Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface Science 544 (2003) 1–4

SURFACE SCIENCE

www.elsevier.com/locate/susc

Surface Science Perspectives

Extending surface science studies to industrial reaction conditions: mechanism and kinetics of methanol oxidation over silver surfaces

Israel E. Wachs *

Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, 7 Asa Drive, Bethlehem, PA 18015, USA

Received 4 August 2003; accepted for publication 4 August 2003

Keywords: Models of surface kinetics; Oxidation; Alcohols; Silver; Catalysis

The selective oxidation of CH_3OH to H_2CO over the noble metals Cu, Ag and Au represents one of the oldest industrial catalytic technologies dating back to the 1880s [1,2] and also the first non-Pt based catalytic industrial process. Initially, the catalyst employed for methanol oxidation was metallic Cu and subsequent research three decades later comparing the noble different metal catalysts found that Ag was the most efficient catalyst for this reaction. The commercial Ag catalysts are unsupported and are in the form of pure needles, wires or gauzes and are of very high purity (99.999% Ag) with very low surface areas (BET $\ll 0.1$ m^2/g). Currently, more than 50% of the world's H_2CO is manufactured employing metallic Ag catalysts. Bulk mixed iron-molybdate catalysts account for the remaining H_2CO production and commercially introduced in the middle of the 20th century. The advantage of the Ag-based technology is that it is a very flexible and simple process to start, operate (adiabatic reaction conditions), shut down and change the catalyst. Analogous alcohol oxidation reactions over the noble metal catalysts are also employed in the chemical industry to synthesize higher molecular weight aldehydes such as C_{10}–C_{20} fragrances.

The proposed reaction mechanism of methanol oxidation over Ag catalysts has also undergone significant changes over the years and has attracted much attention in the past 25 years by many leading surface science and catalysis research groups (more than 250 publications, which corresponds to an average of ~10 papers/year). The initial proposed mechanism consisted of two sequential steps:

$$CH_3OH \leftrightarrow H_2CO + H_2 \tag{1}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2}$$

Whereas the methanol dehydrogenation reaction (step 1) is an endothermic reaction with limited equilibrium yield, the subsequent hydrogen combustion reaction (step 2) was thought to provide the exothermic

---

[*] Tel.: +1-610-758-4274; fax: +1-610-758-6555.
E-mail address: iew0@lehigh.edu (I.E. Wachs).

doi:10.1016/j.susc.2003.08.006

heat required for this process as well as to push the dehydrogenation equilibrium (step 1) to the right. Minor direct combustion of methanol could also provide the exothermic heat required by methanol dehydrogenation, but this reaction path is rather limited since commercial H_2CO selectivity of ~90% is routinely obtained. The above simple reaction mechanism was accepted by everyone for about 100 years until the appearance of fundamental surface science studies on methanol oxidation over Ag(1 1 0) single crystals 25 years ago [3].

The surface science investigation involved temperature programmed reaction spectroscopy with the aid of isotopes to trace the various functionalities and the following reaction mechanism was discovered for methanol oxidation to formaldehyde over Ag:

$$^{18}O_2 \leftrightarrow 2\,^{18}O_{ads} \tag{3}$$

$$CH_3OD + {}^{18}O_{ads} \leftrightarrow CH_3O_{ads} + {}^{18}OD \tag{4}$$

$$CH_3OD + {}^{18}OD_{ads} \leftrightarrow CH_3O_{ads} + {}^{18}OD_2 \tag{5}$$

$$CH_3O_{ads} \leftrightarrow H_2CO + H_{ads} \text{ (rate-determining-step)} \tag{6}$$

$$H_{ads} + H_{ads} \leftrightarrow H_2 \tag{7}$$

$$CH_3O_{ads} + H_{ads} \leftrightarrow CH_3OH \tag{8}$$

It was the selective formation of $^{18}OD_2$ and H_2 as well as the appearance of CH_3OH from CH_3OD that revealed that the hydroxyl end of the methanol molecule underwent oxidation to water and that the methyl hydrogen underwent dehydrogenation to H_2CO and H_2. Thus, both ends of the methanol molecule are responsible for the simultaneous oxidation and dehydrogenation of CH_3OH to H_2CO, H_2 and H_2O. In addition, CO_2 formation originates from over-oxidation of H_2CO on Ag via a surface formate, $HCOO_{ads}$, intermediate. This new reaction mechanism suggested several new directions to further improve the commercial efficiency of the H_2CO synthesis reaction and were successfully immediately implemented in industry [4,5] within a few years of its discovery. The oxidation of CH_3OH to H_2CO over Ag is considered to be the first successful example of the impact of surface science studies upon heterogeneous catalysis.

The above surface reaction mechanism and associated kinetics were supported by the numerous surface science investigations over the years. In recent years, however, high temperature and atmospheric pressure investigations of the oxidation of Ag single crystals and methanol oxidation by Ag concluded that the previous surface science studies cannot be extrapolated to industrial conditions because of the restructuring of the Ag surface with the creation of unique active surface oxygen species and surface sites that are not present under UHV conditions over single crystals [6–8]. Although these investigations were performed at high temperatures and atmospheric pressures, the chosen experimental conditions were net oxidizing conditions (either pure oxygen or $O_2/CH_3OH \sim 100$) [6–8] in sharp contrast to the net reducing conditions employed commercially ($O_2/CH_3OH \sim 1/3$ as well as the significant production of byproduct H_2) [1,2] and, consequently, resulted in the proposal that there existed a unique reconstructed oxidized surface with selective surface oxygen species directly responsible for H_2CO formation and unselective surface oxygen species directly responsible for CH_3OH combustion to CO_2. *In situ* and *operando* [1] Raman spectroscopy

---

[1] *Operando* spectroscopy is new term coined by Miguel A. Banares to describe simultaneous catalyst spectroscopic measurement and online GC or MS analysis of the reaction products under actual reaction conditions [21,22]. The term *operando* comes from Latin and means "working." The first International Conference on *Operando* Spectroscopy was already held earlier this year in Lunteren, The Netherlands (March 1–6, 2003) and was organized by Bert M. Weckhusyen. *Operando* spectroscopy will undoubtedly further bring surface science studies and heterogeneous catalysis studies closer together in the coming years as more fundamental mechanistic and kinetic information is obtained on actual operating industrial catalysts.

studies under conventional methanol oxidation catalytic reaction conditions revealed that the Ag surface was essentially in a reduced state and much closer to the surface Ag state present under UHV surface science investigations [9].

The microkinetic modeling paper in this issue by Andreasen et al. [10] contributes significantly to this discussion by examining in detail the fundamental kinetics and proposed surface reaction mechanisms of methanol oxidation over Ag catalysts. It elegantly demonstrates and confirms how the fundamental surface science kinetic and mechanistic studies with single crystals under UHV conditions and low temperatures can be "scaled-up" with microkinetic modeling to predict catalytic operation under high temperature and atmospheric reaction conditions. The microkinetic model assumptions are clearly and quantitatively described and the simulations over a wide range of catalytic reaction conditions reveal no significant deviations when compared to actual catalytic reaction data. This paper is an excellent example of the ability of the new microkinetic analysis approach, based on surface science molecular level details, to bridge the temperature, pressure and materials gap between UHV single crystal surface science studies and corresponding conventional powdered heterogeneous catalytic studies. Thus, the authors have successfully achieved the objective of their investigation: "to demonstrate that the reaction mechanism established at UHV can explain kinetic experiments near industrial conditions".

Microkinetic modeling is an emerging area of research that has already demonstrated success in bridging surface science and catalysis studies for several different industrial catalytic reactions: ethane hydrogenolysis, water–gas shift reaction, methanol synthesis, ammonia synthesis, CO oxidation, high temperature hydrocarbon cracking reactions [11–20]. For an extensive review of microkinetic modeling and recent developments see the outstanding chapter by Cortright and Dumesic [20]. The recent microkinetic modeling studies to date confirm the close relationship between surface science mechanistic and kinetic conclusions and industrial catalysis. Many more such microkinetic modeling studies based on UHV surface science studies should be forthcoming in the coming years. The paper in this issue of Surface Science by Andreasen et al. [10] has successfully extended microkinetic modeling to selective oxidation reactions and Ag catalysts. In the case of Ag catalyzed selective oxidation reactions, it would be very nice to further extend such microkinetic modeling studies to olefin epoxidation reactions because of the enormous effort expanded over the past three decades on this specific topic as reflected in the hundreds of publications and the numerous conflicting models proposed in the literature. I am confident that such a microkinetic model will be developed in the coming years given the significant industrial importance of the unique silver epoxidation catalytic reaction and the enormous base of fundamental mechanistic and kinetic data already available in the literature. Indeed, a preliminary version of a microkinetic model for ethylene epoxidation over Ag has recently appeared [23]. Much remains to be done, however, to better understand the working state of this catalyst and to account quantitatively for the reaction selectivity.

References

[1] Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., vol. A11, VCH Verlagsgesellschaft, Wien, 1988.
[2] Kirk-Othmer Encyclopedia of Chemical Technology, vol. 11, John Wiley & Sons, New York, 1994.
[3] I.E. Wachs, R.J. Madix, Surf. Sci. 76 (1978) 531.
[4] DuPont, private communication, 1979.
[5] Celanese, private communication, 1980.
[6] X. Bao, M. Muhler, T. Schedel-Niedrig, R. Schlogl, Phys. Rev. B 54 (3) (1996) 2249.
[7] T. Schedel-Niedrig, X. Bao, M. Muhler, R. Schlogl, Ber. Bunsenges. Phys. Chem. 101 (7) (1997) 994.
[8] A.J. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann, R. Schlogl, J. Catal. 182 (1999) 417.
[9] C.-B. Wang, G. Deo, I.E. Wachs, J. Phys. Chem. B 102 (1999) 5645.
[10] A. Andreasen, H. Lynggaard, C. Stegelmann, P. Stoltze, Surf. Sci. 544 (2003) 5.
[11] S.H. Oh, G.B. Fischer, J.E. Carpenter, D.W. Goodman, J. Catal. 100 (1986) 360.
[12] V. Zhdanov, B. Kosemo, Surf. Sci. Rep. 20 (1986) 111.

[13] P. Stoltze, Phys. Scr. 36 (1987) 824.

[14] N. Waletzko, L.D. Schmidt, AIChE J. 34 (1988) 1146.

[15] J. Dumesic, D. Rudd, L. Aparicio, J. Rekoske, A. Trevino, The Microkinetics of Heterogeneous Catalysis, ACS Book Series, 1993.

[16] D.A. Hickman, L.D. Schmidt, AIChE J. 39 (1993) 1164.

[17] T. Askgaard, J.K. Norskov, C.V. Ovesen, P. Stoltze, J. Catal. 156 (1995) 229.

[18] C.T. Campbell, Topics Catal. 1 (1995) 353.

[19] C.V. Ovsen, B.S. Clausen, B.S. Hammershoi, G. Steffensen, T. Askgaard, I. Chorkendorff, J.K. Norskov, P.B. Rasmussen, P. Stoltze, P. Taylor, J. Catal. 158 (1996) 170.

[20] R.D. Cortright, J.A. Dumesic, Adv. Catal. 46 (2001) 161.

[21] B.M. Weckhuysen, Chem. Commun. (2002) 97.

[22] I.E. Wachs, Cattech 7 (4) (2003) 142.

[23] S. Linic, M.A. Barteau, J. Catal. 212 (2002) 200.