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Carbon Dioxide Photocatalytic Hydrogenation by Water on Well-Defined Non-stoichiometric Molybdenum Oxide Surface

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Abstract: Reaction between carbon dioxide and water on molybdenum oxide surface, induced by ultraviolet photons, has been studied in ultra-high vacuum by a set of surface sensitive techniques. On oxygen deficient Molybdenum oxide (IV), carbon dioxide quite efficiently hydrogenates via sequential conversion steps: formic acid – formaldehyde – methoxide – methanol. Molybdenum oxide should be only partly nonstoichiometric, while a certain part of the substrate surface should retain the MoO_2 stoichiometry to accommodate reaction intermediates.

Keywords: Surface Reaction, Model Catalysts, Metal Oxides, Carbon Dioxide, Water, Surface Science Techniques

1. Introduction

Synthesis of methanol as one of the most technologically relevant products deserves considerable interest from the scientific and technological viewpoints. Particularly important is its synthesis from the waste gases like carbon dioxide [1]. In this regard the main challenge is to develop corresponding new efficient catalysts which moreover do not contain precious metals, like Pt, Au, Pd, Ir. In this regard, the Cu/ZnO catalyst system is widely used for several important industrial processes, which include the synthesis of methanol, as one of the top-ten industrial products, and the forward and reverse water-gas-shift reactions [2, 3]. The system is complicated with the active catalyst being a coprecipitate of ZnO and Cu on an Al_2O_3 support [4]. Different works have looked at the various components of this system in order to illuminate their role in the catalytic process. These include investigations into the contribution of the copper nanoparticles [5, 6], the various facets of the ZnO substrate [7-9], the oxidation state of Cu [10-13] and alloying of Cu with Zn [14]. Despite of the very extensive research of CO_2 surface chemistry there are still some unresolved problems relating, for instance, to exact determination of the reaction sites and linking the nature of this sites to specific reaction pathways [2, 14]. To address the latter issue in view of metal/oxide model catalysts, one can use easy and controllably reducible oxides providing a set of metal ionic charges: Metal ionicity is considered to be an important factor in molecular surface reaction [15]. In this regard, MoO_3 is promising support because of the possibility of controllable reduction of Mo^{+6} to Mo^{+5}, Mo^{+4}, Mo^{+3}, Mo^{+2}.

The present work deals with the design of molybdenum oxide MoO_2 with a specific density of anionic vacancies for methanol synthesis from carbon dioxide and water. The choice of molybdenum oxide is motivated by the fact that this material, as stated above, is easily tunable in terms of defect nature and density, for instance by electron and ion bombardment or thermal treatment. The defects, in turn, considerably affect the catalytic behavior of the oxide.

2. Experimental

Investigations have been carried out in ultra-high vacuum chamber (base pressure: 10^{-10} Torr) by means of atomic force microscopy (AFM), reflection-absorption infrared spectroscopy (RAIRS), X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) using Al K_α (1486.6 eV) and He II (40.8 eV) irradiation, respectively [16, 17]. RAIRS was designed in reflection-absorption configuration, using p-polarized infrared beam. In this configuration the technique is sensitive to the molecular vibrations oriented along the surface normal. Amplification of electric field of incident and reflected waves at the surface plane enhances sensitivity of the technique at grazing incident and reflection angles. In the present configuration they were 83 degrees. A Mo(110) crystal serving as a substrate was mounted on a holder, which enabled cooling and heating of a sample to 90 and 2400 K, respectively. The sample was cleaned to remove foreign admixtures by the standard procedure of high-temperature annealing in an atmosphere of, first, oxygen and, then, hydrogen. Molybdenum oxide film was grown on Mo(110) bulk crystal by its oxidation in an oxygen ambient at partial pressure of 10^{-6} Torr and at a substrate temperature ranging from 1000 to 1300 K. According to previous results [18], thin surface oxide MoO_2(010) film grows at a substrate temperature of 1300 K, while thicker three-dimensional film grows after reducing the substrate temperature to 1000 K. Thick film develops into a periodically faceted surface with nanowirelike structures composed of MoO_2 (021) and (02-1) faces. The corresponding XPS spectra characterizing transition from Mo(110) substrate to thick MoO_2 film and reduced MoO_x ($x<2$) are shown in figure 1. The fact that the XPS spectrum contains no lines associated with Mo (110) evidences that the oxide film fully covers the surface of Mo (110) and has a sufficient thickness for retaining photoelectrons from the substrate. Taking into account the 1200 eV kinetic energy of these electrons, one can consider that the thickness of the oxide film is no less than 7 nm.

To reduce the as-grown MoO_2 oxide it was bombarded by Ar ions at energy of 1 keV and current density of 10 mA/cm^2 to produce oxygen vacancies of approximately of 1/4 of their initial concentration in surface region. It can be seen in figure 1 that the exposure to the ions results in a partial reduction of the oxide, which is manifested in the appearance of new low-energy photoelectron signals. Qualitative analysis of how the intensity of these lines varies under the ion bombardment indicates that about one-quarter of anionic vacancies are formed relative to the initial density of oxygen ions. After cooling the sample down to 90 K the carbon dioxide was admitted into the vacuum chamber up to 10^{-8} Torr, followed by subsequent inlet of water until the base pressure reached 10^{-6} Torr. Further, the sample was irradiated by laser light from pulsed ArF eximer laser (photon energy: 6.4 eV, fluence: 4 mJ/cm^2, pulse duration 9 ns, repetition rate: 10 Hz).

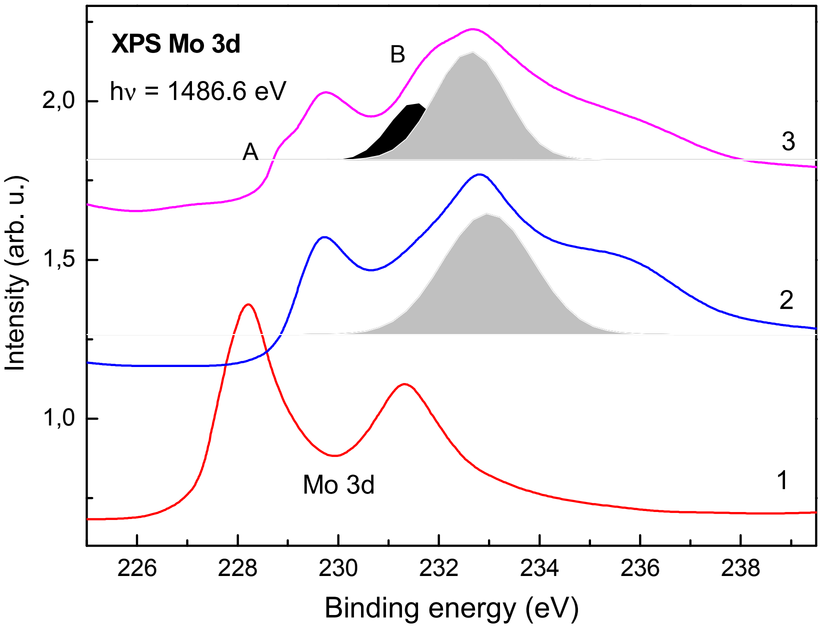

Figure 1. *X-ray photoelectron spectra of (1) Mo (110), (2) MoO_2 film with a thickness of about 7 nm, and (3) oxide film upon irradiation with 1 keV argon ions at a beam current density of 10 mA/cm^2 for 5 min.*

3. Results and Discussions

The UPS spectrum of $(CO_2+H_2O)/MoO_x$ after laser irradiation for 5 min and subtracted from UPS of bare MoO_x is shown in figure 2 (curve 1). To account for the observed spectral features this spectrum is compared with the spectrum of multilayer methanol film (curve 2). The qualitative agreement between these two spectra indicates that methanol molecules are formed when the $(CO_2 + H_2O)/MoO_x$ system kept at low temperature is exposed to photons. Some observed discrepancy between these two spectra is presumably due to the fact that along with the methanol there are some reaction intermediates at the surface. Nevertheless, the close intensities of the main photoelectron lines in spectra 1 and 2 demonstrate that carbon dioxide and water molecules are converted to methanol to a noticeable extent and a corresponding condensed layer is formed. It should be noted that the characteristic spectrum of CH_3OH is hardly observed in the absence of photons. Similarly, using a stoichiometric MoO_2 film as a substrate under the same experimental conditions does not lead, either, to formation of spectral features characteristic of methanol.

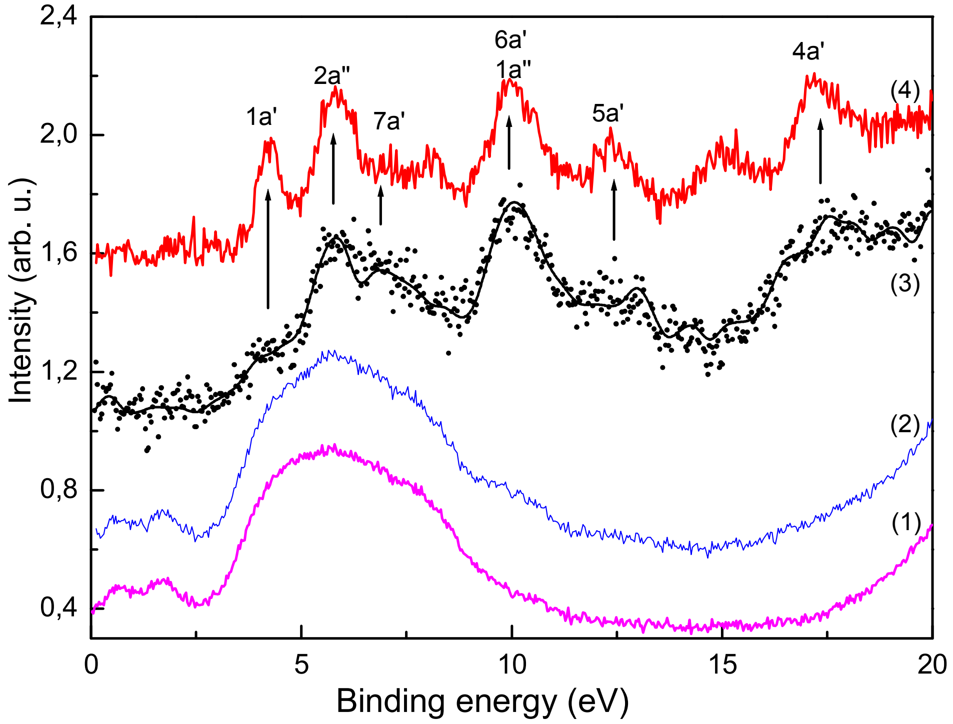

Figure 2. *UV photoelectron spectra of Mo (110) (curve 1) and Mo (110) on its being kept in the* $CO_2 + H_2O$ *atmosphere at 95 K, total partial pressure of* 10^{-6} *Torr, and exposure to laser light pulses with a photon energy of 6.4 eV for 5 min(curve 2). For clarity, the differential spectrum 2–1 (curve 3) is compared with the spectrum of a methanol film condensed on the* MoO_x *surface (curve 4).*

Vibrational properties of CO_2 on stoichiometric and non-stoichiometric oxide films are notably different. In the former case, as seen in figure 3, the RAIRS spectrum has no features, whereas for non-stoichiometric oxide there is absorption band observed at 1420 cm^{-1}. It means that defect sites are favorable adsorption sites, where molecular axis has non-zero dynamical dipole moment projection along the surface normal. As such, the defect sites may cause CO_2 molecular bond activation, leading to certain reaction intermediates. The known mechanisms of adsorption of CO_2 and H_2O molecules on the surface of oxides can be invoked as a possible explanation of the observed effect [4, 5]. For example, it has been well established that the CO_2 molecule is adsorbed on the stoichiometric metal oxide surface to yield carbonate-like compounds via formation of bonds between an oxygen atom of the molecule and an oxygen atom of the substrate and between the carbon and the substrate metal. At the same time, in the presence of anionic vacancies, the predominant adsorption configuration is that in which an anionic vacancy is filled by an oxygen atom of the carbon dioxide molecule. In both cases, the charge transfer from the substrate to the π-orbital of the molecule results in the molecular axis of CO_2 becoming deformed and the unstable configuration forming. The probability of formation of such a negatively charged configuration becomes higher due to filling of anionic vacancies by photoexcited electrons. When an H_2O molecule is adsorbed on the molybdenum oxide surface, it dissociates into H^+ and OH^- [4]. In the presence of an excess charge, which is generated in the given case via photoexcitation of carriers in the substrate, there occurs effective formation of the formate ion $CHOO^-$, which, interacting with the hydrogen ion released via $H_2O \rightarrow H^+ + OH^-$, yields CHOOH. It has been found that further conversion of CHOOH in the presence of an excess amount of hydrogen ions generated via dissociation of H_2O, enhanced by photons and substrate defects, occurs by the $CHOOH \rightarrow CH_2O \rightarrow CH_3O \rightarrow CH_3OH$ mechanism [3]. In this case, accommodation by the substrate of hydroxide ions formed in the reaction $H_2O \rightarrow H^+ + OH^-$ is necessary, which is enabled by the formation of oxy-hydroxide ions of the metal, $MoO(OH)^-$. These complexes are formed with the highest probability on the stoichiometric surface of the oxide [4]. This accounts for the fact that, for the above transformations to occur, molybdenum oxide should be only partly nonstoichiometric, while a certain part of the substrate surface should retain the MoO_2 stoichiometry. Otherwise, one can expect quite high poisoning of the substrate by hydroxylation of active sites.

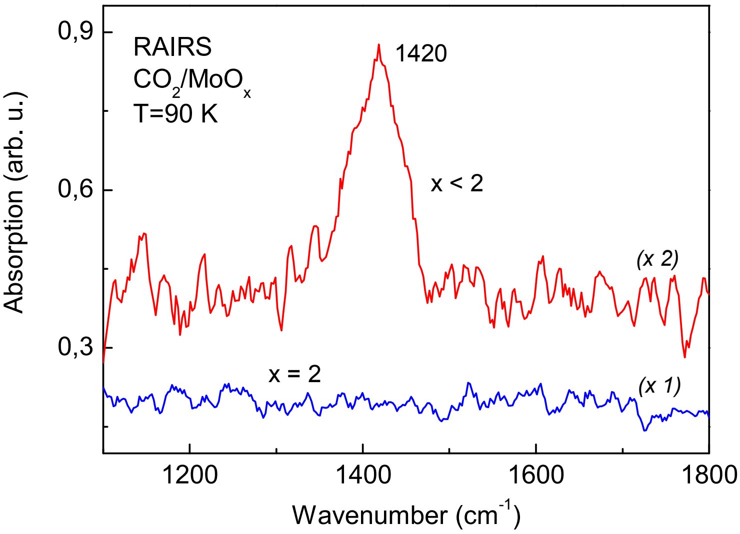

Figure 3. *RAIRS spectra of CO_2 at an exposure of 300 L adsorbed on stoichiometric (x=2) MoO_2 and non-stoichiometric (x<2) MoO_x held at 90 K.*

Formation of certain reaction intermediates is evidenced by reflection infrared absorption spectra recorded after successively increasing laser irradiation time (figure 4). It is seen that initially methoxy and formaldehyde, characterized by C-O stretch vibration wavenumbers of 1000 cm^{-1} and 1725 cm^{-1}, respectively, are formed. At higher irradiation time these species are almost totally converted to methanol, characterized by the wavenumber of 1050 cm^{-1}. An apparent red shift of the band in curve 5, compared to the band of multilayer condensed methanol (curve 6) and a trace intensity of the band at 1725 cm^{-1}, indicates that there are still some intermediates, like methoxy and formaldehyde, remaining at the surface. This also explains some observed discrepancy in UPS spectra of (CO_2+H_2O) irradiated film and condensed overlayer of methanol (figure 4). At the same time, qualitative analysis of infrared intensities implies that the amount of reaction intermediates is at the level not exceeding 10 %. Thus, MoO_2 with submonolayer concentration of anionic vacancies (c.a. 25%) is an efficient model catalyst for methanol photosynthesis from carbon dioxide and water.

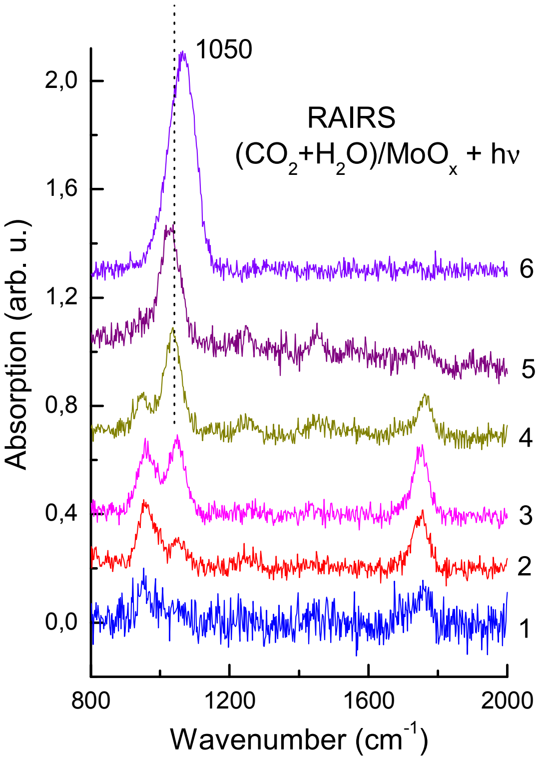

Figure 4. *Infrared spectra in CO stretch region during laser irradiation of mixture of CO_2 and H_2O on the surface of MoO_x at 90 K (1-5). Irradiation time, min: 1-1, 2-2, 3-3, 4-4, 5-6. Curve 6 corresponds to condensed methanol overlayer.*

4. Conclusion

By means of surface sensitive techniques, it has been shown that CO_2 hydrogenates by H_2O on non-stoichiometric Molybdenum oxide surface under the effect of ultraviolet photons via sequential conversion steps: formic acid – formaldehyde – methoxide – methanol. The key role is played by the processes of adsorption and bond activation of CO_2 and H_2O molecules on surface defects of the substrate enhanced by the exposure to photons.

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References

[1] Burghaus U; *Progr. Surf. Sci.*; 2014, 89, 161.

[2] Saito M; Murata K; *Catal. Surv. Asia*; 2004, 8, 285.

[3] Karelovic A; Bargibant A; Fernández C; Ruiz P; *Catal. Today*; 2012, 197, 109.

[4] Ertl G; Knotzinger H; Weitkamp J; *Handbook of Heterogeneous Catalysis*; VCH; Weinheim, Germany, 2008.

[5] Koplitz L. V.; Dulub O; Diebold U; *J. Phys. Chem.*; 2003, B 107, 10583.

[6] Kroll M; Köhler U; *Surf. Sci.*; 2007, 601, 2182.

[7] Meyer B; Marx D; *Phys. Rev.*; 2003, B 67, 03540.

[8] Schiek M; Al-Shamery K; Kunat M; Traeger F; Wöll C; *Phys. Chem. Chem. Phys.*; 2006, 8, 1505.

[9] Wöll C; *Prog. Surf. Sci.*; 2007, 82, 55.

[10] Dulub O; Batzill M; Diebold U; *Top. Catal.*; 2005, 36, 65.

[11] Lazcano P; Batzill M; Diebold U; Haberle P; *Phys. Rev.*; 2008, B 77, 035435.

[12] Dai X. Q.; Yan H. J.; Wang J. L.; Liu Y. M.; Yang Z; Xie M. H.*; J. Phys.: Condens. Matter*; 2008, 20, 095002.

[13] Ozawa K; Oba Y; Edamoto K; *Surf. Sci.*; 2009, 603, 2163.

[14] Behrens M; Studt F; Kasatkin I; Kühl S; Hävecker M; Abild-Pederson F; Zander S; Girgsdies F; Kurr P; Kniep B. L.; Tovar M; Fischer R. W.; Nørskov J. K.; Schlögl R; *Science*; 2012, 33, 893.

[15] Freund H-J; Roberts M. W.; *Surf. Sci. Reports*; 1996, 25, 225.

[16] Tvauri I. V.; Gergieva B. E.; Magkoeva V. D.; Grigorkina G. S.; Bliev A. P.; Ashkhotov O. G.; Sozaev V. A.; Fukutani K; Magkoev T. T.; *Solid State Commun.*; 2015, 213, 42.

[17] Magkoev T. T.; *Surf. Sci.*; 2007, 601, 3143.

[18] Radican K; Berdunov N; Shvets I. V.; *Phys. Rev.*; 2008, B77, 085417.