Investigation of the Molecular Structure of Nanoscale, Binary $Fe/M/Al_2O_3$ catalysts by XAFS and Mössbauer Spectroscopy

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In situ XAFS Spectroscopy

A major problem in determining catalytic reaction mechanisms is assessing the state of the catalyst during the reaction and relating that to the product distribution. While measurements of catalyst structure before and after reaction often provide significant insight, active metal-based catalysts often have an extremely fine particle size distribution and undergo spontaneous oxidation when they are removed from the reactor and exposed to air prior to examination.

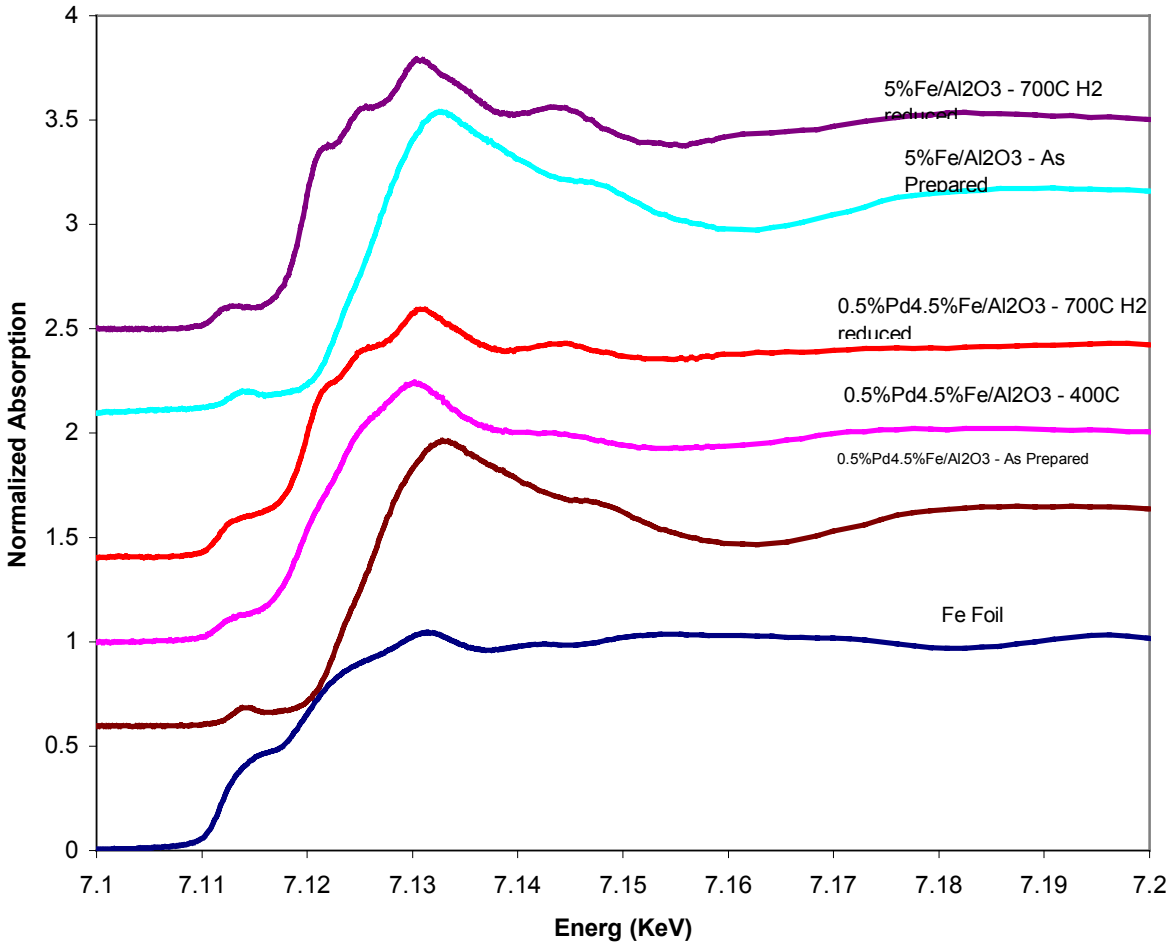


Figure 1. Fe K-edge in situ XAFS of as prepared and reduced under flowing hydrogen spectra of $5\%Fe/Al_2O_3$ and $0.5\%Pd4.5\%Fe/Al_2O_3$ catalysts.

A novel in situ XAFS cell optimized for investigation of C1 chemistry processes has been built and tested. Figure 1 shows Fe K-edge XAFS spectra of a 5%Fe/Al_2O_3 catalyst and a 0.5%Pd-4.5%Fe/Al_2O_3 catalyst in their as-prepared state and during reduction in flowing hydrogen at 700 °C. Both catalysts show partial conversion of the ferrihydrite phase to a metallic phase under reducing conditions.

Mossbauer Spectroscopy

To better understand the effect of pre-reduction treatment on the behavior of catalysts, 5%Fe/Al_2O_3, 0.5%Mo-4.5%Fe/Al_2O_3, 0.5%Ni-4.5%Fe/Al_2O_3 and 0.5%Pd-4.5%Fe/Al_2O_3 catalysts were treated under flowing hydrogen at 700 °C and 1000 °C and examined using Mossbauer spectroscopy. Figures 2-5 are for the catalysts reduced at 700 °C and figures 6-9 are for the catalysts reduced at 1000 °C. The following tables show the distribution of iron phases in these various catalysts. All catalysts in as-prepared state show the iron to present as ferrihydrite.

Catalysts reduced at 700

MK	Catalyst	Fe^{++}	Fe^{+++}	Fe Alloy	Fe Metal
2675	5%Fe/Al_2O_3	72	17		11
2602	0.5%Mo4.5%Fe/Al_2O_3	66	15	16(♣)	3
2678	0.5%Ni4.5%Fe/Al_2O_3	68	24		8
2673	0.5%Pd4.5%Fe/Al_2O_3	54	23		22

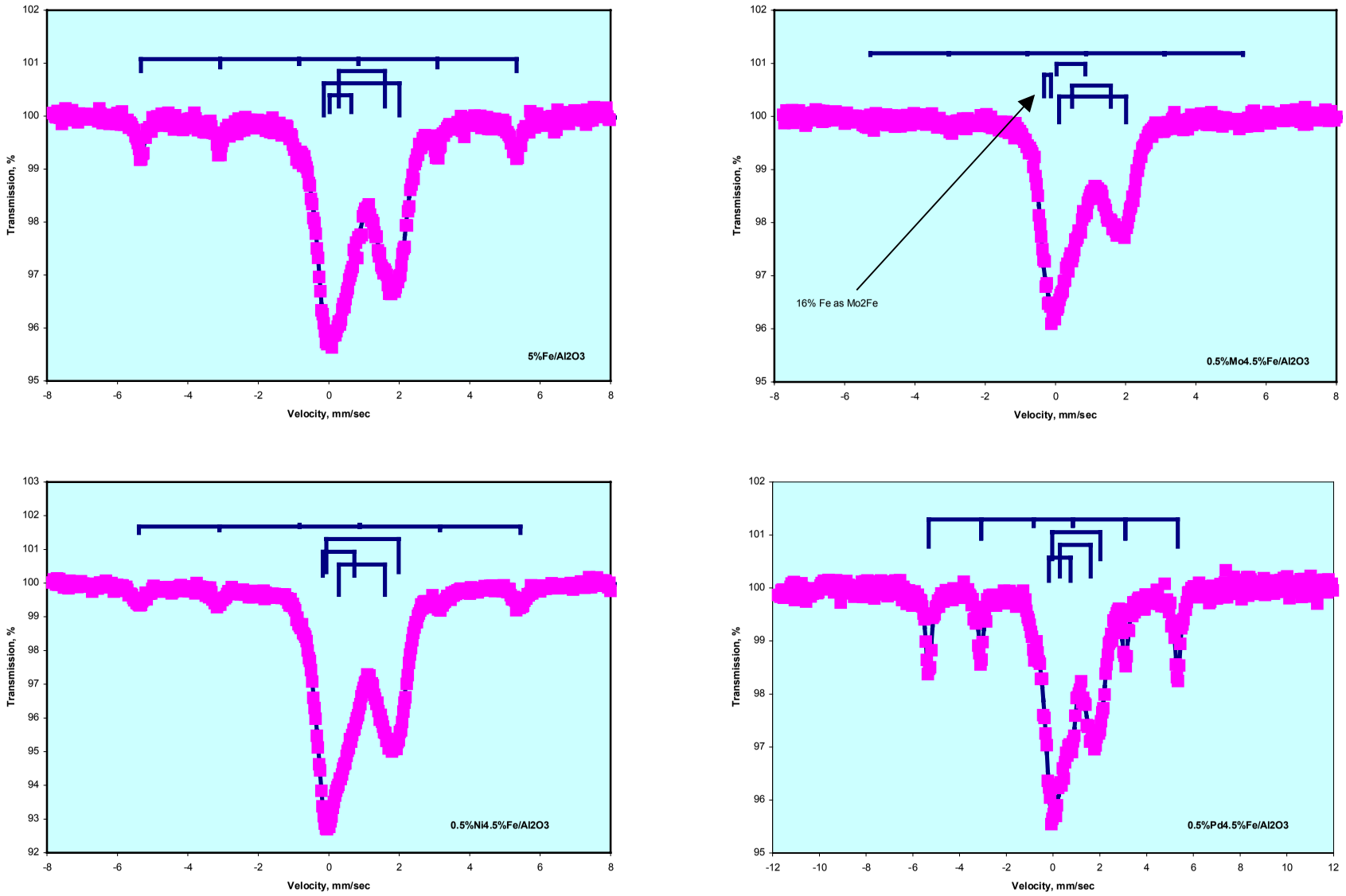
Catalysts reduced at 1000

MK	Catalyst	Fe^{++}	Fe^{+++}	Fe Alloy	Fe Metal
2625	5%Fe/Al_2O_3		4		96
2600	0.5%Mo4.5%Fe/Al_2O_3		29	48.5(♣)	22.5
2679	0.5%Ni4.5%Fe/Al_2O_3			46(♥)	54(♦)
2666	0.5%Pd4.5%Fe/Al_2O_3			1	99

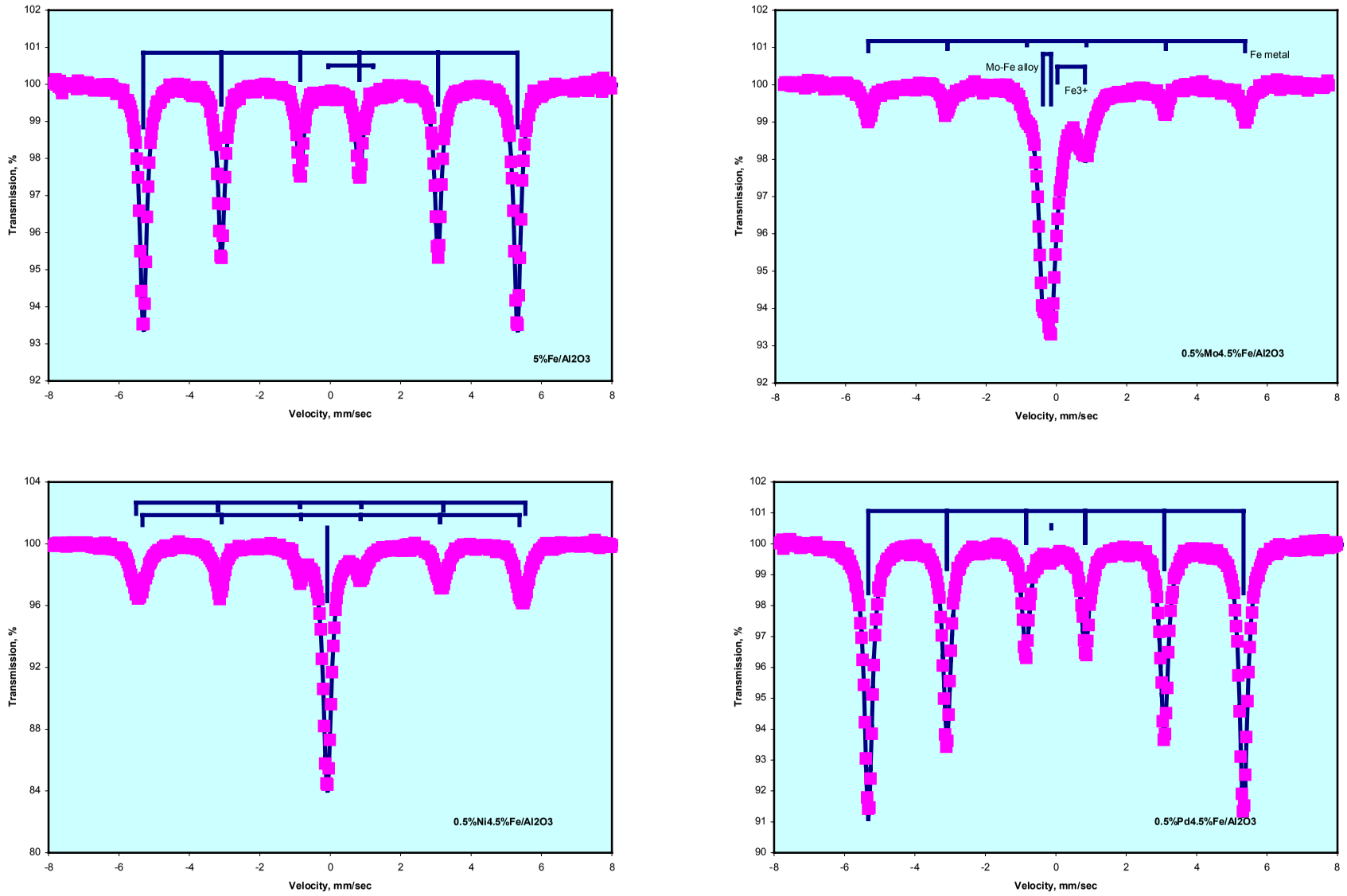
(♣) Fe exists as Mo_2Fe

(♥) Ni is substituted for Fe in austenite phase

(♦) evidence of Ni substitution for Fe in Fe metal



Figures 2-5: Fe Mossbauer spectra of catalysts reduced at 700 C in flowing hydrogen.



Figures 6-9: Fe Mossbauer spectra of catalysts reduced at 1000 C in flowing hydrogen.