

## Mössbauer and XAFS Investigation of C1 Catalysts

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**Mössbauer spectroscopy:** As described elsewhere in this report, various C1 catalyst formulations are being prepared, treated, and reacted. In addition, considerable catalyst characterization is being undertaken to determine the chemistry and properties of these catalysts. Although such work is incomplete at this time, significant Mössbauer and x-ray absorption fine structure (XAFS) spectroscopic examination of various catalysts have been undertaken. In this section, we report a preliminary account of the iron Mössbauer spectroscopy of various C1 catalysts prepared and treated in the C1 laboratory at the University of Kentucky (UK).

As described elsewhere, the catalysts are prepared as either binary ferrihydrites or as impregnated alumina ( $\text{Al}_2\text{O}_3$ ). Table 1 summarizes Mössbauer results for the two types of catalyst. As can be seen from this table, the as prepared catalysts are found exclusively as ferrihydrite or similar species. Selective spectra are shown in Figures 1-3.

The most interesting result is the formation of iron carbide in the 5%Fe/ $\text{Al}_2\text{O}_3$  catalysts after reaction under a methane atmosphere, regardless of how the catalyst was prepared (Figure 1). There is no evidence for iron carbide formation under any other conditions. There appear to be some remnant phases left over that clearly reflect the initial treatments of the catalyst. For example, the 5%Fe/ $\text{Al}_2\text{O}_3$  catalyst heated to 1000°C in air before methane reaction (not shown) exhibits a ferric doublet in its spectrum, whereas the same catalyst reduced at 1000°C exhibits  $\text{Fe}^{2+}$  phases and metallic iron, in addition to the carbide spectrum (Figure 1). These ferrous and ferric phases are thought to have formed by reaction of the iron oxide with the alumina support and prevent complete reduction of the iron to the metallic state. The temperature of reduction makes a significant difference as the Mössbauer spectrum of the 0.5%Mo/4.5%/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 1000°C (Figure 3) is clearly much different from that obtained from the catalyst reduced at 700 (Figure 2) or 500°C (not shown). Further work is needed to identify the very narrow doublet in Figure 3 that has an unusually low value for the isomer shift of -0.23 mm/sec. We have tentatively identified it as a Fe-Mo alloys phase.

**Table 1: Summary of Mössbauer Results on Prepared and Treated Catalysts**

Sample ID	Treatment	Fe metal	Fe <sub>3</sub> C	Austenite	Fe <sup>2+</sup>	Fe <sup>3+</sup>
10%Mo/0%Si/FHYD MK2608	As rec'd	--	--	--	--	100 (fhyd)
5%Mo/5%Si/FHYD MK2607	As rec'd	--	--	--	--	100 (fhyd)
#12 5%Fe/Al <sub>2</sub> O <sub>3</sub> MK2598	R @ 1000 C CH <sub>4</sub> rxn	13	43	10	34	--
#13 5%Fe/Al <sub>2</sub> O <sub>3</sub> MK2606	C @ 1000 C CH <sub>4</sub> rxn	33	19	11	37	--
#14 5%Fe/Al <sub>2</sub> O <sub>3</sub> MK2597	O @ 1000 C CH <sub>4</sub> rxn	Trace	65	15	--	20
#23 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2599	R @ 1000 C C @ 725 C	18	--	25	--	57
#27 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2603	O @ 1000 C	--	--	--	--	100 (spinel?)
#28 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2600	R @ 1000	22	--	--	--	29*
#29 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2601	R @ 500 C	5	--	--	61	34
#30 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2602	R @ 700 C	4	--	30	--	66
#31 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2604	R @ 500C C @ 500C	11	--	--	39	50
#32 Mo/Fe/Al <sub>2</sub> O <sub>3</sub> MK2605	R @ 700C C @ 700C	13	--	--	40	47
0.5%Mo/4.5%Fe/Al <sub>2</sub> O <sub>3</sub> MK2596	As prep'd	--	--	--	--	100 (fhyd)

\*Includes 49% unknown doublet (-0.23,0.37) Mo-Fe alloy?

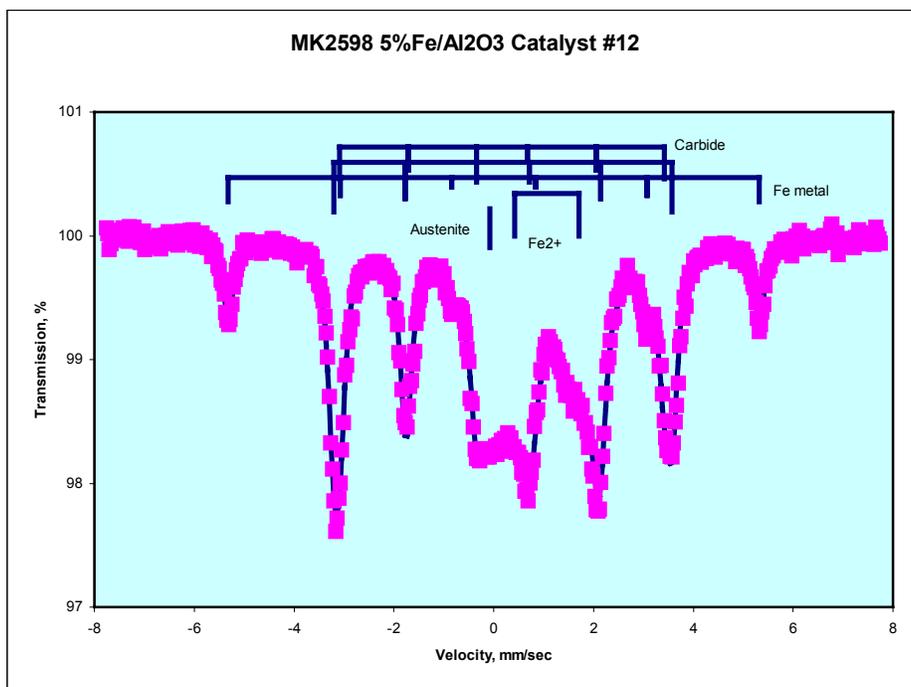


Figure 1: Mössbauer spectrum of 5%Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. Sample 12 after reduction in hydrogen at 1000°C followed by reaction in a methane atmosphere.

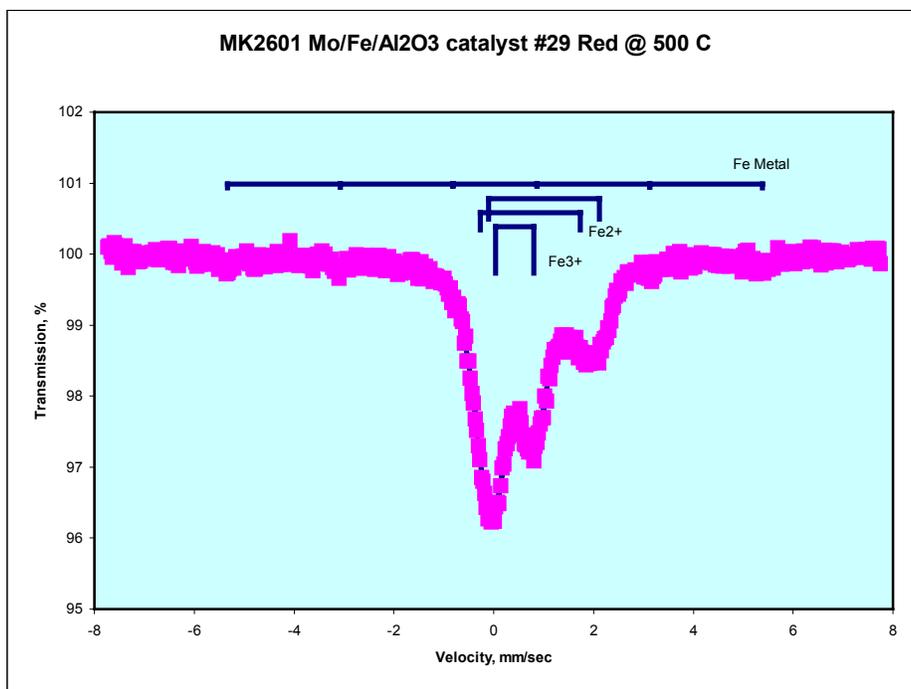


Figure 2: Mössbauer spectrum of 0.5%Mo/4.5%Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. Sample #29 after reduction at 500°C in hydrogen.

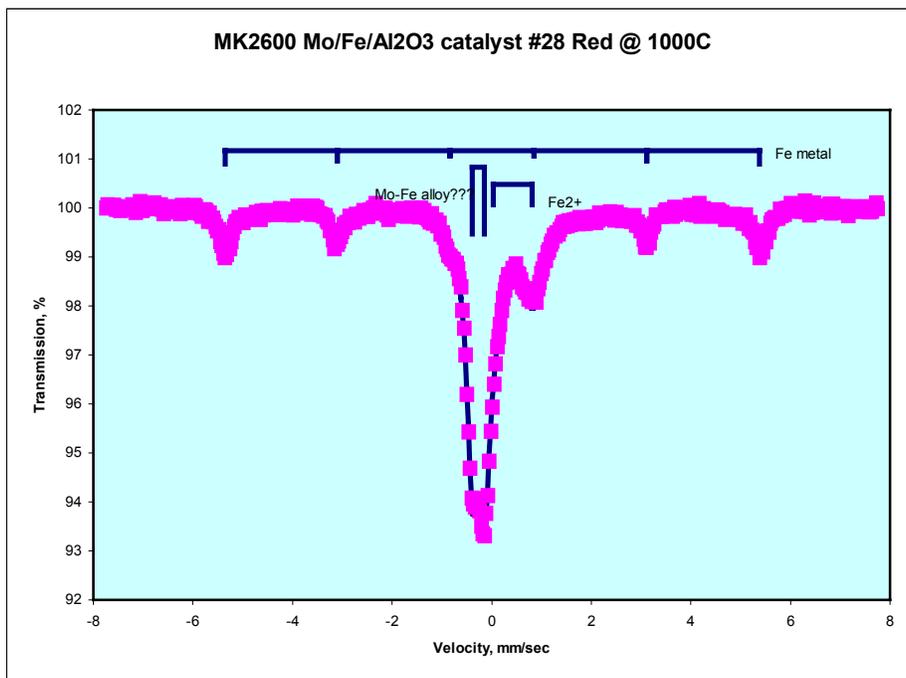


Figure 3: Mössbauer spectrum of 0.5%Mo/4.5%Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. Sample 29 after reduction in hydrogen at 1000°C.

**XAFS spectroscopy:** X-ray absorption fine structure (XAFS) spectra have been obtained from a number of the catalysts synthesized and reacted in the C1 laboratory at UK. Although detailed analysis and interpretation of these spectra is incomplete, some preliminary conclusions can be reported. Qualitative interpretations of the XAFS spectra obtained from 5%Fe/Al<sub>2</sub>O<sub>3</sub>, 4.5%Fe/0.5%Mo/Al<sub>2</sub>O<sub>3</sub>, and 0.5%Mo/Al<sub>2</sub>O<sub>3</sub> catalysts at both the Fe and the Mo K-edges are given in Table 2. The Mössbauer results for several samples are also indicated in the table. Briefly, it is found that the catalysts subjected to reduction treatments at 700 and 1000 °C or to reduction treatments followed by carburization at 700 °C exhibit ~20-50% Fe metal in their Fe K-edge XAFS spectra, and some evidence of metallic forms of Mo in their Mo K-edge XAFS spectra. However, there is little indication of carbide formation for either metal. For the four samples reacted in methane subsequent to reduction or reduction plus carburization, the Fe XAFS data indicate that Fe metal is the dominant component. The as-prepared 4.5%Fe/0.5%Mo/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits spectra consistent with the Mo being present in the form of a molybdate anion, MoO<sub>4</sub><sup>-2</sup>. Subsequent reduction appears to produce lower oxides and a

metallic form of Mo. For the 4.5%Fe/0.5%Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, the Mo generally appears to be less reduced than the Fe after reducing treatments. More detailed analysis of these spectra is in progress.

Unfortunately, the analysis of catalyst samples after reaction may be deceptive, since exposure of small metallic catalyst particles to air when they are removed from the reactor may convert them to oxide. Therefore, much of the current effort in XAFS analysis is focused on the development of an in situ XAFS cell that will allow structural data to be obtained from catalysts during C1 reactions. An in situ cell has been designed and built that should allow investigation of C1 catalysts at temperatures up to 700 °C. It will be tested at the National Synchrotron Light Source at Brookhaven National Laboratory in mid-July of this year.

**Table 2. Mössbauer & XAFS Data Summary for C1 Catalysts**

Sample no. and description	MK no.	XAFS elem	Mössbauer results	XAFS results (qualitative analysis)
47 – AP 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2596	Mo	100% Fe <sup>+3</sup> (ferrihydrite)	XANES edge at ~ same location as MoO <sub>3</sub> with similar shoulder. FT - large peak at 1.3 Å (O), small at 2.9 Å. Very similar to Mo <sub>0.05</sub> /FHYD data (MoO <sub>4</sub> <sup>2-</sup> ).
27 - O-1000 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Mo		Nearly identical to as prepared sample (47).
48 - AP 0.5Mo/Al <sub>2</sub> O <sub>3</sub> & 40 - O-700 0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Mo		Both show an O FT peak at 1.5-1.55 Å and an XANES and an XANES shoulder at ~7 eV, similar to MoO <sub>3</sub> .
41 - R-700 0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Mo		Both XANES and FT look like mixture of MoO <sub>3</sub> and Mo metal.
42 - R & C – 700 0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Mo		FT peaks at 1.37, (~1.7), & 2.4 Å, slightly different from 41. XANES very similar to 41. FT suggests some Mo carbide.
28 - R-1000 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2600	Mo	28% Fe metal, 29% Fe <sup>3+</sup> , 49% Fe-Mo alloy.	Mixture of oxide and metallic forms of Mo. Mo appears to be mainly molybdate (MoO <sub>4</sub> <sup>2-</sup> ).
30 - 0 R-700 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2602	Mo	4% Fe metal, 66% Fe <sup>3+</sup> , 30% austenite.	XANES and FT indicate Mo is still predominantly molybdate (MoO <sub>4</sub> <sup>2-</sup> ).
32 - R-700, C-700 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2605	Mo	13% Fe metal, 40% Fe <sup>2+</sup> , 47% Fe <sup>3+</sup> .	FT – strong peak at 1.57 Å (MoO <sub>3</sub> or MoO <sub>2</sub> nn O shell) and weaker peak at ~2.5 (Mo <sub>2</sub> C nn metal shell). XANES more metallic but still show an oxide shoulder like MoO <sub>3</sub> .
28 - R-1000 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2600	Fe	28% Fe metal, 29% Fe <sup>3+</sup> , 49% Fe-Mo alloy.	Both FT and XANES indicate partial conversion (~50%) to metallic form.
30 - R-700 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2602	Fe	4% Fe metal, 66% Fe <sup>3+</sup> , 30% austenite.	FT indicates ~20-30% conversion to Fe metal, balance hematite. XANES is consistent with this estimate.
32 - R-700, C-700 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>	2605	Fe	13% Fe metal, 40% Fe <sup>2+</sup> , 47% Fe <sup>3+</sup> .	FT and XANES about the same as 30.
33 - R-700, CH <sub>4</sub> rxn 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Fe		FT – strong peak at 2.12 Å (Fe metal) and broad weak peak at ~4.0. XANES close to Fe metal, missing edge shoulder. Appears to be mostly Fe metal.
34 - R-700, C-700, CH <sub>4</sub> rxn, 4.5Fe/0.5Mo/Al <sub>2</sub> O <sub>3</sub>		Fe		Virtually identical to 33.
17 - R-1000, CH <sub>4</sub> rxn 5%Fe/Al <sub>2</sub> O <sub>3</sub>		Fe		Both FT and XANES indicate Fe metal with minor secondary component.
18 - R-1000, C-725, CH <sub>4</sub> rxn 5%Fe/Al <sub>2</sub> O <sub>3</sub>		Fe		Both FT and XANES indicate Fe metal with minor secondary component.
39 - R-700, C-700, 5%Fe/Al <sub>2</sub> O <sub>3</sub>		Fe		FT – strong O peak 1.5 Å, weaker Fe metal peak, 2.17 Å, oxide Fe peak – 2.85 Å. XANES - mixture of oxide and metal.
37 - R-700, 5%Fe/Al <sub>2</sub> O <sub>3</sub>		Fe		Nearly identical to 39.

AP – as prepared.

O – oxidized in air.

R – reduced in H<sub>2</sub>.

C – carburized in 20% CH<sub>4</sub>, 80% H<sub>2</sub>.

CH<sub>4</sub> rxn – reacted in CH<sub>4</sub>.

FT – Fourier transform.

XANES – x-ray absorption near edge structure.

700, 1000 – 700 °C, 1000 °C.