Reduced molybdenum oxide MoO$_x$ (x<2) as a model catalyst for methanol photosynthesis from carbon dioxide and water

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ABSTRACT

By means of X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), atomic force microscopy (AFM) and reflection-absorption infrared spectroscopy (RAIRS) it is shown that methanol is formed from carbon dioxide and water on the surface of reduced molybdenum oxide substrate MoO$_x$ (x<2) under pulsed laser irradiation at photon energy of 6.4 eV, pulse duration 9 ns and laser fluence of 4 mJ/cm^2. The key factor is MoO$_x$ defect enhanced photoinduced substrate mediated CO$_2$ and H$_2$O bond activation, leading to formation of reaction intermediates: CH$_2$O$_2$ → CH$_2$O → O–CH$_3$, forming finally methanol.

Keywords: surface reaction, model catalysts, metal oxides, methanol synthesis, carbon dioxide, water, surface science techniques

1 INTRODUCTION

Synthesis of methanol as a top ten industrial 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$_2$O$_3$ 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 [1,14]. 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

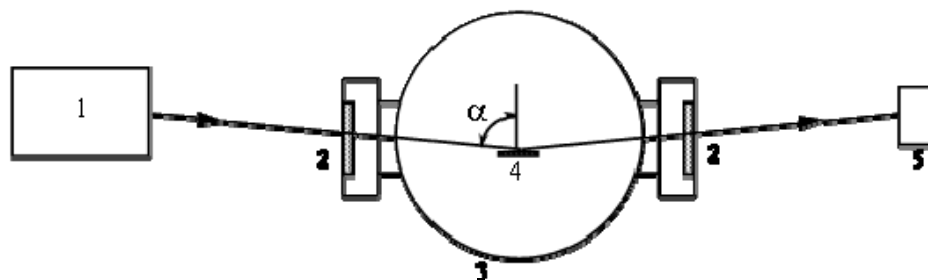Figure 1: RAIRS scheme. 1-interferometer, 2-CaF$_2$ windows, 3–UHV chamber, 4–sample, 4–CdHgTe detector

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 configuration, shown in Fig. 1,   using p-polarised 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 prsent configuration they were 83 degrees. A Mo (110) crystal serving as a substrate was mounted in a holder, which enabled cooling and heating of a sample to 95 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)
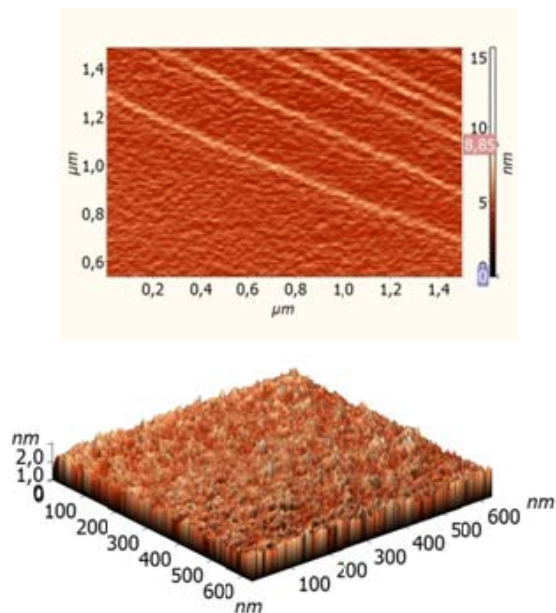

Figure 2: AFM image of MoO_2 11 nm thick film on Mo(110) crystal before (upper image) and after Ar ion bombardment (lower image).

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 AFM image of MoO_2 as-grown thick film and the XPS spectra characterizing
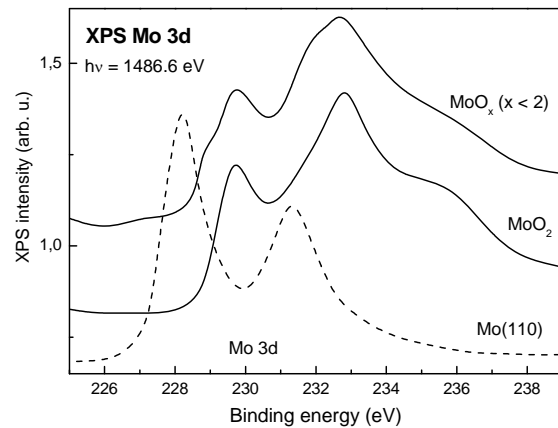

Figure 3: XPS spectra of Mo(110) crystal, MoO_2 11 nm thick film and reduced by about 25% of oxygen density the MoO_x.

transition from Mo(110) substrate to thick MoO_2 film and reduced MoO_x (x<2) are shown in Figs. 2 and 3, respectively. 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 Fig. 2 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. Additionally, as seen in Fig 2, ion bombardment causes smoothing of rough relief of the surface, still leaving surface roughness at nanometer scale. 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).

3 RESULTS AND DISCUSSION

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 Fig. 4 (curve 1). To account for the observed spectral featurtes 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 intermedietaes 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
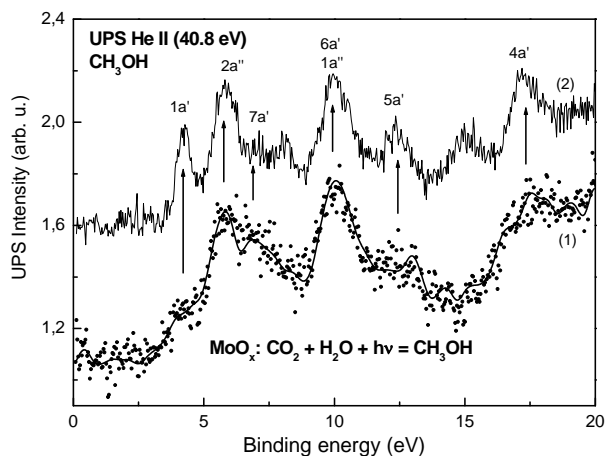
atom of the molecule and an oxygen atom of the substrate and between the carbon and the substrate metal. At the same time, in the presence of anionic vacancies, the predominant adsorption configuration is that in which an anionic vacancy is filled by an oxygen atom of the carbon dioxide molecule. In 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,

Figure 4: Comparison of UP spectrum of methanol multilayer condensed film on MoO_x (2) with the spectrum obtained after exposure of MoO_x in an ambient of CO_2 and H_2O to photons (1).
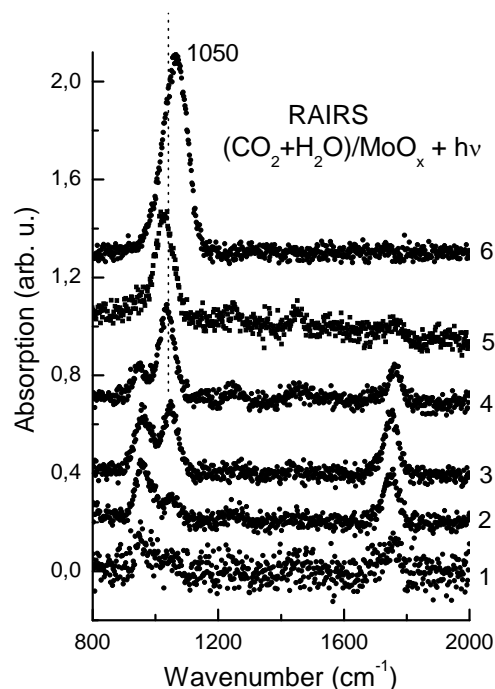

Figure 5: Infrared spectra in CO stretch region during laser irradiation of mixture of CO_2 and H_2O on the surface of MoO_x at 90 K (1-5). Irradiation time, min: 1-1, 2-2, 3-3, 4-4, 5-6. Curve 6 corresponds to condensed methanol overlayer.

characteristic of methanol. In this context, it should be assumed that the key factors responsible for the formation of methanol from carbon dioxide and water are the presence of anionic vacancies and exposure to photons. 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

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 hydroxilation of active sites. Formation of certain reaction intermediates is evidenced by reflection infrared absorption spectra recorded after succesively increasing laser irradiation time (Fig. 5). 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 still some intermediates, like methoxy and formaldehyde, remaining at the surface. This also epxlains some observed discrepancy in UPS spectra of (CO_2+H_2O) irradiated film and condensed overlayer of methanol (Fig. 4). At the same time, qualatative analysis of infrared intensities implies that the amount of reaction intermediates is at the level not exeeding 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.

4   CONCLUSION

By means of surface sensitive techniques it has been shown that methanol is effectively formed from carbon dioxide and water in an ultrahigh vacuum on the surface of molybdenum oxide MoO_2 with a submonolayer concentration of anionic vacancies at a substrate temperature of 95 K under the action of laser light with a photon energy of 6.4 eV. 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.

5   ACKNOWLEDGEMENTS

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