface. Although this nanocluster might appear relatively small, its size falls within the range of NPs experimentally observed,³⁰ and, since we first used this model, it has been successfully employed by others to model the same interface,⁴⁹ as well as in studies of Cu/CeO_x/TiO₂(110) catalysts.³⁷ The K atom might anchor the surface at different sites and we found that it slightly prefers to be located near the Cu NP (See Figure 11a). The adsorption energies of K atom on the Cu/TiO₂(110) surface range between -3.7 and -3.9 eV, close to the values computed for the adsorption on bare TiO₂(110) surface (-3.6 eV).⁴³ Analysis of the charge density shows that K atom is also oxidized.

To examine the interaction of water with this surface we start by comparing the adsorption on bare TiO₂(110), K/TiO₂(110) and Cu/TiO₂(110) models. As can be seen in Table 3, the adsorption energies for pristine titania and K-modified titania surface are moderate and close each other (-1.02 and -1.06 eV)⁴³. In both cases the dissociation is

exothermic (-0.15 and -0.39 eV). In the case of Cu/TiO₂(110), the water molecule might interact directly with a copper atom of the cluster (Figure 11b) or with a copper atom and the titania interface simultaneously (Figure 11c). In the first case, the adsorption energy is -1.08 eV close to that reported by Peng *et al.*⁴⁹ using a similar Cu nanocluster, while in the second case, the adsorption energy increases to -1.45. Finally we address the interaction of water with the Cu/K/TiO₂(110) model. We have considered several possibilities and in Figure 11d we report a representative structure. As can be seen, water molecule simultaneously interacts with the Cu NP and the K ion, as well as a titanium surface atom. The adsorption energy at this site is moderate, -0.87 eV, midway of those computed for the Cu₈/TiO₂(110) model. However, what is outstanding in this case is the large dissociation energy that we have found: -0.72 eV. This value shows that the system is able to adsorb water and efficiently split it to give hydroxyl groups ready to participate in the reaction. Bearing in mind that the limiting step of the WGS reaction is the water dissociation, this result agrees with the high activity experimentally observed for the Cu/K/TiO₂ system.

Table 3. Adsorption (E_{ads}) and dissociation energies (E_{dis}), of water computed from different surface models. All values in eV.

Model surface	E_{ads}	E_{dis}
TiO ₂ ^a	-1.02	-0.15
K/TiO ₂ ^a	-1.06	-0.39
Cu/TiO ₂ (Interface)	-1.45	-0.21
Cu/K/TiO ₂	-0.87	-0.72

^a Reference 43

We can now try to compare the energies of water dissociation (limiting step) computed for the different models employed here with the experimental activity. Taking the average value for the high K coverage of the K/Cu system, we find that values of E_{dis}

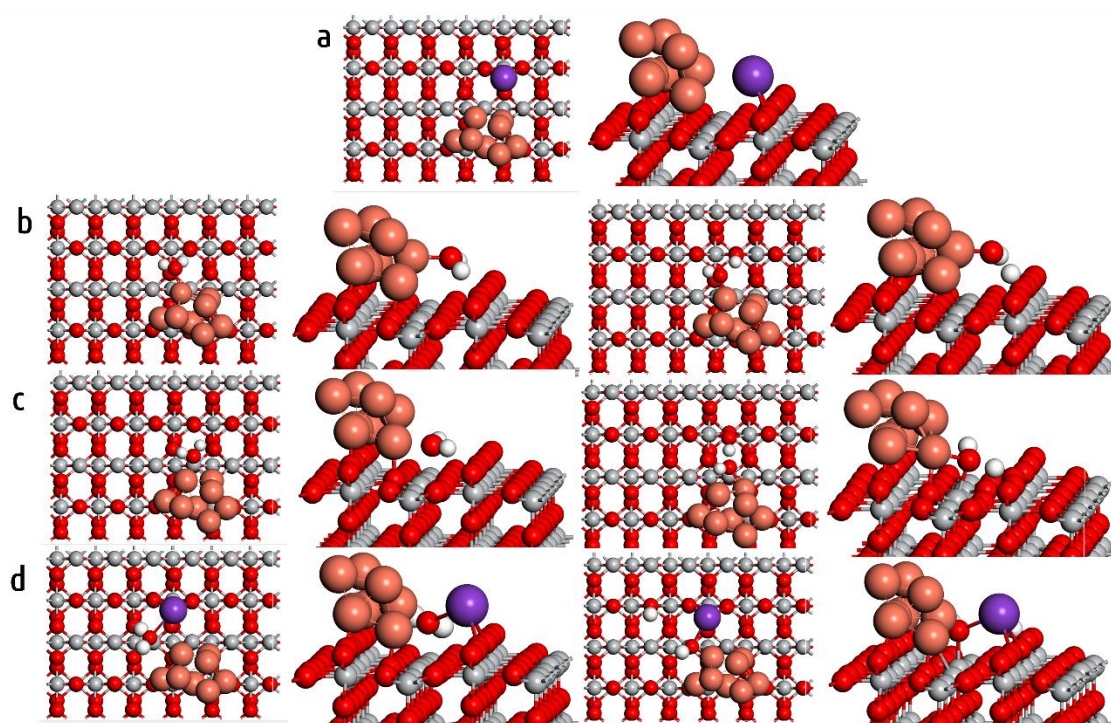


Figure 11. a) Model for adsorption of K and copper cluster top view (left image) and side view (right image). b) Water adsorption on Cu/TiO₂ on copper cluster from left to right molecular top and side view and dissociated water top and side view. c) Water adsorption on Cu/TiO₂ interface from left to right molecular top and side view and dissociated water top and side view d) Water adsorption on Cu/K/TiO₂ from left to right molecular top and side view and dissociated water top and side view. Colors code: Cu (light brown), K (violet), O (red), H (white).

follow the order $K/Cu \leq Cu/TiO_2 \ll Cu/K/TiO_2$, in agreement with the trend observed in Figure 5. Thus, in the Cu-K/TiO₂ interface, there is a synergy that clearly favors the dissociation of water and leads to an enhanced activity for the WGS reaction. Although the alkali certainly affects the metal, by far the major effect is on the metal-oxide interface. Indeed, a [metal-alkali-oxide] unit is present in highly active catalysts for the WGS.^{22,23,24} In Figure 5, Cu/K/TiO₂(110) is much more active than K/Cu(111). One finds changes which enhance the rate of hydrogen production by several orders of magnitude when going from a plain metal to an alkali-promoted metal-oxide interface. Thus, when optimizing the performance of a metal/oxide catalyst with a promoter, one must focus on the effects of the alkali on the metal-oxide interface. An optimization based on considering only alkali-metal interactions is a weak approximation from experimental and theoretical viewpoints. Therefore, the generation of [metal-alkali-oxide] units is essential to obtain catalysts which have an excellent performance for the WGS process.^{22,23,24}

Summary and conclusions

The addition of K atoms to Cu(111) and Cu/TiO₂(110) surfaces substantially enhances the rate for water dissociation and the production of hydrogen through the WGS reaction. In the range of temperatures investigated, 550-625 K, Cu/K/TiO₂(110) exhibits a WGS activity substantially higher than those of Cu(111) and a Cu/ZnO(000 $\bar{1}$) system used to model an industrial Cu/ZnO catalyst. The apparent activation energy for the WGS drops from 18 Kcal/mol on Cu(111) to 12 Kcal/mol on K/Cu(111) and 6 Kcal/mol on Cu/K/TiO₂(110). The results of density functional calculations show that K adatoms substantially favor the thermochemistry for water dissociation on Cu(111) and TiO₂(110).

Furthermore, at the Cu-KTiO₂ interface there is a clear synergy not seen at the Cu-K interface, and the alkali-metal-oxide interface has an unique ability to dissociate the water molecule and catalyze hydrogen production through the WGS process.

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