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Methanol decomposition on Ru(0001) during continuous exposure at room temperature

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ABSTRACT

Using infrared vibrational spectroscopy, we have studied the chemical reactivity of methanol on Ru(0001) under experimental conditions closer to real catalysts than those existing in most of the literature. We have performed experiments in the pressure range from 10^{-8} to 10^{-3} mbar, exposing the surface to large gas doses at room temperature. We show the co-existence of two active paths: one involves the complete dehydrogenation of methanol into CO, the other one promotes the scission of the C–O bond of methanol, leaving carbon and oxygen on the surface, which, after large exposures, deactivate the surface towards a further evolution of the molecular adlayer. In no case, the presence of stable reaction intermediates is detected along either of the two reaction paths. We have compared the behavior of flat ruthenium surfaces with those having a variable concentration of controlled surface defects. Surface defects, mainly steps, seem to accelerate the rate of both reaction paths, but do not activate any new reaction path or stabilize intermediates.

1. Introduction

Methanol is a simple hydrocarbon and the smallest alcohol. Yet, it shows a variety of molecular bonds: C–O, C–H and O–H. The selective activation of each of these chemical bonds on different types of substrates makes methanol a good model molecule for fundamental research. In addition, and from the point of view of technical applications, the use of methanol in direct methanol fuel cells (DMFCs) has boosted a lot of applied research. Moreover, this alcohol is one of the most important raw materials in industry. Thus, the interactions of methanol with solid surfaces are of great interest and have been widely studied in basic and applied research, both theoretically and experimentally.

Methanol adsorption has been mostly investigated on transition metal surfaces, such as Pt [1,2], Pd [3,4], Rh [5], Co [6] or Mo [7], to name a few examples. Studies of methanol adsorbed on ruthenium surfaces are specially significant since ruthenium is one of the two main components of commercial catalysts in the anode of DMFCs, where the extraction of hydrogen from methanol takes place. Several groups have studied the reactivity of methanol adsorbed on Ru(0001), either on clean surfaces [8–16], or in surfaces modified with preadsorbed oxygen [17–19]. The latter are mainly motivated by the possibility of stabilizing intermediate species such as formaldehyde.

There is a general consensus in the literature [8–16], that methanol easily dehydrogenates on clean Ru(0001), leaving CO on the surface. However, some serious discrepancies arise about the specific decomposition mechanisms and kinetics. Some authors [11] report that, under certain conditions along the dehydrogenation path, formaldehyde (CH_2O) is stabilized at the Ru(0001) surface by surface carbon, up to temperatures as high as 420 K. More recent works [15,16], however, have not observed formaldehyde stabilized on Ru(0001) under the conditions reported in the previous research [11]. Since formaldehyde is a key raw material, the ability of the surface to activate specific reaction channels to produce it and the conditions under which the activation may take place are issues with potential industrial application.

Another controversial issue in the literature is the possible existence of a second path during methanol decomposition: the scission of the C–O bond on the Ru(0001) surface. This scission would lead to the growth of hardly removable surface carbonaceous species, a process which, in turn, might lead to the catalyst deactivation. On other metal surfaces, such as Pd(111) [20] and Ir(111) [21], the activation of the C–O bond scission in methanol has been recognized. In the case of the alcohol adsorbed on Ru(0001), whereas some authors [8,11] have reported the existence of this channel, in a very recent work, other authors [16] have discarded it. To develop an understanding of methanol fuel cell surface chemistry, further investigations are clearly needed to clarify the existing discrepancies in the methanol/Ru(0001) system.

The influence of surface defects on chemical reactivity, often invoked but seldom systematically addressed, can be hardly overemphasized. Several works have reported an enhanced chemical activity of surface steps on ruthenium surfaces for certain reactions, such as NO dissociation [22]. Theoretical studies using DFT calculations suggest that, on a Ru(0001) surface, both a preferred chemisorption of O or N

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[23] and an enhanced activity towards CO oxidation [24] take place at the steps. Experimental work also points out at the presence of active oxygen at surface steps, where it is adsorbed with a higher local coverage and promotes the oxidation of CO [25]. Furthermore, a very recent work [26] provides evidence that on a ruthenium surface, CO dissociates just at surface steps. With respect to methanol adsorption, Schauermann et al. [27] provide evidence of the preferential C–O bond scission of methanol at the edges and steps of Pd nanoparticles and other authors [20] also observe an influence of surface defects on the scission when the molecule is adsorbed on Pd(111). Moreover, it has been reported that methanol dehydrogenation on Pt(111) takes place exclusively at the surface steps [1].

Here, we report the results of our investigation of methanol adsorption and evolution on the Ru(0001) surface. Results of oxygen and methanol co-adsorption will be deferred to a forthcoming publication. We address, specifically, these fundamental and controversial issues:

1. the stabilization of intermediates during methanol dehydrogenation on the surface.
2. the scission of the C–O bond as another possible reaction path.
3. the role of surface defects on methanol reactivity.

Most previous work has taken place under conditions far from those existing on the surface of real catalysts in terms of gas pressure, environment, temperature and catalyst structure and composition. In an attempt to bridge this *gap*, we have carried out most of the experiments at room temperature, at relatively high pressures and exposures and both on flat and defective Ru surfaces.

We have covered a wide range of pressures, from 10^{-8} to 10^{-3} mbar while keeping untouched the surface sensitivity of the IRAS technique. The surface has been exposed to the gas continuously, for long times (of the order of hours) and long exposures (up to the order of 10^7 L). Note that certain reaction events may remain undetected at low temperatures and short exposures due to their low probability. However, after long exposures, they may even control the evolution of the surface. Surface poisoning species may also build up by these slow growth processes. Regarding the issue of *real* surfaces, note that an atomically flat surface of a single crystal cannot fully capture the structural, morphological and compositional complexity of the surfaces of real catalysts. To check whether the defects act as active sites and promote new reactions, we have carried out parallel experiments on both flat and defective surfaces, the latter assembled in a controlled way.

2. Experimental

The experimental system is composed of two UHV chambers: a preparation chamber with some common surface analytical and preparation techniques and an infrared cell (connected to but isolated from the main chamber) where Fourier-Transform Infrared Reflection-Absorption Spectroscopy (FT-IRAS) is carried out. This chamber, routinely kept in UHV conditions, can also reach higher pressures. The pressure attained is limited by the optical absorption of the gas phase which can hide, undesirably, the absorption bands of surface species. In the present study, we can reach methanol background pressures of 10^{-2} mbar without reaching that limit. To avoid unwanted reactions from hot filaments, the pressure is measured with a cold cathode gauge.

The ruthenium surface is routinely cleaned with argon ion bombardment, with an energy of 1 keV, followed by low pressure (5×10^{-7} mbar) oxygen exposures and several high temperature flashes up to 1350°C. After pumping out the oxygen, a final flash, reaching 1400°C is carried out to remove the oxygen from the surface. The surface defects on the Ru(0001) surface are generated by controlled low energy Ar^+ bombardment, with a differentially pumped ion gun. The beam is rastered to ensure a homogeneous ion dose all over the surface. The Atomic Force Microscopy (AFM) images, recorded ex-situ, were taken in air with a Nanotec instrument in non-contact mode.

The interferometer is a Bruker Vertex 80v instrument, with a MCT external detector, fully evacuated to reduce atmospheric perturbations. FT-IRAS spectra are carried out in a grazing incidence configuration, with the incident and reflected beams passing through BaF_2 windows. A typical measurement consists of the acquisition of about 1600 spectra, with a resolution of 4 cm^{-1}. The exposure of the surface to the gases (methanol 99.8%, CO 99.995%, O_2 99.999% and H_2 99.999%) is carried out by backfilling the system with a background pressure. Methanol is purified by several freeze-pump-and-thaw cycles before each experiment. To reduce the possibility of introducing impurities, all the gas lines and the flask containing the methanol are evacuated with a turbomolecular pump.

3. Results and discussion

3.1. Methanol reactivity on flat Ru(0001)

The first set of experiments consists of a continuous exposure of the flat Ru(0001) surface to a methanol background pressure, at room temperature, while infrared spectra are continuously taken.

We attempt to cover a large set of exposures, from a few langmuirs (where the molecular adlayer on the ruthenium surface qualitatively changes) to long exposures, of the order of 10^7 L. To capture in reasonable experimental times such a wide range of exposures, the pressure is increased between successive spectra. Table 1 shows all the methanol pressures and exposures used in the present work. The acquisition of each spectrum lasts 12 min. The cumulative exposures appearing in the graphs are those at the end of the acquisition of the corresponding spectrum. As the surface adlayer is evolving in time, and the spectra acquisition lasts 12 min, each IRAS spectrum reflects the corresponding temporal average.

Fig. 1 shows the evolution of the IRAS spectra as the pressure and the exposure increase. At the lowest exposures, a broad peak around 2020 cm^{-1}, with a shoulder at higher wavenumbers, evolves into a clear double peak, growing both in frequency and intensity.

These bands correspond to the stretching mode of CO, placed on-top, adsorbed in different symmetries [28]. Furthermore, the fact that the double peak is present in consecutive spectra implies that two types of CO adlayers (or domains) indeed coexist on the surface. For exposures around 50 L, the double band evolves into a single band, which gradually decreases. After 1.4×10^4 L this band splits into a double band again which, for higher coverage, decreases both in frequency and intensity. The LEED pattern taken after the acquisition of spectrum number 14 is shown in Fig. 1b. While the CO coverage

Table 1
Methanol pressures during the acquisition of each successive IRAS spectrum with the corresponding cumulative methanol exposures.

Spectrum	Pressure (mbar)	Exposure (L)
1	1.0×10^{-8}	5.4
2	2.5×10^{-8}	19
3	6.3×10^{-8}	53
4	1.6×10^{-7}	1.4×10^2
5	4.0×10^{-7}	3.6×10^2
6	1.0×10^{-6}	9.0×10^2
7	2.5×10^{-6}	2.2×10^3
8	6.3×10^{-6}	5.6×10^3
9	1.6×10^{-5}	1.4×10^4
10	4.0×10^{-5}	3.6×10^4
11	1.0×10^{-4}	9.0×10^4
12	2.5×10^{-4}	2.2×10^5
13	3.0×10^{-4}	5.6×10^5
14	1.6×10^{-3}	1.4×10^6
15	$>10^{-3}$	$>1.0\times10^7$
16	$>10^{-3}$	$>2.0\times10^7$