



Methanol on Co(0001): XPS, TDS, WF and LEED results

K. Habermehl-Ćwirzeń^{a,b,*}, J. Lahtinen^a, P. Hautojärvi^a

^a *Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02150 HUT, Helsinki, Finland*

^b *Department of Material Science, Darmstadt University of Technology, Petersenstr. 23, D-64287 Darmstadt, Germany*

Received 23 June 2005; accepted for publication 23 August 2005

Available online 21 October 2005

Abstract

The adsorption and decomposition of methanol on clean Co(0001) was studied as a function of temperature and exposure by means of TDS (thermal desorption spectroscopy), XPS (X-ray photoelectron spectroscopy), WF (work function measurements) and LEED (low energy electron diffraction). Methanol was adsorbed by OH-bond scission as methoxide on the cobalt surface. TD and XP spectra revealed that beside a small amount of molecularly desorbing methanol, it decomposed during heating to the final products: CO and H₂. Desorption of H₂ took place around 356 K and desorption of CO around 390 K. These temperatures are characteristic for desorption of these species on clean cobalt. Work function measurements showed that the adsorption of methanol resulted in a lowering of the WF by 1.1 eV. Heating – and therewith decomposition – led to an increase in the WF of +0.4 eV. After all decomposition products had desorbed, the WF returned to the value for the clean Co(0001) surface. LEED exhibited a combination of two ordered structures: $p(2 \times 2)$ and $(\sqrt{7} \times \sqrt{7})19.1^\circ$. The $(\sqrt{7} \times \sqrt{7})19.1^\circ$ pattern was formed by methoxide or hydrogen and vanished below 340 K. The $p(2 \times 2)$ structure was still found above 380 K and was therefore assigned to CO. © 2005 Elsevier B.V. All rights reserved.

Keywords: Methanol; Cobalt; Low energy electron diffraction (LEED); Low index single crystal surfaces; Thermal desorption spectroscopy; X-ray photoelectron spectroscopy; Work function measurements

1. Introduction

In the past decade fuel cell technology became one of the environmentally friendly developments

in the automobile related industry. Liquid methanol is a promising fuel, but the decomposition of methanol on board to CO and hydrogen is an even cleaner and more efficient process [1]. Commonly used catalysts in fuel cells are Ru-based or Pd-based. As these materials are expensive, alternatives with similar capabilities towards the decomposition of methanol are needed; and here cobalt is a promising candidate [2]. The pres-

* Corresponding author. Address: Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02150 HUT, Helsinki, Finland. Fax: +358 9 451 3116.

E-mail address: kha@fyslab.hut.fi (K. Habermehl-Ćwirzeń).

ent work gives insight as to why cobalt might successfully replace the traditional materials used in fuel cell catalysts.

The research of cobalt catalysts as a support for methanol decomposition is rather limited. So far, the adsorption of methanol has been studied only on Mo-supported cobalt [3,4]. The results show competition between molecular methanol desorption and O–H bond scission at 210 K. Above that temperature methoxide and hydrogen are found on the surface. Methoxide further decomposes to hydrogen and CO, which desorb at 350 K and 430 K, respectively. C–O bond scission – resulting in atomic carbon and oxygen – is detected but related to presumable defects in the cobalt overlayer enabling methanol adsorption and dissociation on Mo.

Transition metals, which prevent CO bond scission from occurring during CO adsorption, are also believed to retain the C–O bond in the case of methanol adsorption [3]. This holds for Ni(100), Pd(111) and Cu(110) where the CO adsorption as well as methanol adsorption is molecular and for Fe(110) where the adsorption of both species is dissociative. In this respect cobalt should be an interesting material, as dissociation of CO has been detected on open surfaces and surface defects but not on close packed surfaces [5].

Besides these studies, the adsorption of methanol has been investigated on some other metal surfaces, given below in the order of onset of the dissociation temperature. The activation energy for desorption of methanol ranges from 40 kJ/mol on Ag(111) [6] 41 kJ/mol on Cu(100) [7], 45 kJ/mol on Pd(100) [8], 46 kJ/mol on Cu(110) [9], 47 kJ/mol on Pt(111) [7] to 54 kJ/mol on Cu(111) [10].

On Ni(100) methanol starts to dehydrogenate at 160 K to form methoxide species, which further decompose above 240 K to CO adsorbed on the bridge sites [11]. On Pd(111), at low coverages methanol decomposes via methoxide intermediates and then dehydrogenates completely to desorb as CO. At near monolayer coverage the methanolic C–O bond dissociates at 175 K to produce $\text{CH}_{3,\text{ads}}$, which is stable up to 400 K. A stepwise dehydrogenation of $\text{CH}_{3,\text{ads}}$ to form $\text{CH}_{2,\text{ads}}$ (methylene) and CH_{ads} (methylidyne) is observed above 400 K [12].

On Cu(110) annealing causes dissociation into methoxide and formaldehyde around 200 K before all molecular species eventually desorb from the surface [13].

On Al(111) [14] and Fe(110) [15] the adsorption is dissociative already at 100 K. On clean Fe(110) methoxide dehydrogenates around 400 K, yielding gaseous H_2 and CO. The hydroxyl hydrogens leave the surface as H_2 at the slightly lower temperature of 375 K. Carbon–oxygen bond scission competes with CO evolution at 400 K, accounting for about 25% of the CO yield on clean Fe(110).

Our study deals with the adsorption, dissociation and desorption behaviour of methanol on Co(0001). This fundamental study should be helpful in developing new cobalt-based methanol decomposition catalysts.

2. Experimental

All experiments were carried out in an UHV system equipped with facilities for TDS, LEED, XPS and work function measurements. The operating base pressure was of 2×10^{-10} Torr.

The cobalt sample was fixed to the sample holder by 0.25 mm tantalum wires, which in addition served for resistive heating and conducting heat to the liquid-nitrogen-cooled heat sink. The temperature range for the measurements was between 160 K and 690 K. The lower temperature was restricted by the cooling system, the upper by the phase transformation of cobalt from hcp to fcc. The temperature of the sample was monitored continuously by using a chromel–alumel thermocouple spot welded on the sample surface. For a detailed description of the apparatus the reader is referred back to our previously published articles [16–19].

A disc-shaped Co(0001) single crystal with a diameter of 11 mm served as the sample. The initial cleaning procedure was published in an earlier paper [17]. To obtain a clean surface the sample underwent sputtering and subsequent annealing before each experiment. This procedure removed all surface contamination and an atomically smooth vacuum–solid interface was obtained. The cleanliness was controlled by XPS and LEED.

Download English Version:

<https://daneshyari.com/en/article/9594997>

Download Persian Version:

<https://daneshyari.com/article/9594997>

[Daneshyari.com](https://daneshyari.com)