Methanol oxidation on Ru catalysts: reaction pathways and catalytically active states

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Abstract

Surface composition and corresponding catalytic activity and selectivity of model Ru catalysts in methanol oxidation have been studied in the 10^{-1} mbar pressure range for three oxidation regimes, combining in situ synchrotron based X-ray photoelectron spectroscopy (XPS) with simultaneous monitoring by online mass spectrometry the products released to the gas phase. Ru $3d_{5/2}$ and O1s XP core level spectra provide clear evidence that the composition of catalytically active steady states exhibiting different activity and selectivity originate from interactions with reactants and are dynamically controlled by the reactants partial pressure and temperature.

Introduction

Selective oxidation of methanol (CH_3OH) to formaldehyde (CH_2O) has attracted a lot of interest because formaldehyde is a primary reagent in many organic syntheses. Along with the most commonly used metallic Ag and Cu or Mo and V oxide catalysts, a remarkable activity for CH_2O production at rather low temperature (300 K -400 K) has been recently reported for supported RuO_2 catalysts [1]. Their high catalytic activity is attributed to fast redox cycles. Recent studies focusing on identification of catalytically active states in redox reactions have provided strong evidence that both structure and chemical state of the catalyst can be far different from those of the stoichiometric oxide compounds used as models for explaining Mars-van Krevelen oxidation mechanism. A Ru transient "surface oxide" (TSO) state, Ru_xO_y, has been found to be active for CO oxidation at mbar pressures [2]. Extensive structural, photoemission and TPD studies characterized the TSO state as a disordered phase with 1-4 ML oxygen incorporated within the top few Ru layers, which precedes the nucleation and growth of the stoichiometric RuO_2 phase [3,4]. The TSO state exists in a pressure-temperature range, where the formation of the thermodynamically stable RuO_2 is kinetically hindered and it can also coexist with the growing RuO_2 islands.

In contrast to CO oxidation, the reaction mechanism in CH_2O production from CH_3OH is complicated by multiple possible reaction pathways. The present study of CH_3OH oxidation on model Ru(0001), Ru(10$\bar{1}$0), and polycrystalline Ru catalysts addresses the catalytically active states under different reaction conditions. Ru 3d and O1s X-ray photoelectron core level spectra (XPS) were used as fingerprints for the dynamic response of the catalysts surface active state to changes in temperature and CH_3OH/O_2 molecular mixing ratio.

Experimental

The experiments have been performed at the synchrotron facility BESSY in Berlin in the high pressure XPS station designed and constructed in FHI-MPG. The gas phase products were monitored by a differentially pumped HIDEN mass spectrometer. The MS response was used as a measure of the catalytic activity. Ru3d and O1s XP spectra were measured with photon energies of 450eV and 650eV, respectively. This results in an effective escape depth for the O1s and Ru3d photoelectrons of ~5Å, which limits the probing depth to the top few layers (~10Å). The catalyst temperature was changed stepwise. The investigations were carried out in the pressure range of $10^{-2} – 10^{-1}$ mbar using different CH_3OH / O_2 mixing molecular ratios.

Results and discussion

Our results clearly show that the $CH_3OH:O_2$ mixing ratio controls the Ru reduction-oxidation equilibrium attaining the steady catalyst states independently of the initial pre-catalyst state. Fig. 1A shows Ru $3d_{5/2}$ XP spectra taken at steady state conditions corresponding to different catalyst selectivity. The deconvolution of the Ru $3d_{5/2}$ core level reveals 3 components that can be assigned to the bulk metallic component Ru_{bulk}, Ru with adsorbed oxygen Ru_{ad} and transient "surface oxide" Ru_xO_y (TSO), respectively. $Ru_{ad\&TSO}/Ru_{bulk}$ abundance ratios higher than 0.3 mark the incorporation of oxygen and the formation of the TSO state. For the catalytically active states favouring partial oxidation of methanol to: $CO+H_2+H_2O$ (a) and CH_2O+H_2O (b), and full oxidation to CO_2+H_2O (c) we evaluated the $Ru_{ad\&TSO}/Ru_{bulk}$ abundance ratios 0.15, 0.46, and 0.56, respectively. Apparently, the only difference in the catalytically active TSO states for partial oxidation to CH_2O and full oxidation to CO_2 is in the amount of accumulated oxygen, whereas the partial oxidation to $CO+H_2+H_2O$ occurs on metallic Ru only with submonolayer of adsorbed oxygen. The established steady states exhibit different activity and favour specific reaction pathways (Fig. 1B). The figure

compares the catalytic activities of the three catalyst states elucidated from the total yield of C-containing products (CO, CH_2O, CO_2) and from the corresponding methanol consumption.

A)

B)
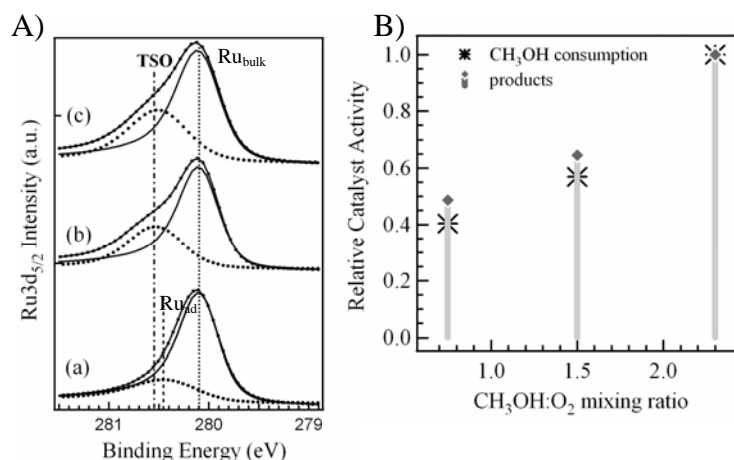
Figure 1 (A): *Deconvoluted Ru $3d_{5/2}$ XP spectra of the catalyst steady states measured in the temperature range 570K-620K, representing the oxidation regimes favouring oxidation to $CO+H_2+H_2O$ (a), CH_2O+H_2O (b), and CO_2+H_2O (c).*

Figure 1 (B): *Catalyst activity at 580K-600K for the RuO_2 pre-catalyst state as a function of the $CH_3OH:O_2$ ratio.*

Conclusions

The catalytically active states of Ru catalysing different CH_3OH oxidation pathways are formed by interaction with the reactants in the gas phase under specific (T, p_{CH3OH}, p_{O2}) conditions, independently of the initial pre-catalyst. Non-stoichiometric transient "surface oxide" ("Ru_xO_y"), differing only by the amount of accumulated oxygen was found to catalyze both partial oxidation to CH_2O and total oxidation to CO_2. The dramatic changes in the selectivity correlate to relatively small differences in catalyst chemical state demonstrate the compositional complexity of the catalyst surface under dynamic reaction conditions and the important role of the T,p range in tuning the catalyst performance.

Acknowledgements

References

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