5.3.5.2.6 Overall Summary of Used Catalyst Characterization

After soxhlet extraction of the overwhelming majority of Fischer-Tropsch wax, the used catalysts showed, by XPS, two types of carbon with different chemistry. The majority of the carbon on the surface was hydrocarbon-like, while the other type appeared to be associated with oxygen. This second type of carbon may be part of an organic oxygenate molecule or may be carbon bound to the oxygen of the support.

Further soxhlet extraction of the used catalyst with methylene chloride/methanol resulted in a decrease of both types of carbon on the surface, according to XPS measurements. HRMS, IR and fluorescence analyses of this final extract material showed three types of carbon compounds.

Part of the extract contained long chain olefinic or cyclic oxygenates which appeared to be acids and/or esters with carbon numbers up to 35. This result is consistent with XPS measurements which indicated that a carbon apparently bound to oxygen was removed during the final extraction and furthermore, suggests that part of the oxygen-bound carbon detected by XPS indeed may be long chain acids and/or esters.

The second type of carbon compound detected in the final extracts was paraffinic hydrocarbons, which typically makes up the Fischer-Tropsch wax. This result is also consistent with XPS measurements which indicated that carbon in a hydrocarbon-type environment was removed during the final extraction.

The third type of detected carbon compound, which amounted to the minor material in the extracts, was aromatics, which consisted of aromatic hydrocarbons, aromatic oxygenates and polynuclear aromatics. These paraffinic and aromatic hydrocarbons would not be easily distinguished by XPS and are possibly related to the hydrocarbon-like carbon detected by XPS.

Examination of the alkylbenzene distribution in the extracts indicated that the aromatization tendency of Fischer-Tropsch olefins and/or paraffins increased with carbon number. It was also determined that the formation of polynuclear aromatics from alkylbenzenes was very favorable.

Aromatics amounted to the minor material in the extracts. However, aromatics may be harder to remove with the extraction techniques used here, and therefore, may be present at a relatively higher concentration on the catalyst surface.

NMR could not detect the carbon bound to oxygen. However, NMR detected two types of hydrocarbon-type carbon with similar chemistry but with different mobility. The mobile carbon species had the same features as Fischer-Tropsch wax. This carbon could be a small portion of the wax retained in the used catalyst despite the soxhlet extraction steps and is not expected to be chemically bound to the catalyst surface. The carbon with higher restriction to motion is possibly chemically bound to the catalyst surface. Alternatively, the 2 ppm NMR shift observed here between the two carbon species may be caused by different restrictions for motion of wax-type hydrocarbons inside or outside the catalyst pores or with waxes of different crystallinity. However, the immobile carbon could also be removed during soxhlet extraction with methylene chloride/methanol and, therefore, should be one of the three compounds detected in the final extracts.

According to results reported by A. Bell's group α-type carbidic carbon connected to ruthenium and β-type carbon bound to ruthenium with a methylene group had about 7 ppm shift in the NMR spectra. The 2 ppm shift in NMR spectra observed here probably is not caused by the presence of α-type and β-type carbon on the catalyst.

The presence of multiple types of carbon on the used catalysts after Soxhlet extraction with cyclohexane was also confirmed by differential scanning calorimetry (DSC) measurements. According to DSC measurements, two types of carbon were present, which burned at ~30°C different temperatures. Extraction with toluene and with methylene chloride/methanol resulted essentially in the disappearance of the low temperature peak and shifted the high temperature peak to lower temperatures.

Organic molecules are expected to burn at different temperatures depending upon the hydrogen:carbon ratio in the molecule. The presence of multiple DSC maxima with used catalysts may then be explained by the presence of carbon species with different hydrogen contents.

The major DSC maximum occurred at a lower temperature with the modified ruthenium catalyst relative to the unmodified catalyst. This may then suggest that coke on the modified catalyst has a higher hydrogen content. However, it is important to point out that, according to NMR, the two types of carbon species observed here had similar chemistry, therefore, similar hydrogen:carbon ratios. Therefore, another factor may have caused the presence of multiple DSC maxima. It is not presently clear whether the two carbon species with different mobilities, as detected by NMR, would burn at different temperatures.

5.3.5.3 Elucidation of the Role of Modifier in the Improved Catalytic Stability Observed

At least three criteria are needed for stable catalyst performance:

1. The catalyst must not lose metal surface area by agglomeration.

2. The coverage of active sites by the active carbon species should not indefinitely increase. This carbon species may form via CO dissociation on vacant active sites. This, then, implies that catalytic stability may be improved when the catalyst is modified in a manner that balances the CO dissociation rate relative to the hydrogenation rate of this active carbon into methyl and methylene species.

3. The hydrocarbons on the surface should not be converted into polynuclear aromatic (PNA) compounds. Therefore, a modifier which suppresses the dehydrogenation/cyclization reaction of hydrocarbons into PNA's may improve catalytic stability.

The extent of ruthenium metal surface area loss through agglomeration observed at the end of Run 46 with the new modified ruthenium catalyst can explain the observed deactivation. This may indicate that, for this catalyst, deactivation by coking is minimal. These results are in sharp contrast to those observed with unmodified ruthenium catalysts. One such example is the unmodified ruthenium Catalyst 4966-198. This catalyst gradually deactivated during Run 47 although the ruthenium particle size remained 4-6 nm during the 825-hour run, indicating that deactivation probably was via coking.

Examination of used catalysts indicates that the amount of coke on the modified catalyst was much less than the amount on the unmodified catalyst, although the test with the modified catalyst was 886 hours longer. The modified ruthenium catalyst showed a lesser amount of hydrocarbon-type carbon and carbon associated with oxygen, according to XPS. A carbon with restricted motion was also present in lesser quantities on the modified catalyst. Finally, low quantities of aromatics and no polynuclear aromatics were detected, which are in sharp contrast to results obtained with unmodified ruthenium catalysts.

These results indicate that the modifier may have improved catalytic stability by controlling the surface concentration of the active carbon species. This may have been possible if attenuation of ruthenium's initial activity was caused by a decrease in the rate of CO dissociation. A slower rate of formation of the active carbon species may then be more easily balanced by the hydrogenation rate of this carbon species.

It is important to note that there was an apparent inverse correlation between ruthenium's initial activity and the binding energy of ruthenium's $3p_{3/2}$ electrons, as determined by XPS. The ruthenium's binding energy appeared to increase with modification of ruthenium, which also resulted in attenuation of ruthenium's initial activity. For example, Ir appeared to increase ruthenium's binding energy to a greater extent than the proprietary modifier identified in this work, and also caused more attenuation of initial activity. However, differences between modified and unmodified catalysts were small, and, therefore, definite conclusions are not possible.

Alternatively, the modifier may have improved catalytic stability by preventing the transformation of the active carbon species into polynuclear aromatic compounds via dehydrogenation/cyclization reactions.

It is not presently clear whether the alternative deactivation pathway observed with the modified ruthenium catalyst is directly caused by the modifier or is the result of the relatively severe operating conditions that prevailed during the second part of the test with the modified catalyst and would have occurred also with the unmodified catalyst.

6.0 APPENDIX

In an attempt to determine the source of CO_2 observed with ruthenium catalysts, two possible reaction pathways were compared. The first reaction pathway resulted in CO_2 formation via the water gas shift reaction, which may occur subsequent to the hydrocarbon synthesis reaction. The second reaction pathway resulted in CO_2 formation via the Boudouard reaction. In each case the relation between CO_2 selectivity and the H_2 conversion, the CO conversion and $r = H_2{:}CO$ feed ratio was determined. Here, x was defined as the conversion of CO in the hydrocarbon synthesis reaction, y as the conversion of CO in the water gas shift reaction and 2z as the conversion of CO in the Boudouard reaction. Then, plant data in Runs 18 and 21 were used to determine which of these two reaction pathways predicted better the CO_2 selectivities.

Reaction Pathway 1

	CO	+	$2H_2$	$\rightarrow$	CH_2	+	H_2O
initial moles	1		r		o		o
final moles	1-x		r-2x		x		x

	CO	+	H_2O	$\rightarrow$	CO_2	+	H_2
initial moles	1-x		x		o		r-2x
final moles	1-x-y		x-y		y		r-2x+y

H_2 conversion/100 = $2x-y/r$

CO conversion/100 = $x+y$

CO_2 selectivity/100 = $y/x+y$

Reaction Pathway 2

	CO	+	$2H_2$	→	CH_2	+	H_2O
initial moles	1		r		o		o
final moles	1-x		r-2x		x		x

	$2CO$	→	CO_2	+	C
initial moles	1-x		o		o
final moles	1-x-2z		z		z

H_2 conversion/100 = $2x/r$

CO conversion/100 = $x+2z$

CO_2 selectivity/100 = $z/x+2z$

In Run 21 at 3 hours on stream the H_2 and CO conversions were 34% and 77%, respectively. With a H_2:CO feed ratio = r, the first reaction pathway via the water gas shift reaction predicts the CO_2 selectivity to be 24%, while the actually measured CO_2 selectivity was 25.5%, indicating very good agreement. According to the second reaction pathway which involved the Boudouard reaction, the predicted CO_2 selectivity was 18%, much lower than the actually measured value.

Similarly, in Run 18 at 7 hours on stream the H_2 and CO conversions were 8% and 33%, respectively. With a H_2:CO feed ratio = r, the water gas shift reaction pathway predicts 43% CO_2 selectivity which agrees with the actually measured value of 44%. The Boudouard reaction pathway, on the other hand, predicts 32% CO_2 selectivity, which is much lower than the actually measured value.

These results indicate that the water gas shift reaction and not the Boudouard reaction is the most likely source of CO_2.

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