

Mechanism for methane steam reforming over transition metals

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Introduction

Catalytic steam reforming of hydrocarbons is an important process for generating synthesis gas. Typically nickel based catalysts are used for industrial steam reforming but increasing interest in low O/C steam/CO₂ reforming have prompted renewed interest in steam reforming over more noble and precious metals. Here a theoretical and experimental study of methane steam reforming over transition metals are reported [1].

Materials and Methods

Density Functional Theory (DFT) is used as implemented in the computer code DACAPO using the RPBE exchange correlation functional [2]. In order to establish the adsorption energies of hydrogenated intermediates scaling relationships were combined with the relative energies from Ref. [3] for adsorption on the fcc{211} surface for the close-packed (fcc and hcp) metals and bcc{210} surface for the bcc metals. Linear scaling relationships were used as discussed in reference [4]. An overview of the methane steam reforming reaction over transition metals was developed using scaling relations for adsorption energies of simple molecules. Combined with thermodynamics and micro kinetic modeling it was possible to determine reactivity trends for methane steam reforming of the pure metals.

18 catalysts have been prepared using 6 different metals (Ru, Rh, Ir, Pt, Ni and Pd) by impregnation of ZrO₂, Al₂O₃ and MgAl₂O₄ support. The activity was measured at 773K and ambient pressure using a 19%CH₄, 7%H₂ and 74% H₂O gas mixture. TEM measurements have been performed *in situ* and *ex situ* on a Philips CM300 FEG electron microscopy. *In situ* TEM experiments proved critical for Ru catalysts to get the right average particle size and were performed in reducing conditions of 1.2-1.6 mbar H₂ at 773 K. The particle sizes have been determined assuming spherical particles (>400 particles per sample).

Results and Discussion

The scaling relations show that to a first approximation only two independent variables, $\Delta E(C^*)$ and $\Delta E(O^*)$, characterize the activity of the metals. All other adsorption energies and reaction barriers depend linearly upon these underlying variables. Fig. 1 depicts a 2D plot of the influence of the C and O adsorption energies on the activity. The peak of this volcano plot (i.e. where the rate is highest) lies close to the region of the Ni, Rh and Ru adsorption energies.

The activity measurements combined with the particle sizes from TEM give turn over frequencies (TOF), which are proportional to the dispersion. The active sites are therefore primarily under-coordinated surface sites. The overall agreement between theory and experiments is found to be excellent with Rh and Ru being the most active metals for methane steam reforming, while Ni, Ir, Pt, and Pd are significantly less active at equal dispersion [1].

Significance

The ranking of the most active metals for methane steam reforming is important for the choice of metal for industrial low O/C applications. This work is the first to give a combined theoretical and experimental picture of the steam reforming reaction.

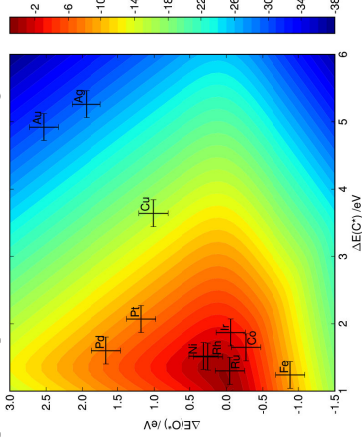


Figure 1. Two-dimensional volcano-curve of the turn over frequency (log10) as a function of O and C adsorption energy. T = 773 K, P = 1 bar; 10% conversion.

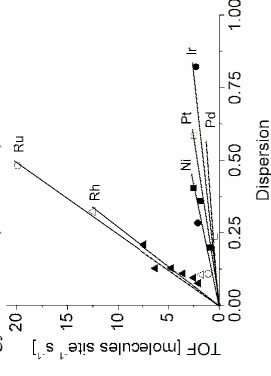


Figure 2. Reaction rate as a function of dispersion for CH₄-H₂O reforming (773 K). Ru (○), 5 wt%Rh (▲), 1 wt% Rh (Δ), Ni (■), Pt (□), Ir (●) and Pd (◆).

References

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