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

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Introduction

Heterogeneous catalytic reactions occur by definition on the surface of a catalyst. However, numerous industrially important reactions such as HCN synthesis, ammonia oxidation or many hydrocarbon oxidations are performed at reaction temperatures beyond 1000 °C and at atmospheric or higher pressure. Under these conditions, surface reactions may induce gas phase reactions with both processes coupled by exchange of heat and reaction intermediates [1-4].

Energetic coupling will result if exothermic surface reactions rise the temperature of the surrounding gas phase so high that homogeneous reaction pathways become feasible. In most cases, radicals are generated by homolytic bond cleavage in the gas phase (high activation barrier) and can start radical chain reactions involving carriers like H·, R·, RO·, RO_2·, HO_2· and OH· [1,5,6]. Heterogeneous catalytic oxidations for example are very fast and exothermic, reactors operate often close to the adiabatic limit, and high surface and gas phase temperatures are common [3,7].

Coupling via reactive species will occur if the catalyst surface acts either as a source or a sink of reactive intermediates. Among the species reported in the literature, again radicals seem to play the pivotal role for this kind of coupling. According to the few reviews available [1,2,8,9], the generation of radicals on catalytic surfaces followed by their desorption into the gas phase seems to be more widespread in heterogeneous oxidation catalysis than generally assumed. Besides for non-redox type oxides (e.g. MgO), radical desorption was also reported for redox-type oxides of all period IV transition metals [10] and for noble metal surfaces (e.g. Pt [11,12]).

In addition to radicals also closed shell reactive intermediates might be involved in the coupling between surface and gas phase chemistry [4].

The Molecular Beam Mass Spectrometer (MBMS) presented here has been developed to investigate reactions proceeding via steps on the surface and in the gas phase (`heterogeneous-homogeneous' reactions) under high temperature and atmospheric pressure conditions by detecting gas phase radicals above the catalyst surface [13].

Experimental

The MBMS apparatus 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 up to 1300 °C (Fig.1). If the reaction supplies enough heat, the reactor can also be operated autothermally after reaction light off. The temperature 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 ($\approx$ 100 µm) drilled into the catalytically active wall. The evolving supersonic expansion (free jet) permits quenching of any occurring gas phase reaction on a millisecond timescale. A downstream arrangement of skimmer and collimator cones forms a molecular beam entering the mass spectrometer for analysis of stable species and radicals (Fig. 2). The quadrupole mass spectrometer used in the MBMS allows for specific detection of radicals in presence of other gas phase constituents by the threshold ionization technique [14].

Results and Conclusions

To verify the performance of the MBMS we determined first 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/z, 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 (1) which involves at high temperatures the formation of higher hydrocarbons as a side reaction as showed exemplarily for ethane (2):

$$CH_4 + ½ O_2 \rightarrow CO + 2 H_2 \quad (1)$$

$$2 CH_4 + ½ O_2 \rightarrow C_2H_6 + H_2O \quad (2)$$
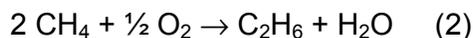
C_2 hydrocarbons are suspected to be formed by recombination of two $CH_3\cdot$ radicals in the gas phase (3) because this mechanism has been verified for the oxidative coupling of methane over strong basic oxides [15,16].

$$CH_3\cdot + CH_3\cdot \rightarrow CH_3\text{-}CH_3 \quad (3)$$
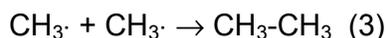
At high temperatures ethane can be further dehydrogenated to ethylene and acetylene (4)

$$C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + 2H_2 \quad (4)$$
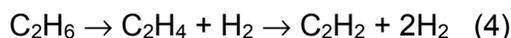
Using surface and gas phase microkinetic models developed for numerical simulation of the methane CPO on Pt [16,17] and a boundary layer simulation in CHEMKIN$^{\copyright}$ the accessible experimental space was screened for conditions that could maximize the concentration of $CH_3\cdot$ radicals in the gas phase. It was found that high temperatures, high flow rates and low concentration of inert collision partners maximize the radical concentration in the gas phase.

To reach a high operating temperature, a mixture of 600 ml/min CH_4, 500 ml/min O_2 (C/O = 0.6) and 200 ml/min He (standard for energy axis) was used. In addition, 80 A were passed through the Pt tube leading to a reactor temperature of 1250 °C. The reactor pressure was slightly above atmospheric. Under these conditions, $CH_3\cdot$ radicals were successfully detected at m/z = 15 amu (Fig. 2). The ionization energy of the radical, (IE ($^{12}C^1H_3^+$ / $^{12}C^1H_3\cdot$ = 9.84 eV), is more than 4 eV lower than the appearance energy of the CH_3^+ fragment from CH_4 (AE ($^{12}C^1H_3^+$ / $^{12}C^1H_4$ = 14.01 eV). With the reaction on, the ionization efficiency curve at m/z = 15 amu rises linearly from about 9.6 eV which agrees well with the ionization energy of $CH_3\cdot$ (9.84 eV) before it increases steeply at about 13.5 eV caused by CH_3^+ formation from fragmentation of C_2H_6 (IE (CH_3^+ / C_2H_6) = 13.65 eV) and CH_4 (14.01 eV). Without the reaction, the IE-curve remains close to zero until fragmentation of C_2H_6 and CH_4 occur. Reactor off-gas analysis using gas chromatography revealed that acetylene is the main C_2 reaction product obviously formed by consecutive dehydrogenation of C_2H_6 according to Eq. (4).

Hence, it could be demonstrated that with the novel apparatus highly reactive gas phase species, present in a catalytic wall reactor under flow conditions at high temperatures, can be sampled and identified.
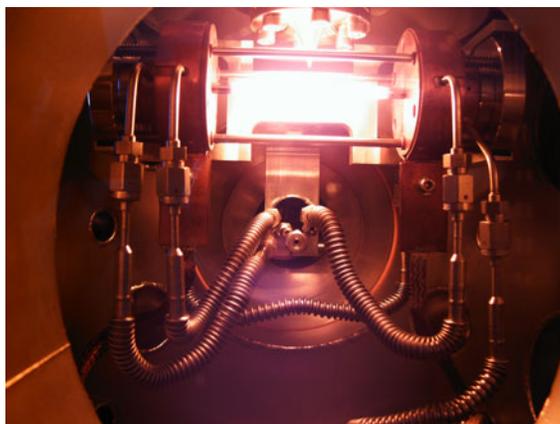
Fig. 1 Catalytic wall reactor in operation, T=1250°C.
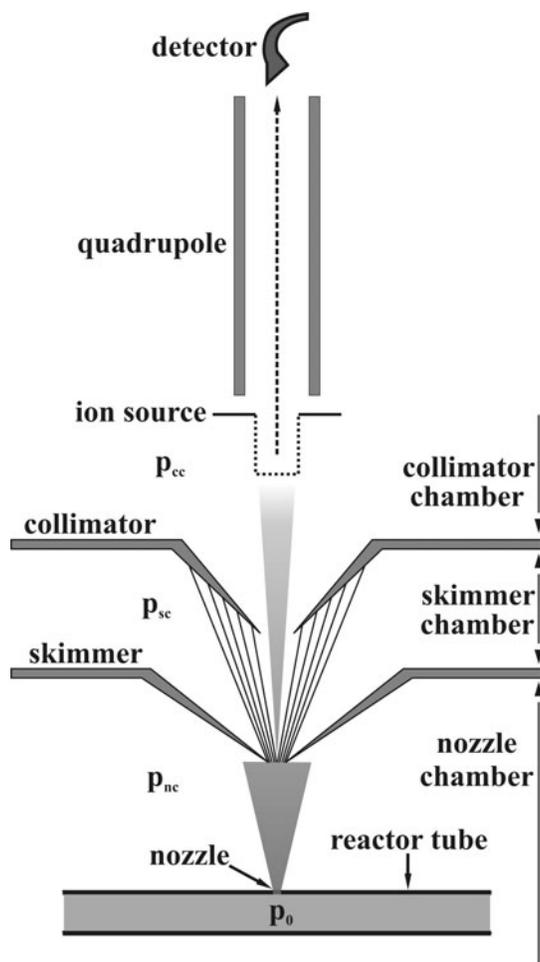
Fig. 2 Molecular Beam Formation in the MBMS.
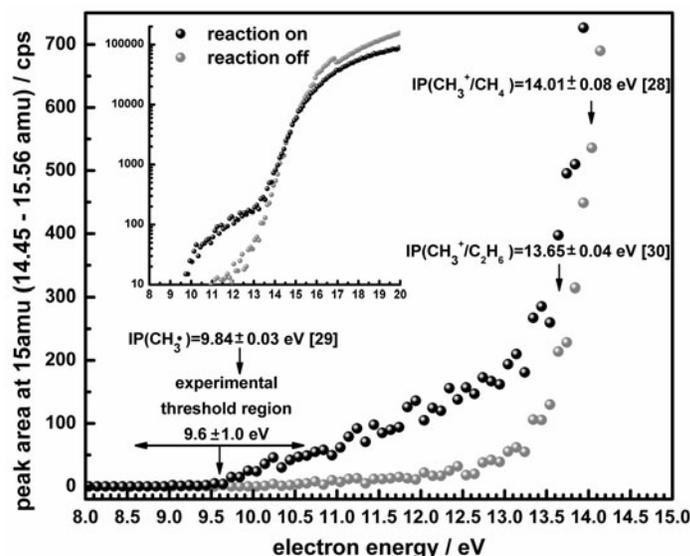
Fig. 3 Detection of CH$_3$· radicals at 15amu by threshold ionization.

[1] Cavani F.;Trivirò F. *Catal. Today* **1999**, *51*, 561-580.

[2] Driscoll D. J.; Campbell K. D.; Lunsford J. H. *Adv. Catal.* **1987**, *35*, 139

[3] Olsen R. J.; Williams W. R.; Song X.; et al. *Chem. Eng. Sci.* **1992**, *47*, 2505

[4] Horn R.; Mestl G.; Thiede M.; et al. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4514

[5] Beretta A.; Forzatti P.; *J. Catal.* **2001**, *200*, 45

[6] Henning D. A.; Schmidt L. D.; *Chem. Eng. Sci.* **2002**, *57*, 2615

[7] Arpentinier P.; Cavani F.; Trifiró F. *Catal. Today* **2005**, *99* 15

[8] Garibyan T. A.; Margolis L. Y. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 355

[9] Krylov O. V. *React. Kinet. Catal. L.* **1987**, *35*, 315

[10] Ismagilov Z. R.; Pak S. N.; Krishtopa L. G.; et al. *Stud. Surf. Sci. Catal. A* **1993**, *75*, 231

[11] Selwyn G. S.; Lin M. C. *Langmuir*, **1985**, *1*, 212

[12] Marks C. M.; Schmidt L. D. *Chem. Phys. Lett.* **1991**, *178*, 358

[13] Horn R.; Ihmann K.; Ihmann J.; F. C. Jentoft et al. *Rev. Sci. Inst.* **2006**, *77*, 054102

[14] Sablier M.; Fujii T. *Chem. Rev.* **2002**, *102*, 2855-2924.

[15] Lunsford J. H. *Angew. Chem. Int. Edit. Engl.* **1995**, *34*, 970-980.

[16] Mims C. A.; Mauti R.; Dean A. M.; Rose K. D. *J. Phys. Chem.* **1994**, *98*, 13357-13372.

[17] Zerkle D. K.; Allendorf M. D.; Wolf M.; Deutschmann O. *J. Catal.* **2000**, *196*, 18-39.