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XAFS Analysis of Supported Binary Catalysts for Catalytic Decomposition of Methane

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Beamline(s): X18B, X19A

Introduction: Traditionally, hydrogen is produced by reforming or partial oxidation of methane to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO₂ and produce more hydrogen, followed in turn by a purification or separation procedure. Nanoscale, binary, Fe-M (M = Pd, Mo or Ni) catalysts supported on alumina reduced undiluted methane decomposition temperature by 400-500 °C relative to non-catalytic thermal decomposition and exhibited significantly higher activity than Fe or any of the secondary metals (Pd, Mo, and Ni) supported on alumina alone. We observed that the efficient removal of the carbon from the catalyst surface in the form of nanotubes might be the key factor influencing catalyst performance.¹ To better understand the role of these catalysts, we carried out ex-situ XAFS analysis on as prepared, pre-reduced and after on-stream catalysts. We also carried out in-situ XAFS analysis at 700 °C under flowing hydrogen and flowing methane atmospheres.

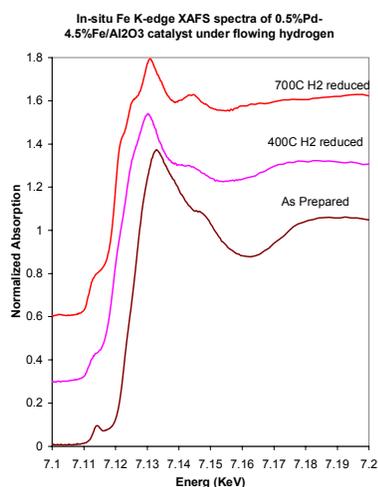
Results:

As-prepared catalysts: EXAFS spectroscopy confirmed that the iron in vacuum-dried, alumina-supported catalysts exists in ferrihydrite structure.² Radial structure function (RSF) of Pd EXAFS indicate presence of only one nearest neighbor shell implying very small particles of PdO either on alumina or ferrihydrite. XAFS analysis indicated that Mo exists in +6 oxidation state probably as MoO₄²⁻. Similar to Pd, Ni is present as small particles of NiO in the as-prepared catalysts.

Pre-reduced catalysts: As-prepared catalysts are not active for methane decomposition. The catalysts were activated by reduction at 700 °C for two hours and cooling in flowing hydrogen. Fe EXAFS showed, and Mössbauer spectroscopy confirmed that in all the catalysts, reduction of Fe to metallic-Fe state is not complete at 700 °C. Pre-reduction at 1000°C is required to complete the reduction of all Fe present. Both Pd XANES and Fe Mössbauer data showed that at 700 °C, Pd is easily reduced to metallic state and that Pd promotes reduction of Fe. Both Ni and Mo are partially reduced to metallic state. Mössbauer spectroscopy showed presence of Fe₂Mo phase in Mo-Fe/Al₂O₃ catalysts and substitution of Fe by Ni and thereby stabilization of austenitic phase in ni-Fe/Al₂O₃ catalysts.

Catalysts after on-stream exposure: Exposure of the pre-reduced catalysts to flowing methane at 700 °C did not show any changes in XAFS. Though methane is a carburizing atmosphere and catalysts are very active in decomposing methane to produce large amounts of elemental carbon in form of nanotubes, the catalysts retained their metallic states. Iron carbide phase was observed by Mössbauer spectroscopy only in the case of Fe/Al₂O₃ catalyst pre-reduced at 1000°C.

In-Situ experiments: We have designed, constructed and tested an in-situ cell for XAFS analysis of these catalysts at temperatures up to 700°C under flowing hydrogen and/or methane atmosphere. To prevent heat losses, this cell has heavy insulation with a small aperture for fluorescent x-ray measurement. The accompanying figure shows in-situ Fe K-edge XANES for Fe/Al₂O₃ and Pd-Fe/Al₂O₃ catalysts under flowing hydrogen with a PIPS detector capturing about 0.2% of the solid angle. All in-situ observation are in agreement with the ex-situ experiments indicating little or no change in the form of catalysts during cooling and storage.



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References:

- [1] N. Shah, D. Panjala, G.P. Huffman; *Hydrogen production by catalytic decomposition of methane*; **Energy & Fuels**, **15(6)**, (2001), to be published.
- [2] N. Shah, J. Zhao, F.E. Huggins, G.P. Huffman; *In-situ XAFS spectroscopic studies of direct coal liquefaction catalysts*; **Energy & Fuels**, **10(2)**, (1996) 417-420.