

Ni-W-C and Co-W-C as Alternative Catalysts for Dry Reforming and Steam Reforming of Methane

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Introduction

Steam reforming of methane (SRM) over supported Ni is the preferred route for stationary production of synthesis gas or hydrogen on a large scale. Dry reforming of methane (DRM), *i.e.*, using CO₂ as a reactant in place of H₂O, is of value for stranded natural gas or recycling of the vapor stream in Fischer-Tropsch reactions, and has the added advantage of reacting CO₂ rather than sequestering it. However the conventional Ni catalyst is quickly deactivated under DRM conditions due to coke deposition.

In our previous work, bimetallic η -carbides of Co and W such as Co₆W₆C have been successfully used for DRM and SRM. These materials were prepared by reduction and carburization of a precursor with a flowing mixture of CO₂ and CO. The material structure and properties depend upon the ratio CO₂/CO (= x). After exposure to flowing CH₄, the catalysts are active, selective and stable [1], with specific reaction rates per surface area equivalent to supported Ni. After exposure to methane at 800°C, the catalyst is significantly more active and stable at 600-700°C than before such exposure [2]. This treatment removes surface oxides, and carbon deposition converts the bimetallic carbide to Co + WC in the bulk. Even though Co and WC are found in the bulk when the catalyst is active, a simple mixture of these two components does not lead to a useful catalyst [3]. In this work, parallel research is reported for the Ni-W-C family of materials.

Materials and Methods

Ni-W-C was made analogously to Co-W-C. Precursor Ni(en)₃WO₄ was carburized while the temperature was ramped in a CO₂-CO mixture. DRM and SRM reactions were carried out in a computer-controlled unit and products were continuously sampled. XRD, SEM and EDAX were used to characterize the catalyst, before and after reaction. In addition, Professor Jingguang Chen's group (U Delaware) performed NEXAFS studies on selected materials. More details can be found in Ref. [3].

Results and Discussion

While Co₆W₆C is formed when the ratio CO₂/CO (= x) \geq 0.5, the value of x needs to be \geq 0.75 before Ni₆W₆C is formed. At lower values of x , Ni and WC are formed, whereas the corresponding phases are not seen for Co-W-C, at least for $x > 0.1$. Ni + WC are the catalytically active phases for Ni-W-C, corresponding to Co + WC for Co-W-C catalysts. SEM, EDAX and NEXAFS before and after reaction indicate that surface oxides are not present. This implies that, for the Ni-W-C system, exposure to methane at high temperatures is not required to form an active, stable catalyst.

DRM reactions were run using Ni-W-C catalysts with $x = 0.5$ and 0.75. Both catalysts were found to be active, selective and stable for the life of their respective runs, each over 100 h. However, the former catalyst (Figure 1) requires less lag time than the latter, again consistent with the above hypothesis.

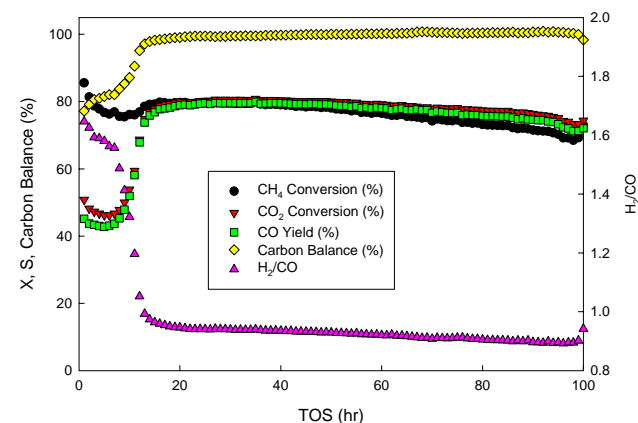


Figure 1. Reactivity for Ni-W-C ($x = 0.5$) 850°C, 3.4 atm, 9,000 sec h⁻¹ g.cat⁻¹

low temperature after exposure to high temperature. Again, this indicates that the Ni-W-C catalyst does not require exposure to methane at high temperatures to be in its active form.

Rate constants for both loss of methane and formation of hydrogen during DRM and SRM were calculated on a surface-area basis. Methane loss rates for the conventional supported Ni catalyst (initial values) are lower than steady-state values for Ni-W-C, which in turn are lower than those of Co-W-C after exposure to methane at 850°C. SRM rates for hydrogen production are lower than DRM rates.

Significance

Both Co-W-C and Ni-W-C are not only active and selective for dry reforming of methane, but are also stable catalysts. Both compare favorably with supported Ni for steam reforming. Surface oxides are not present in the Ni-W-C catalyst, so exposure to methane at high temperatures is not required for this catalyst to show high activity, as it is for Co-W-C.

References

1. Iyer, M.V., Norcio, L.P., Kugler, E.L., and Dadyburjor, D.B., *Ind. Eng. Chem. Res.* 42, 2712 (2003).
2. Shao, H.F., Kugler, E.L., Ma, W.P., and Dadyburjor, D.B., *Ind. Eng. Chem. Res.* 44, 4914 (2006).
3. Shao, H.F., Ph.D. Dissertation, West Virginia University, Morgantown WV (2006).

The latter catalyst was subjected to reaction at temperatures from 600°C to 850°C and back down. Unlike the Co-W-C catalyst, reaction rates are fairly high even at the low temperatures before exposure to the highest temperature, and do not change significantly when returned to the