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The Use of Catalysts in Near-Critical Water Processing

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ABSTRACT:

The use of heterogeneous catalysts in near-critical water processing provides many challenges of material stability in addition to the normal questions of chemical activity. Conventional catalyst materials developed in traditional organic chemistry or petroleum chemistry applications provide a source of information of materials with the required activities but often without the required stability when used in hot liquid water. The importance of the use of catalysts in near-critical water processing plays a particularly crucial role for the development of renewable fuels and chemicals based on biomass feedstocks. Stability issues include both those related to the catalytic metal and also to the catalyst support material. In fact, the stability of the support is the most likely concern when using conventional catalyst formulations in near-critical water processing. Processing test results are used to show important design parameters for catalyst formulations for use in wet biomass gasification in high-pressure water and in catalytic hydrogenations in water for production of value-added chemical products from biomass in the biorefinery concept. Analytical methods including powder x-ray diffraction for crystallite size and composition determination, surface area and porosity measurements, and elemental analysis have all been used to quantify differences in catalyst materials before and after use. By these methods both the chemical and physical stability of heterogeneous catalysts can be verified.

INTRODUCTION:

The use of catalysts in hydrothermal processing (high-pressure, high-temperature liquid water) has received relatively limited study. Catalytic hydrothermal processing (250°C to 350°C, up to 22 MPa) can be used to treat wet biomass, organics-in-water process residues and wastewaters by converting the organic contaminants to gases. In this application, catalysts accelerate the reaction of organics with water and produce methane and carbon dioxide. It has been reported both as a means of recovering useful energy from organic-in-water streams and as a water treatment system for wet organic contaminants. The offset of costs by energy recovery may make this waste treatment process economically attractive. The system is operated as a liquid-phase, heterogeneously catalyzed process at nominally 350°C and 20 MPa to produce a methane/carbon dioxide product gas from the water solutions or slurries of organics. We have published extensively on the issue of catalytic operations and stability at these conditions including discussions of the processing environment (Sealock, 1993), early development of catalyst systems for this environment (Elliott, 1993a), and continuous flow reactor tests with fixed beds of catalyst in a tubular reactor (Elliott, 1994b). Test results in a demonstration scale reactor (Elliott, 1999 & 2004) have addressed the issues of catalyst fouling in the use of a range of “real world” feedstocks. Here we summarize those results and discuss the conclusions related to use of catalysts in near-critical water processing systems.

Developing new, stable catalyst formulations for this processing environment has also been an important factor in making this processing technology viable (Elliott, 1994a). Previous reports of continuous reactor tests with biomass feedstocks provide preliminary short-term processing results (Elliott, 1993b & 1993c), but also show the problems of long-term operation of the process because of catalyst instability and fouling. Attempts to pretreat biomass by removing certain components, like alkaline earths, to allow extended use with catalysts, have also been documented (Elliott 1996). More recently, we have demonstrated more stable catalyst formulations for wet gasification as described in patents claims (Sealock, 1997 & Elliott, 1997).

EXPERIMENTAL:

Gasification tests were carried out in fixed-bed catalytic tubular reactors. The mobile scaled-up reactor system (MSRS) (Elliott, 1999) was based on the bench-scale continuous-flow design also described earlier (Elliott, 1994b). The MSRS was designed at a scale of 10 liters/hr of aqueous feed for obtaining engineering data for further scale-up. As shown schematically in Figure 1, it includes the reactor system mounted in a fifth-wheel trailer unit and also a small operations control and analytical room. Design working conditions for the reactor systems were 350°C at 24 MPa.

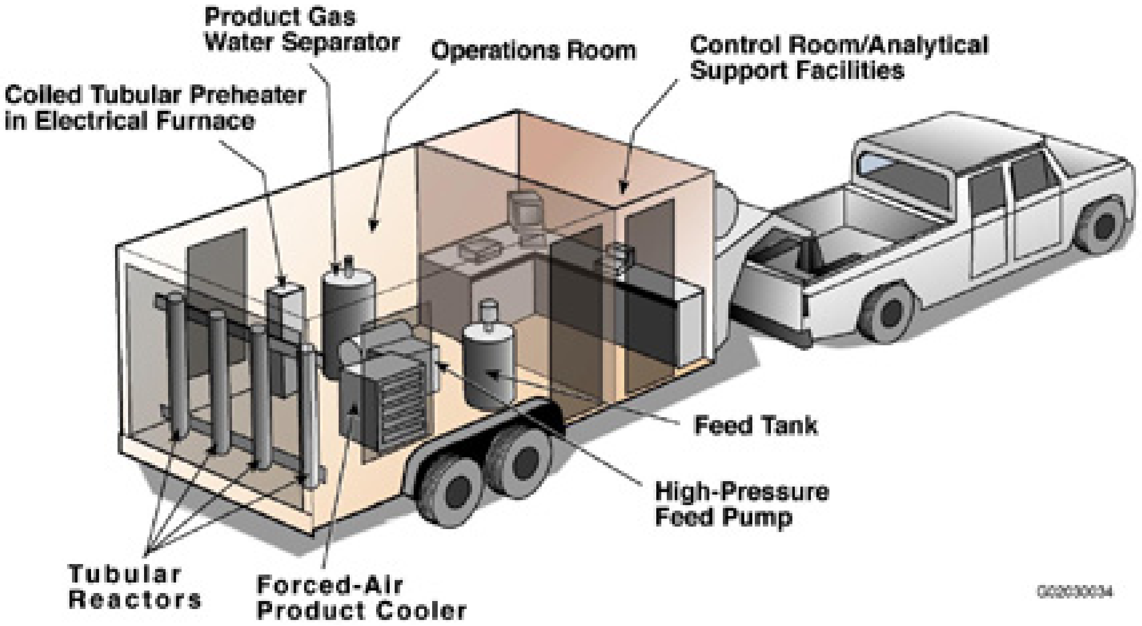

Figure 1. Schematic of Mobile Scaled-Up Reactor System

In the wet gasification process, the wet biomass feedstock was loaded into the feed tank equipped with an electrically driven paddle stirrer to agitate the contents. The feed stream was pumped with a high-pressure reciprocating plunger pump. In the bench-scale unit a progressing cavity pump was used to maintain flow to the high-pressure pump. Preheating of the feedstock was different in the two systems. Initially the bench-scale unit was designed for the initial portion of the tubular reactor to act as the preheater as well. The use of a continuous-flow stirred-tank reactor (CSTR) was required to prevent solids build up at the opening of the reactor when using most biomass slurry feedstocks. In the scaled-up system the feedstock was pumped directly from the feed tank through the tube side of the heat exchanger. The heat exchanger was a double-tube heat exchanger that was constructed of 316SS tubing. With a total length of 17 m, the heat exchanger could bring the feedstock to within 100°C of the final operating temperature when using biomass feedstocks. The final heating of the feed (and start-up heating of the scaled-up system) was accomplished in the coiled tubular preheater. The catalytic gasification reactors were of a tubular fixed-bed design. After leaving the reactor(s), the product stream was routed through a heat exchanger (to provide heat for preliminary heating of the feed stream in the scaled-up version). Downstream of the exchanger, the process pressure was reduced to ambient over a back-pressure regulator. The product stream then entered a liquid/gas separator tank, where process water was reclaimed and combustible gases were sampled for analysis, measured and then vented.

RESULTS AND DISCUSSION:

Results are provided for continuous-flow processing of wet gasification at bench-scale and in a scaled-up reactor system.

Catalyst Development The G1-80 steam reforming catalyst from BASF Corporation has served as a basis for much of our nickel catalyst development research. It is a nickel oxide on proprietary support. It is a thermally stable catalyst with a good resistance to degradation in steam. This catalyst was the first identified with long-term activity in low-temperature catalytic gasification. As shown in Table 1, it retained activity for up to four weeks of operation. The nickel metal exhibited the same crystallite growth seen in other nickel metal catalysts except that after an initial period of growth (up to 40 hours) the crystallites stabilized at 400Å, up from <50Å (see Figure 2). This compared with growth to >700Å or 1000Å in the same time period or less with other nickel metal catalysts (Elliott, 1994a). Our studies have now included 0.1 % Ru and 1% of either Ag, Cu, or Re doped on the G1-80 commercial catalyst and have led to issuance of patents describing the stabilized catalysts (Elliott, 1999) and their use (Elliott, 2000).

Table 1. Results with G1-80 and Stabilized G1-80 Catalysts

	3 weeks		4 weeks		6 weeks		9 weeks		24 weeks		33weeks	
catalyst	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV
G1-80	95.1	1.55	93.6	1.41	--	--	--	--	--	--	--	--
0.1% Ru	--	--	93.1	2.3	94.4	2.05	93.7	1.75	--	--	--	--
1% Ru	99.99	1.9	--	--	99.8	1.9	99.8	1.8	99.0	1.7	73	1.74
5% Ru	99.9	1.97	99.8	2.2	--	--	--	--	--	--	--	--
1% Ag	99.8	1.66	99.8	1.66	--	--	--	--	--	--	--	--
1% Cu	98.0	1.67	96.6	1.68	98.7	1.68	99.2	1.66	--	--	--	--
1% Re	99.8	1.69	(plugged after <5 days on stream)					--	--	--	--	--

Ruthenium was added to the G1-80 catalyst in an attempt to stabilize the nickel metal and reduce the crystal growth phenomenon. The first attempt was a 5% loading which produced a very active and longer lived catalyst. After four weeks of operation the catalyst was still very active while maintaining a respectable space velocity, as shown in Table 1. Analysis of the catalyst showed that the nickel crystallites had grown only to 260Å, thus confirming the hypothesis of the test. Actually, a comparison of the relative advantage gained by ruthenium as a catalyst versus the stabilizing effect of the ruthenium on the nickel is difficult to judge. Ruthenium has been shown to be an active catalyst in this system also. A test of ruthenium only on the G1-80 support is not possible as the nickel and support material are coprecipitated.

A second doped version of the G1-80 was the addition of 1% ruthenium instead of 5%. A reduced level of ruthenium would make the catalyst less expensive. This catalyst was also found to be very active in catalytic hydrothermal gasification. As shown in Table 1, a long term test verified high activity for at least 6 months. After 8 months of operation the catalyst activity had decreased markedly, but the loss of activity may have been due to deposits of hypophosphorus compounds on the catalyst from the hypophosphorus acid (H_3PO_2) inhibitor added to the phenol feedstock by the packager. Phosphorus in the liquid process effluent was below the detectable level (0.08 ppm) through most of the test but increased to 1.80 ppm in the last 3 months. BET surface area measurements showed a drop from 160 m^2/g in the fresh catalyst to only 18 m^2/g after the long-term test. Pore volume had been reduced from 0.22 cc/g to only 0.06 cc/g. The average pore diameter had increased from 55Å to 124Å with the loss of most of the pores under 100Å. The nickel crystallite size after 8 months was still <300Å. The stability of the catalyst is further confirmed by the analysis of the liquid process effluent for catalyst components. Ruthenium was below the level of detection (0.08 ppm) in all samples throughout the test. The nickel results ranged from 0.07 ppm up to 1.31 ppm with a spike at the beginning of the test at 15.95 ppm Ni. Chromium levels were also usually below the level of detection (0.02 ppm) but several samples were measured at up to 0.15 ppm Cr. This level of nickel and chromium in the effluent is apparently coming from the reactor wall as it is also found when other catalysts were tested.

A third ruthenium-doped version of the G1-80 was the addition of only 0.1% Ru. This catalyst batch was tested for long-term activity and was found to be significantly less active than the other Ru-doped G1-80s while still somewhat more active than the regular G1-80.

Other metals have similar effects when used in place of the ruthenium. Silver appeared to stabilize the nickel crystallite growth in the G1-80 at least as well as Ru in a batch test followed by a long term batch test with water. The resulting nickel crystallites were only 130Å using a 1% Ag loading. Of course, silver would be a much less expensive additive and more readily available than ruthenium. A long-term test of the Ag-doped G1-80 ran for 32 days before a pressure differential across the catalyst bed ended the test. Throughout the test the catalyst activity remained high. Following the test the nickel crystallite size had increased to only 214Å, a significant improvement over the Ru-doped catalyst. The silver metal crystallites were also measureable at 242Å.

The copper appeared to stabilize the nickel crystallite growth in the G1-80 better than either Ru or Ag in a batch test followed by a long term batch test with water. The resulting nickel crystallites were only 104Å using a 1% Cu loading. Of course, copper would be even less expensive additive and more readily available than silver. The long-term test of the Cu-doped G1-80 demonstrated good activity through nearly 9 weeks, as shown in Table 1. Following the test, the nickel crystallite size was measured at only 181Å, an improvement in nickel stability over either silver or ruthenium doping.

We also evaluated rhenium as a stabilizer for the G1-80. The Re-doped catalyst showed high activity in the batch reactor. In the continuous unit it showed good activity and was still improving when the reactor plugged after <5 days on line. The used catalyst had nickel crystallites of 142Å about the same as with ruthenium doping.

The relationship of crystallite size with time on stream in catalytic gasification is shown in Figure 2 for all the G1-80 catalyst versions tested here. Tin (Sn) was tested as a nickel stabilizer only in the batch rector.

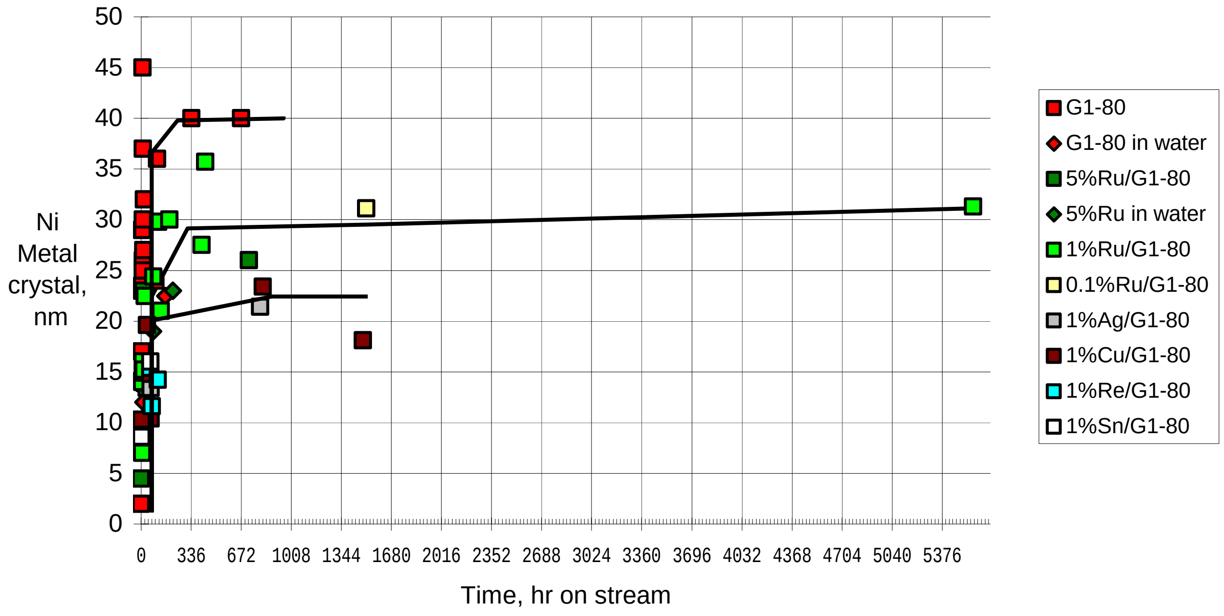

Figure 2. BASF G1-80 Catalyst Lifetime Tests

Our test results (Elliott, 1994b) have shown that ruthenium is a very active catalyst for catalytic hydrothermal gasification. Low metal loadings can still produce highly active catalysts. Alumina supports used in the early tests have been shown to be not stable in the near-critical water environment. High-surface area titania was isubsequently tested as a support for the ruthenium. We found that the anatase-rutile titania formulation used as the support was not stable at higher temperature and reverted to the rutile form preferentially. The data in Table 2 show this transition and the resulting loss of catalyst activity.

Table 2. Ruthenium/Titania Catalyst Long-Term Test Results

Temperature ° C	Time on Stream weeks	Surface Area m^2/g	Pore Volume cc/g	Anatase/ Rutile	LHSV L/L/hr	Reduction of COD %
Unused	0	44	0.20	58/42	---	---
350	1	NA	NA	NA	1.7	99.7
350	6	27	0.14	32/68	1.3	99.95
350	11	25	0.10	36/64	1.95	<95
350	14	21	0.09	18/82	1.4	78

Other supports were subsequently tried for the ruthenium with results presented in Table 3. The zirconia support was loaded with 5% ruthenium. The titania support listed in Table 3 is the mixed anatase and rutile formulation, with 3% Ru. A more useful formulation is based on the rutile form of titania (Elliott, 2001). It shows that high conversion of the COD was accomplished even at the highest space velocities tested. Similarly, a carbon support loaded with about 8% Ru also exhibited extremely high activity. Results are shown at even higher space velocities without actually ever pushing the catalyst bed to its maximum.

Table 3. Results with Ruthenium Catalysts

	1 weeks		3 weeks		6 weeks		11 weeks		14 weeks		19weeks	
Support	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV	conv	LHSV
Zirconia	99.91	2.12	94.0	2.13	--	--	--	--	--	--	--	--
Titania	99.7	1.72	99.8	1.66	99.95	1.3	94.7	1.95	78	1.4	--	--
Rutile	99.99	1.49	99.99	1.66	99.99	1.73	99.99	1.91	low temp.		99.99	1.47
Carbon	99.99	1.15	99.99	1.83	99.99	3.14	low temp.		--	--	--	--

Tests at 350°C & 3000 psig except for those portions marked at lower temperature

Bench-Scale Testing. The bench-scale reactor system was used to generate process information for the catalytic gasification of several wet biomass feedstocks. The process was operated at nominally 21 MPa and 350°C. The slurry feedstock was ground in a stirred ball mill to pass a 60 mesh screen before being pumped. The feed slurry passed through a continuous-stirred-tank reactor (CSTR) which served as a preheater in order to liquefy the biosolids. The 1-liter tubular reactor was filled with a fixed-bed of catalyst particles. The results presented in Table 4 are for three different days of operation. The same catalyst bed was used for the first two days of operation with the manure and Midwest DDG&S; a different catalyst bed was used for the Furst-McNess test.

The test with manure provided very positive results. The feed slurry was pumped smoothly, without interruption or plugging. The reaction proceeded well with good gas production and nearly complete manure gasification. An important result of this test was the passage of the manure-derived inorganic material through the reactor and into the down-stream product collection system where it was simply settled from the product water as a powder. The effect of process rate on the extent of gasification is evident by comparing the three data sets, as they represent a progression to faster throughput over the period of the experiment.

The test with the Midwest Grain DDG&S feed was also relatively problem-free. However, it is noticeable that there is a tendency toward catalyst deactivation over the time of this experiment. The destruction of the organics causing the chemical oxygen demand is reduced, as is the gas yield. Also, there is a shift in gas composition away from methane and toward hydrogen, and higher hydrocarbon gas production, indicating less effective reforming and gas synthesis reactions.

Table 4. Bench-Scale Test Results

	WSU Dairy manure			Midwest Grain DDG&S			Furst-McNessDDG-S		
On stream, hours	6	9	14.5	5(+14.5)	8.5(+14.5)	14.5 (+14.5)	3	5.5	7.5
Feed COD, g/L	47	47	47	79.5	79.5	79.5	65	126	126
LHSV, L/L/hr	1.65	2.09	2.60	1.54	1.73	1.40	1.37	1.59	1.37
Temperature, C	356	355	355	350	350	355	350	350	350
COD Conversion	99.89	99.78	98.30	99.72	99.52	95.48	99.78	99.94	99.91
Gas Yield, L/g DS	0.81	0.76	0.67	0.72	0.67	0.57	40.0	68.0	68.6
Higher Heating Value MJ/m3	21.9	24.9	28.6	24.8	24.3	24.6	24.4	23.3	23.6
Gas Composition, vol %									
methane	54	61	54	59	58	52	60	57	58
carbon dioxide	45	37	39	38	40	42	37	41	40
hydrogen	1.0	1.2	1.5	1.5	1.4	2.0	2.6	2.5	2.6
ethane	<0.1	<0.1	0.5	0.2	0.4	1.7	<0.1	<0.1	<0.1
hydrocarbons	0.4	0.5	6.0	0.8	0.9	2.4	0.3	0.3	0.4

The test with the Furst-McNess DDG&S was similarly successful. There was no sign of loss of catalyst activity over the short period of the run. The same high level of conversion was seen with good gas quality. There were some indications of pumping difficulties, such as loss of pump prime and some pressure drop build-up over the catalyst bed.

Scaled-Up Reactor Operation. A limited amount of scale-up testing has been completed in the engineering demonstration unit using wet biomass feedstocks. Results are shown in Table 5. Engineering issues related to feeding the slurry to the high-pressure reactor were the focus of much of the work. As in the bench-scale unit, a CSTR was installed between the pump and the catalytic reactor beds. Solids build-up at the entrance to the catalyst bed and resulting flow stoppage were to be avoided by the liquefaction caused in the preheating by the CSTR. The progressing cavity pump was not used in the scaled-up system since adequate flow could be achieved by gravity feed. The feed slurry was processed through an Arde Barinco in-line grinder for several hours to achieve pumpable slurry of the Midwest Grain DDG&S feedstock. The tube-in-tube heat exchanger was used as a preheater/liquefier.

Table 5. Scaled-Up Engineering Demonstration Results

	w/CSTR	bypass CSTR		
On stream, hr	3	7.5	7 (+7.5)	2 (+15.5)
Feed COD, ppm	72600	33000	67000	12975
LHSV, L/L/hr	2.46	2.14	2.35	2.66
Temperature, °C	340	345	350	345
COD Conversion	99.96	99.83	50.1	22.93
Gas Yield, L/g DS	0.75	0.68	0.15	0.22
Higher Heating Value of Gas, MJ/m^3	23.5	24.0	17.6	13.8
Gas Composition, %				
methane	56	57	31	2.9
carbon dioxide	40	39	57	12
hydrogen	3.6	3.0	6.6	81*
ethane	<0.1	<0.1	2.5	1.3
hydrocarbons	0.6	0.5	2.9	3.4

* due to low gas yield, not all of the hydrogen had been purged from the system

The first day of operation was plagued by pumping problems. The pumped stopped pumping numerous times principally because of clogged check valves. Plugging at the entrance to the reactor was also a problem. The process operated quite well, chemically, giving high levels of conversion and good gas quality. The use of the CSTR did not appear to provide any advantage relative to the plugging at the reactor entrance. Plugging occurred whether or not the CSTR was on line.

For the second day of operation the reactor entrance was reconfigured to allow better flow into the reactor bed. The system was run without the CSTR. The tube-in-tube heat exchanger provided all the required liquefaction of the biosolids and also provided heat recovery, preheating the feed from 25°C to 250°C while effectively cooling the product from 355°C to 30°C. Following the test, examination of the insides of the tube-in-tube heat exchanger showed only a light powder coating on the tube wall and no significant fouling of the surface. Consistent pumping was less of a problem in this test. By the completion of the 8-hr test, there was an indication of plugging at the front end of the reactor as evidenced by a 1.7 MPa pressure drop.

The catalyst showed evidence of being deactivated at the early stages of the test. One possible explanation for the deactivation was that the opening of the #1 reactor to rebuild the front end may have been sufficient to allow oxygen into the beds to react with the ruthenium metal. As shown in the final column of data in Table 4, it was found that an on-line exposure to warm hydrogen was not sufficient to regenerate the catalyst activity.

Analysis of samples from the plugging materials and the catalysts was performed by TEM, XPS, and XRD methods to determine changes in the catalyst as well as ICP and XRF elemental analysis. These analyses clearly showed that certain of the biomass trace components precipitated and plugged the catalyst bed entrance that a crust of trace components from the biomass was deposited onto the catalyst pellets, and that some of the biomass components passed through the catalyst bed reacting with and poisoning it as it went.

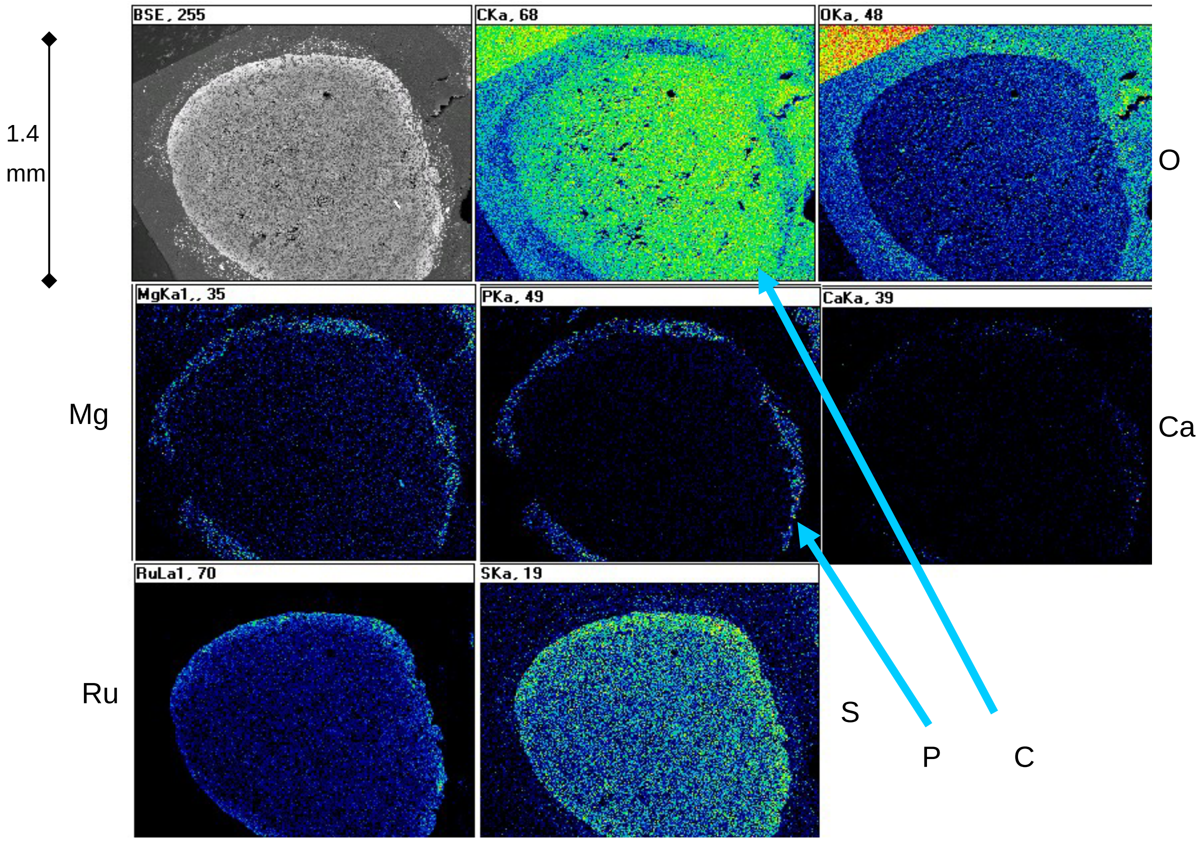

Figure 2. SEM Analysis of a Cleaved Used Catalyst Pellet

A combination of ICP and XRF elemental analysis and XRD showed that the plugging precipitate at the entrance to the catalytic bed in the reactor was composed primarily of hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and iron-chrome stainless steel from the wet grinding media. As seen in Figure 2 (Elliott, 2004), the SEM analysis of the used ruthenium on carbon catalysts shows an outside crust wherein magnesium is associated with phosphorus and lesser amounts of calcium are found. Sulfur contamination only was found within the catalyst pellet and was highly associated with the ruthenium (note particularly the higher concentrations toward the surface of the pellet). In Figure 3 (Elliott, 2004), XPS analysis of the internals of cleaved catalyst pellets (composed of ruthenium on carbon) showed that the contamination of the bulk of the material was limited to sulfur, which was found throughout all 4 of the reactor beds. In the figure, C-3610 indicates the analysis of the fresh catalyst while R-1 through R-4 indicates samples from the four tubular reactors. Some evidence of nitrogen contamination was also found, but it appeared to be limited to the first two reactor beds.

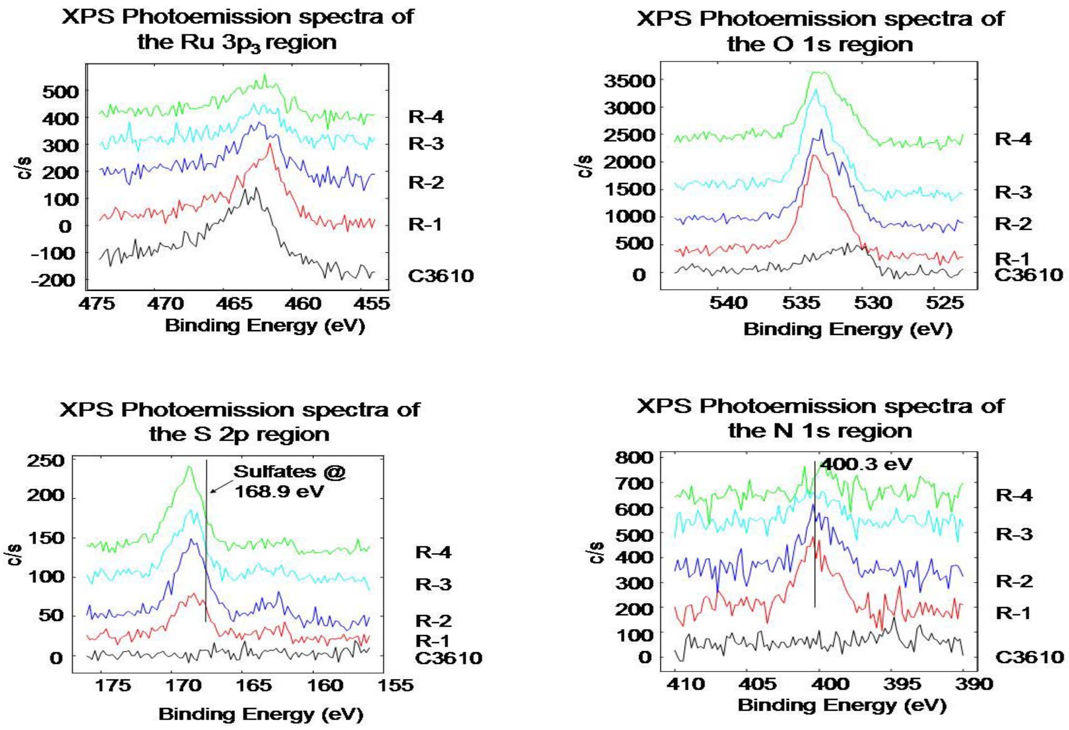

Figure 3. XPS Analysis of Cleaved Catalyst Pellets

CONCLUSIONS:

With proper formulation, heterogeneous catalysts can be used in near-critical water processing systems. Metals are subject to oxidation in this processing environment and only certain metals will remain reduced and active. Stable catalyst supports are required and conventional supports of alumina or silica oxides are not useful. Specific crystalline forms of other oxides such as rutile titania and monoclinic zirconia appear to be stable and useful as is carbon. Deposition of feedstock contaminants onto the catalysts is another issue which needs to be considered. Sulfur poisoning as well as alkaline earth carbonate and phosphate deposition have been studied.

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