Heterogeneous–Homogeneous Catalytic Partial Oxidations Investigated by Molecular Beam Mass Spectrometry

M. Geske, A. Taha, K. Ihmann,† J. Ihmann, K. Pelzer,

R. Horn,[1] F.C. Jentoft, R. Schlögl

Abteilung Anorganische Chemie, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Deutschland

[1]Chemical Engineering and Materials Science Department, University of Minnesota, 421 Washington Avenue SE, Minneapolis MN 55455, USA

Introduction

Heterogeneous catalytic reactions are often insufficiently described by surface reaction steps only; gas phase contributions are neglected. Surface and gas phase reaction steps can take place simultaneously and are coupled by exchange of energy and reaction intermediates. Catalytic partial oxidations are suspected to proceed via combined heterogeneous–homogeneous mechanisms because of high reaction temperatures and the diradical oxygen as reactant. Gas phase radicals are thought to be key intermediates, but there is little understanding of mechanistic details [1]. To study the mechanism of such reactions we have developed a Molecular Beam Mass Spectrometer (MBMS) equipped with a high temperature catalytic wall reactor.

Experimental

Fig. 1: MBMS setup

The new apparatus (Fig. 1) allows us to study reactions performed in a catalytic wall reactor, which is placed in the nozzle chamber of the MBMS system. The reactor consists of a Pt (+10% Rh) tube that can be heated resistively until reaction light off. The temperature profile of the reactor is monitored by line scanning pyrometry. A small gas portion from the reacting surface–gas phase boundary layer expands adiabatically into vacuum through a tiny nozzle (≈ 100 µm) drilled into the catalytically active wall. The evolving supersonic expansion (free jet) permits quenching and MS analysis of any reaction mixture on millisecond timescale (Fig. 2). Spatial resolution is achieved by varying the flow rate and thus shifting the reaction zone relative to the nozzle. The quadrupole mass spectrometer allows specific detection of radicals in presence of other gas phase constituents by the threshold ionization technique [2].

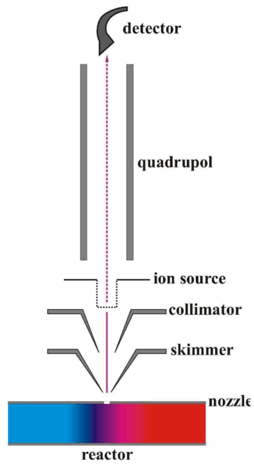

Fig. 2: Working principle

Results

To verify the performance of the MBMS we determined the shape and width of the energy spread of the ionizing electrons as well as the detection limit in threshold ionization. By measuring He and N_2 ionization at the threshold we found the energy spread to be Gaussian with $2\ \sigma \approx 1$ eV and an energy offset of about 1 eV. The detection limit in threshold ionization was determined for the model system CO in N_2 (same m/q, but IP_{CO}=14.01 eV and IP_{N2}=15.58 eV). A detection limit of 230 ppm CO was reached. It follows that in reaction mixtures radicals can be identified if their ionization potentials are at least 1 eV lower than those of all other interfering ions. This prerequisite is fulfilled by most of the simple radicals such as $CH_3\cdot$, $C_2H_5\cdot$ or $OH\cdot$. The target reaction is the catalytic partial oxidation (CPO) of methane over Pt:

$$CH_4 + \frac{1}{2}\ O_2 \rightarrow CO + 2\ H_2$$

C_2 hydrocarbons are suspected to be formed by recombination of two $CH_3\cdot$ radicals in the gas phase [3]. Preliminary experiments operating the wall reactor outside of the MBMS chamber at 500 ml/min CH_4, 450 ml/min, O_2, and $T \approx 1200$ K yielded about 2000 ppm C_2H_6, as measured in the reactor off-gas by online-GC. Simulations using CHEMKIN revealed that, depending on the conditions, $CH_3\cdot$ and $C_2H_5\cdot$ concentrations should be in the range of 100 - 1000 ppm.

Conclusions

Tests of the MBMS apparatus show that we should be able to detect ppm concentrations of gas phase radicals and discriminate them from interfering ions of the same mass. At the expected radical concentrations in the wall reactor, the detection limit will allow their observation.

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