Hydrogen generation through partial oxidation of ethanol or methane over supported well-defined Pt, Rh, and Ru nanoparticles

V.A. Kondratenko,[a]* **A. Malmusi,**[b] **U. Rodemerck,**[a] **U. Karimova,**[c] **A.A. Kasimov,**[c]
F. Cavani,[b] **E.V. Kondratenko**[a]
[a]*Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, Rostock, 18059, Germany*
[b]*University of Bologna, Department of Industrial Chemistry "Toso Montanari“, Viale del Risorgimento 4, Bologna, 40136, Italy*
[c]*Institute of Petrochemical Processes, Khojali Avenue 30, Baku, AZ1025, Azerbaijan Republic*
**Corresponding author: +49(381)1281-51291, Vita.Kondratenko@catalysis.de*

Abstract: Formation of hydrogen through partial oxidation of ethanol or methane was studied over catalysts possessing well-defined supported Pt, Rh, and Ru nanoparticles (NP). As concluded from steady-state tests and temporal analysis of products, catalyst activity and selectivity to hydrogen depend on the kind of metal and support as well as on NP size. These catalyst characteristics govern the rates of selective and non-selective pathways and therefore can be used for tuning catalyst performance.
Keywords: Hydrogen, Methane, Ethanol.

1. Introduction

For over one hundred years hydrogen is used in a wide range of large-scale applications including ammonia and methanol synthesis. Nowadays, it gains in importance as a clean energy carrier. Steam reforming of methane (SRM) is the mature technology for hydrogen generation [1]. Being well optimized, SRM suffers, however, from high energy consumption caused by the strong reaction endothermicity. Exothermic partial oxidation of ethanol (POXE) or methane (POM) can be, therefore, attractive alternatives to SRM. Moreover, the utilization of methane and ethanol from renewable sources (bio-methane and bio-ethanol) is especially advantageous for hydrogen production because it generates no net carbon dioxide. Although catalysts with supported transition metals are known to be active and stable for these reactions [2, 3], direct relationships between the kind of support and supported metal are still not properly established. To close this gap, the effects of (i) the kind of active metal/support and (ii) the size of metal particles on catalyst activity and selectivity in POXE and POM were studied over well-defined Pt, Rh, or Ru NP with a size between 1 and 5 nm supported on TiO_2, $LaZrO_x$, Al_2O_3, SiO_2, and $AlSiO_x$ with different Si content. The catalysts were thoroughly characterized and tested under steady-state ambient pressure conditions at different degree of CH_4 or C_2H_5OH conversion. Mechanistic aspects of product formation were studied in vacuum with sub millisecond time resolution.

2. Experimental

Pt, Rh, and Ru NP were prepared as described in our previous studies [4, 5]. They were deposited on TiO_2, SiO_2, $AlSiO_x$ (1, 10, and 40 wt% SiO_2), Al_2O_3, and $LaZrO_x$ using solution in ethanol. Metal loading amounted to 0.005, 0.05, and 0.1 wt%. The size of NP in the solution and on the support was determined with small angle X-ray scattering and transmission electron microscopy, respectively. Steady-state POXE and POM tests were performed at 800°C using a $CH_4/O_2 = 2$ feed and between 500-700°C using a $C_2H_5OH/O_2/N_2 = 1/1.5/37.5$ feed respectively. Transient mechanistic and kinetic studies were carried out in the temporal analysis of products (TAP-2) reactor at different temperatures using O_2:Ar = 1:1, CH_4:Ar = 1:1, C_2H_5OH:Ar=1:1, C_2H_4:Ar=1:1, CH_4:O_2:Ar = 2:1:2, CH_4:CO_2:Ar = 1:1:1, and CO_2:Ar = 1:1 mixtures.

3. Results and discussion

The catalysts were tested without any reductive pre-treatment. Catalyst activity increased with a decrease in the size of NP in the POM and POXE reactions and regardless the applied support. In POXE,

C_2H_4, C_2H_6, CH_4, CO, CO_2, H_2, and H_2O were formed over all catalysts independent on the size of NP. The hydrocarbons and water were the main products at 500°C. However, the amount of these products decreased with rising temperature in favor of hydrogen and carbon monoxide. Although the effect of temperature was valid for all tested catalysts, the selectivity to individual products depended on the kind of noble metal and support. In terms of H_2 yield, Al_2O_3, TiO_2 and $LaZrO_x$ are the most suitable supports for all metals (Figure 1). The catalysts on the basis of SiO_2 were not active for hydrogen generation but produced methane and carbon dioxide. The performance of Ru and Rh NP supported on $AlSiO_x$ significantly changed when the content of SiO_2 decreased. The yield of hydrogen passed over a maximum at the content of SiO_2 of 1 and 10 wt%, while the yield to methane passed over a minimum. For Pt/$AlSiO_x$, an increase in SiO_2 content in the support led to a smooth increase in the amount of methane, whereas hydrogen yield decreased.

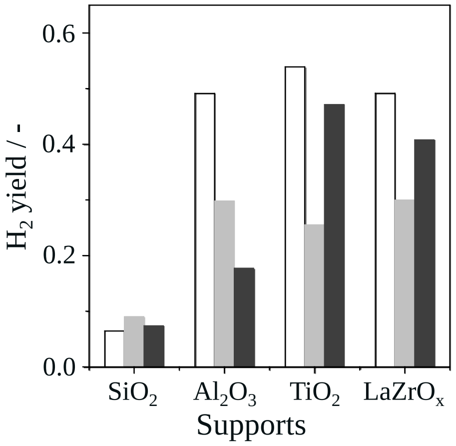

Figure 1. The yield of H_2 at a complete ethanol conversion over Pt (white bars), Rh (grey bars), and Ru NP (dark grey bars) supported over SiO_2, Al_2O_3, TiO_2, and $LaZrO_x$. Reaction conditions: 700°C, 2.5 vol% ethanol and 3.75 vol% oxygen in nitrogen. NP size was around 1 nm.

Similar to POXE, catalyst performance in POM depended on the kind of noble metal and support. Rh NP showed the highest activity followed by Ru and Pt NP supported over Al_2O_3 and $LaZrO_x$. TiO_2-supported catalysts possessed the worst POM performance. The selectivity to hydrogen was also influenced by the support and noble metal. It was the highest over Rh/Al_2O_3 and Rh/$LaZrO_x$.

As concluded from transient and steady state experiments, overall schemes of product formation in both POXE and POM did not depend on the kind of metal, support, and NP size. For the POM reaction, CO_2, CO, and H_2O are the primary products of CH_4 oxidation in the presence of gas-phase O_2 (beginning of the catalyst layer). H_2 was established to be formed through dry and steam reforming of methane in the downstream catalyst layer, where O_2 is not present due to its consumption in the upstream catalyst layer. Similar to POM, H_2 in POXE also originates through reforming reactions. In this case, methane and ethylene primarily formed from ethanol are H_2 precursors. Additionally, hydrogen was formed via water gas shift reaction in the course of POXE. From a kinetic viewpoint, hydrogen formation was established to be the slowest reaction pathways in the course of POXE and POM. The rate of CO oxidation to CO_2 was also slower on Pt and, for all metals, was affected by the support. In general, the ability of metal NP for O_2, CH_4, CO_2, and H_2O activation determine their activity in the downstream catalyst zone. Such catalyst property is affected by the kind of support, metal and NP size.

4. Conclusions

It was shown that supported catalysts possessing well-defined Pt, Rh, or Ru NP with a low metal loading of 0.005-0.1 wt% are promising candidates for H_2 generation through partial oxidation of methane or ethanol. Although the reaction mechanism was not influenced by the kind of metal, NP size, or support, these parameters determined the activity and selectivity of tested catalysts. Such knowledge opens the possibility for tuning catalytic activity and, most importantly, selectivity.

References

1. P. F. v. d. Oosterkamp, in: Encyclopedia of Catalysis, I. Horvath (Ed.), John Wiley & Sons, Weinheim, 2003, vol. 6, p. 770.
2. B. C. Enger, R. Lødeng, A. Holmen, Appl. Catal. A 346 (2008) 1.
3. L.V. Mattos, G. Jacobs, B.H. Davis, and F.B. Noronha, Chem. Rev. 112 (2012) 4094.
4. C. Berger-Karin, M. Sebek, M.-M. Pohl, U. Bentrup, V.A. Kondratenko, N. Steinfeldt, E. V. Kondratenko, ChemCatChem 4 (2012) 1368.
5. V.A. Kondratenko, C. Berger-Karin, E.V. Kondratenko, ACS Catal. 4 (2014) 3136.