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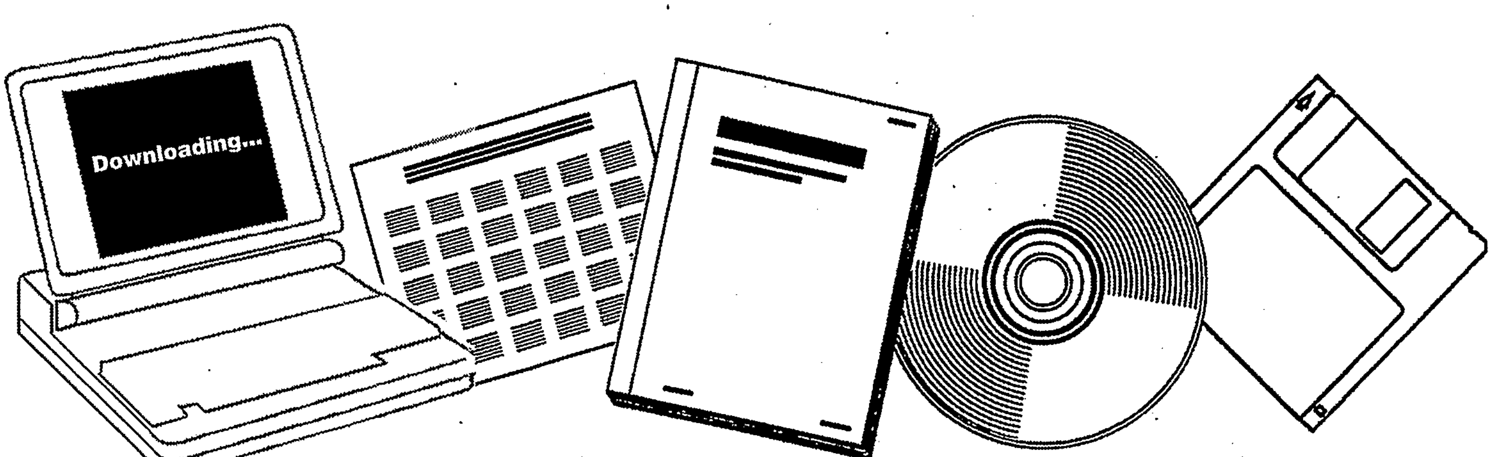

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NEW CATALYSTS FOR THE INDIRECT LIQUEFACTION OF COAL

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Abstract

Some ZSM-5 supported ruthenium catalysts, prepared from $Ru_3(CO)_{12}$ and the acid form of ZSM-5 have been evaluated for their ability to catalyse synthesis gas conversion. The effect of weight percentage ruthenium loading and temperature of evaluation have been studied. Liquid hydrocarbons with varying percentages of aromatics, olefins and saturates are produced.

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A series of ZSM-5 supported ruthenium (Ru/ZSM-5) catalysts, prepared from $Ru_3(CO)_{12}$ and the acid (H^+) form of ZSM-5 have been evaluated for their ability to catalyse synthesis gas conversion. (A previous report has described the characterization of these catalysts). The weight percentage ruthenium loading varies from ~1% to ~8% Ru.

1. Preliminary Evaluation

The initial step in the catalytic evaluation involves reduction of metal species present on the support to metallic ruthenium. Ruthenium is known to be active for the Fischer-Tropsch and water gas shift reactions. Reduction conditions were determined after referring to previous studies on different ruthenium catalytic systems. Kellner and Bell employed 400°C for 8 h in order to reduce their Ru/Al_2O_3 catalysts (1,2). Ru/Y zeolite catalysts investigated by Jacobs and coworkers were reduced at 300°C, and these workers determined that 100% reduction of the metal species was accomplished between 300°C to 500°C (3,4).

The first catalyst to be studied was an 8.13% Ru/ZSM-5 sample which was evaluated over the temperature range of 200°C to 320°C at 20° increments. The catalytic evaluation data were obtained at each temperature for one 48 h period. During this evaluation, a minor problem developed on two occasions causing the pressure in the system to increase above the desired 300 psig. It is believed that the high molecular weight products solidified before the wax trap causing a blockage in the line. To alleviate this problem, the heating tape and insulation between the reactor tube and wax trap were increased to raise the temperature of that section of tubing.

The data from the first evaluation period at 200°C was not reliable due to the blockage; therefore, the reactor was maintained at 200°C for a second 48 h period which was used for the comparison with other evaluation periods. Data from the evaluation of this catalyst are presented in Table 1. The percentages of CO and H_2 conversions increased with increasing temperature up to 280°C where the conversions began to level out. Figure 1 contains the plots of the weight percentages of CH_4, C_{5+}(oil) and wax in the hydrocarbon effluent as a function of temperature. The CH_4 increased from 4% to 77% between 200°C and 320°C; however, the opposite trend was found to be true for the wax which decreased from 84% to 0%. A different trend was observed for the oil yield, one that increased until approximately 260°C, peaked between 260°C and 280°C, but decreased above 280°C. The percentages of aromatics (AR), olefins (OL) and saturates (SAT) were obtained from the FIA analysis of the oil fraction for each evaluation period except for the period at 200°C, due to the lack of available sample, and are depicted in Figure 2 . The trends in aromatic and olefin yields appeared to behave in an opposite manner. Beginning at a high percentage, the olefins rapidly declined after 280°C. Initially, the aromatics are produced in very small yields; however, the aromatic content increased drastically after 280°C. The saturate content varies slightly in comparison to the aromatics and olefins with its peak production at 300°C.

Table 1 : Catalytic Results of the 8.13% Ru/ZSM-5 Catalyst

TEMPERATURE (°C)	CONVERSION (%)		REACTOR EFFLUENT DISTRIBUTION (WT. %)					HYDROCARBON PRODUCT DISTRIBUTION (WT. %)						LIQUID PRODUCT DISTRIBUTION (%)		
	CO	H_2	CO	H_2	CO_2	H_2O	HC	CH_4	C_2	C_3	C_4	C_{5+}	WAX	AR	OL	SAT
200	21	39	76	6	0	7	12	4	0	1	2	9	84			
220	30	54	67	4	0	16	13	5	1	3	3	20	68	3	76	21
240	34	65	61	3	0	20	16	9	1	3	4	31	53	2	79	19
260	36	73	59	3	0	22	16	17	2	5	5	49	23	2	86	12
280	43	90	59	1	1	16	23	31	3	4	6	47	9	7	80	13
300	40	91	55	1	3	23	18	60	5	5	7	23	0	50	14	36
320	37	90	57	1	4	21	18	77	6	4	4	10	0	78	4	18

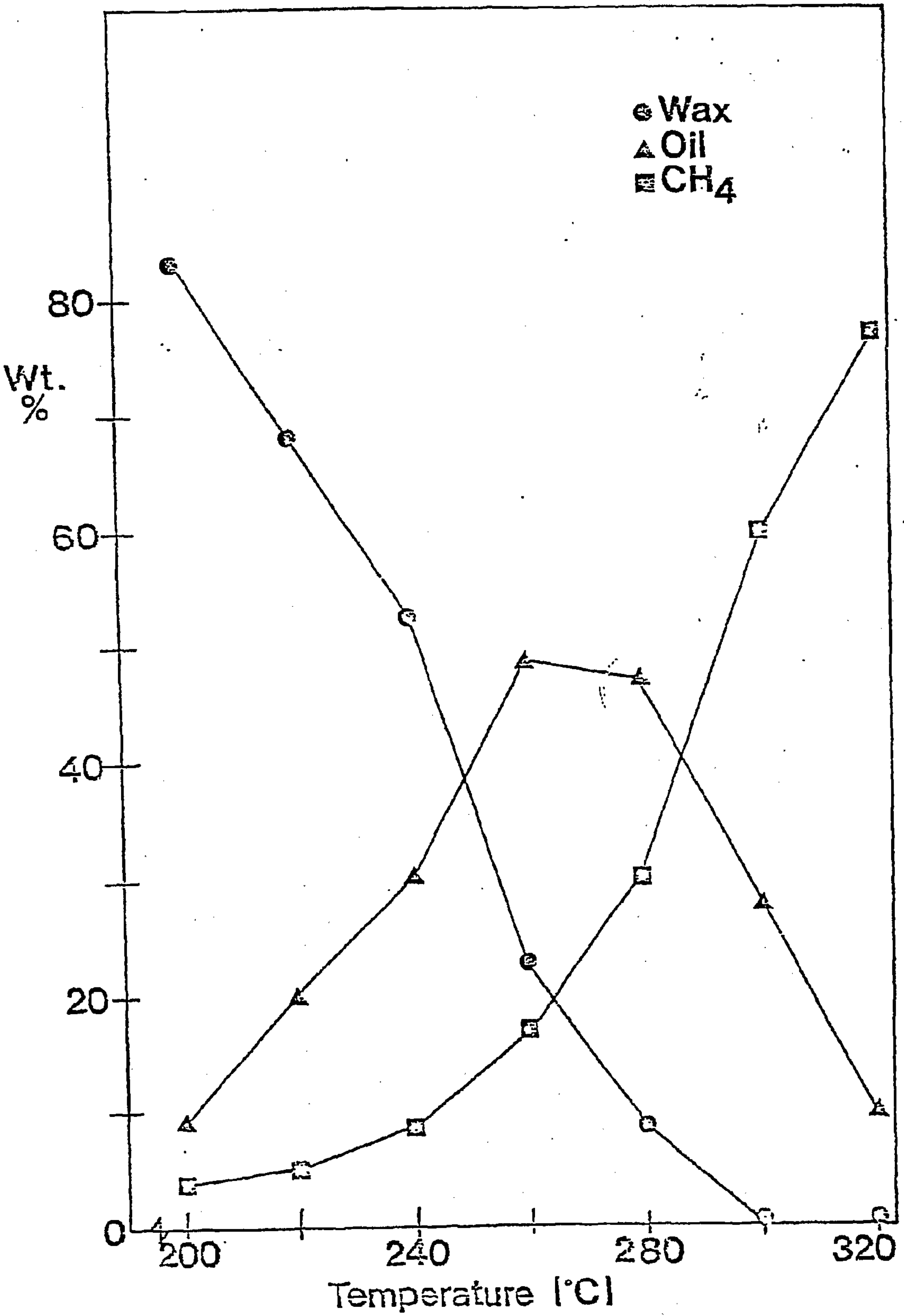

Figure 1. The percentage CH_4, oil and wax in the hydrocarbon (HC) product of the 8.13% Ru/ZSM-5 Catalyst.

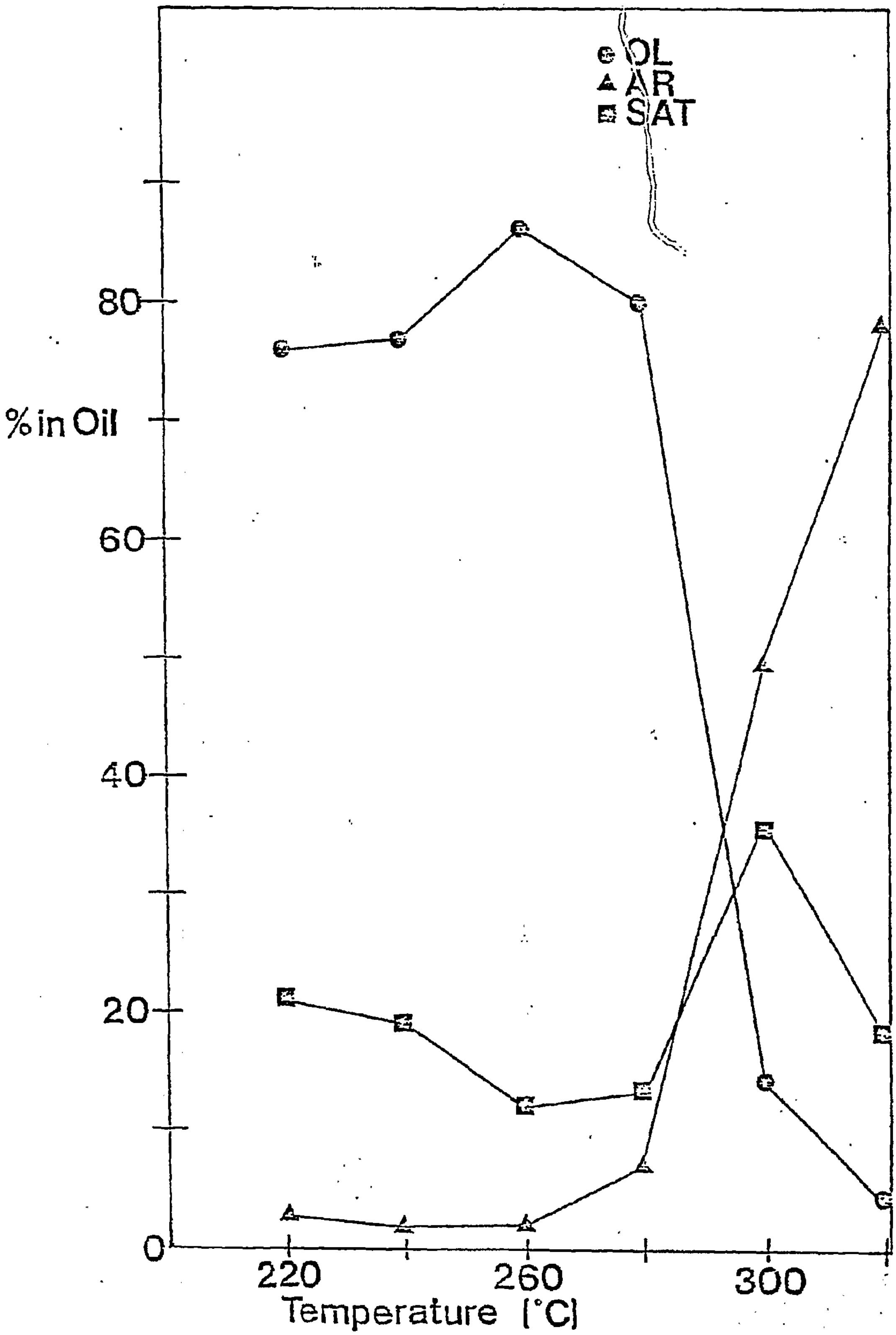

Figure 2. The percentage aromatics, olefins and saturates contained in the oil fractions of the 8.13% Ru/ZSM-5 catalyst.

From this preliminary study, the chosen temperature range for evaluating other Ru/ZSM-5 catalysts was determined to be 260°C to 320°C. The reasons for choosing this temperature range are because the highest yield of oil occurred around 260°C to 280°C, and the highest percentages of aromatics were produced at 300°C and 320°C. These temperatures, also, produced high conversion percentages of H_2 and CO. Thus, during the remainder of this study catalysts were evaluated over the temperature range from 260°C to 320°C with two 48 h evaluation periods at each temperature.

2. Further Evaluations

Three catalysts were evaluated; 0.98% Ru/ZSM-5, 2.88% Ru/ZSM-5 and 7.32% Ru/ZSM-5. Initially, the H_2 and CO conversions were reported, and the plots are represented in Figure 3. The percentages are plotted in reference to the number of days the catalyst was under evaluation conditions with the solid lines joining the two evaluation periods at the same temperature and the dotted lines indicating a change in the temperature. From Figure 3, increases in the conversions are observed as the weight percent loading of ruthenium is increased. However, if the conversions are normalized to 1% Ru when reported, as in Figure 4, the trends are different. From Figure 4, the plots indicate that the 0.98% Ru/ZSM-5 catalyst has the greatest percent conversion when the percentage of Ru is considered, and there is a decrease in the conversions as the amount of Ru increases. These trends indicate that the 0.98% Ru/ZSM-5 catalyst is more efficient for the conversion of the synthesis gas.

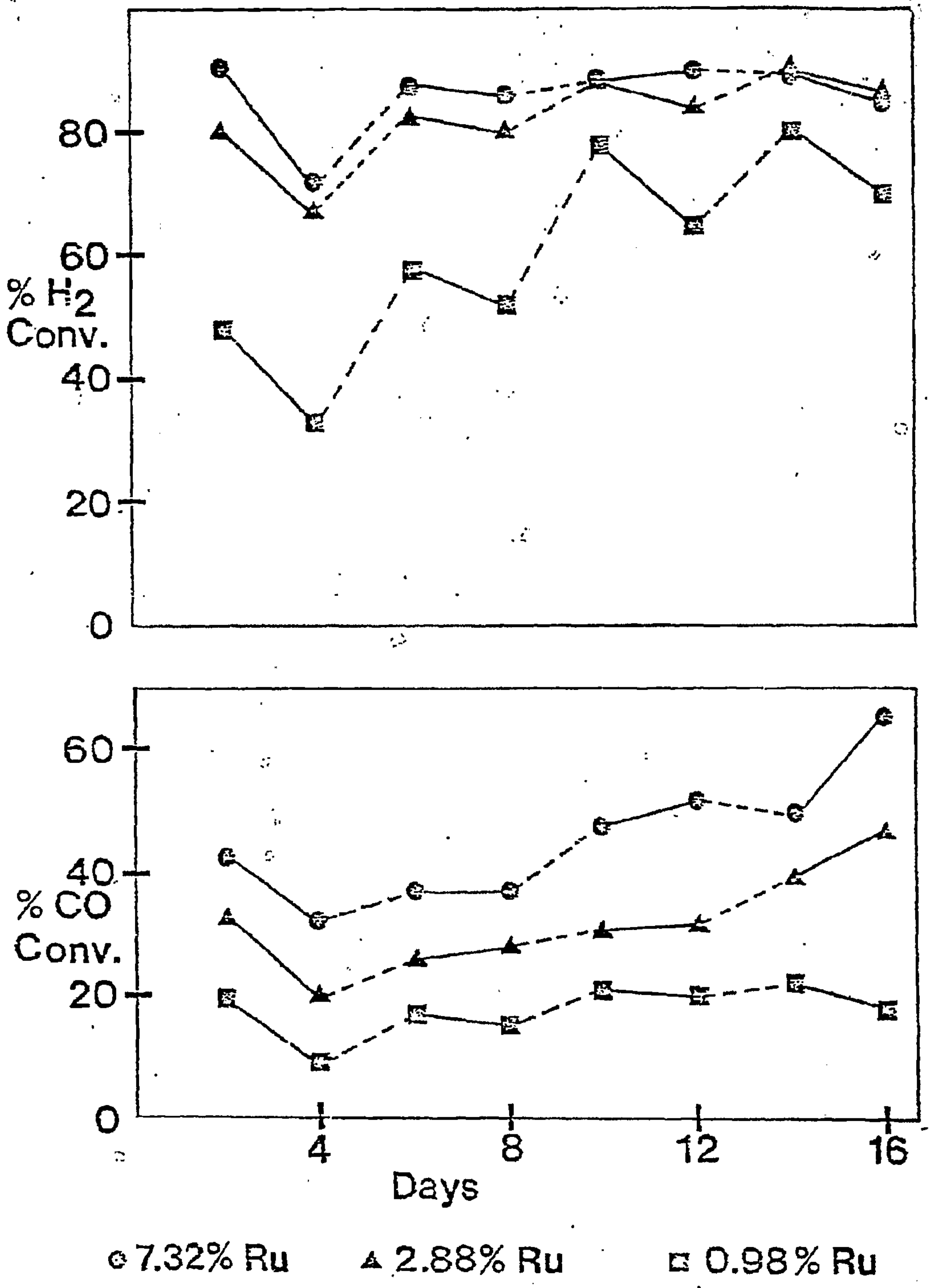

Figure 3. The H_2 and CO conversions for the Ru/ZSM-5 catalysts.

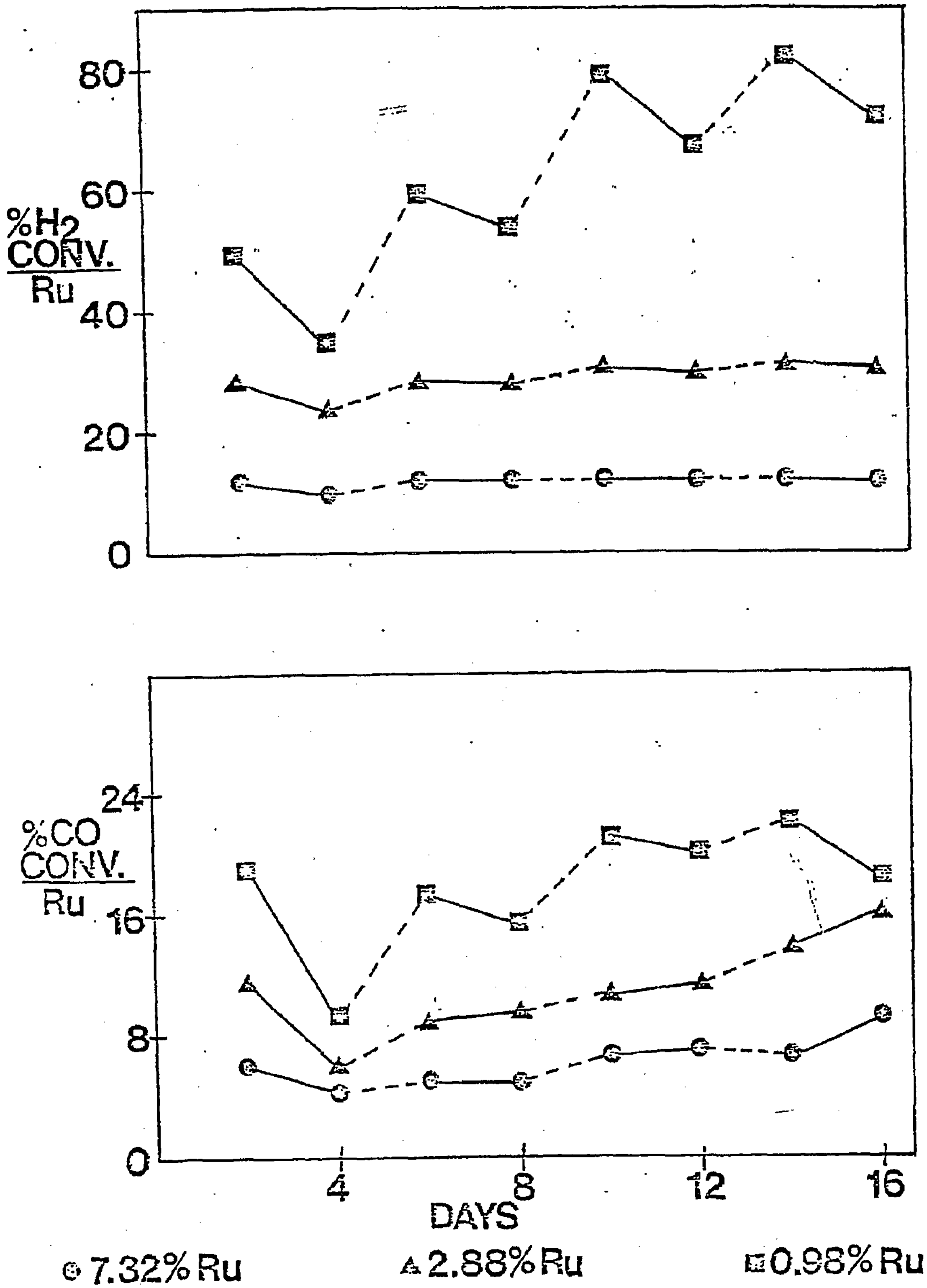

Figure 4. The H_2 and CO conversions normalized to 1% Ru for the Ru/ZSM-5 catalysts.

Due to the expense and limited availability of $Ru_3(CO)_{12}$, the aspect that the lower percentage of Ru is producing the highest conversion per ruthenium is important from an economic viewpoint.

The production of desirable products is another important aspect of the catalytic evaluation. For the total effluent, the weight percentages of hydrocarbons (HC), CO_2 and H_2O are shown graphically in Figure 5. The production of the hydrocarbons remained fairly constant; the rise in the temperature did not produce a drastic change. The yield of hydrocarbons increased with Ru loading, since the overall conversions are higher. The CO_2 production is represented in Figure 5. At 260°C and 280°C there was a low yield of CO_2 which increased with metal loading. The trend of increasing CO_2 with increased Ru loading still exists at 300°C and 320°C; however, the production of CO_2 increased for the 2.88% and 7.32% Ru/ZSM-5 catalysts. The next product to be considered is H_2O which increased with increasing metal loading but decreased with the increase in temperature. The production of the CO_2 and H_2O follow opposite trends, reflecting a shift in the water gas shift reaction above 300°C. Low yields of CO_2 and H_2O, undesirable products, were produced by the 0.98% Ru/ZSM-5 catalyst increasing its desirability as a catalyst for synthesis gas conversion.

The hydrocarbon products were further analyzed, and Figure 6 shows the weight percentages of CH_4, oil and wax in the total hydrocarbon product. From the top two plots, the trends for the percentages of CH_4 and oil appear to be opposite to one another. The CH_4 generally increased with the raise in temperature and with decreasing

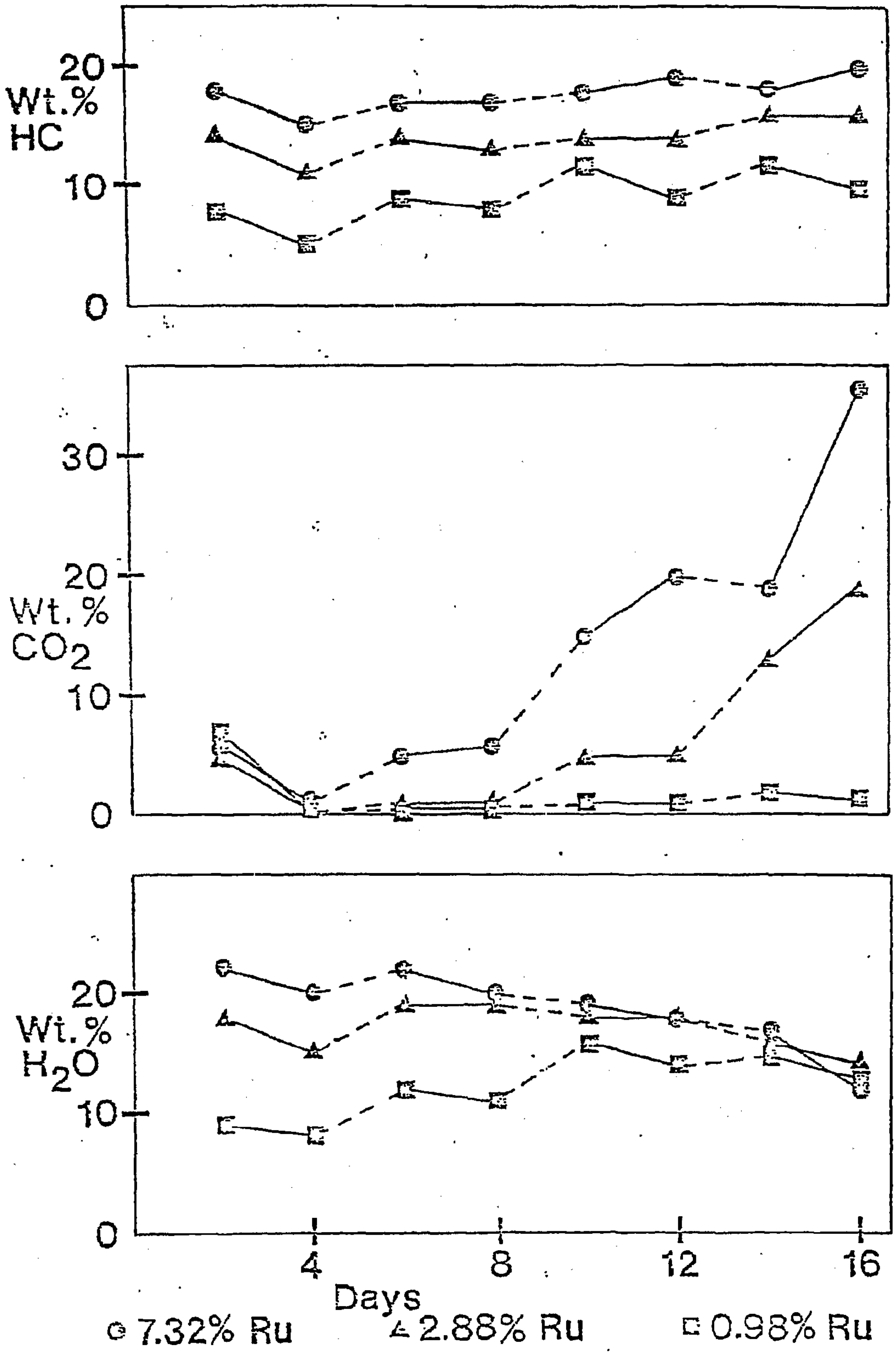

Figure 5. The weight percentages of the hydrocarbons (HC), CO_2 and H_2O.

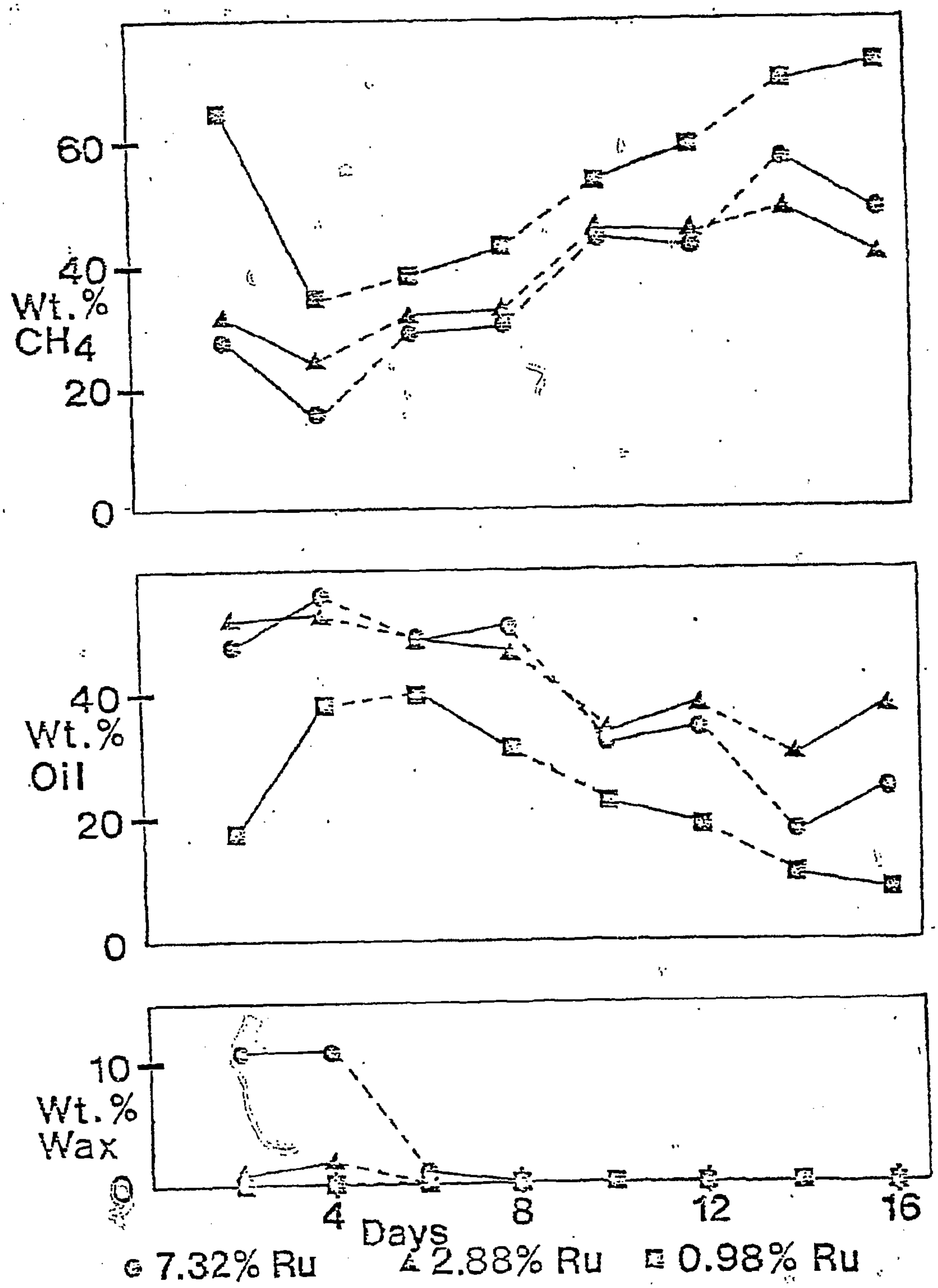

Figure 6. The weight percentages of CH_4, oil and wax in the total hydrocarbon product for the Ru/ZSM-5 catalysts.

Ru percentage. However, the oil fraction decreased with the increase in temperature, but increased with increasing Ru loading. In this study, CH_4 is considered to be an undesirable product while oil is a desirable product. Also, the 7.32% and 2.88% Ru/ZSM-5 samples are quite similar in their CH_4 and oil production with higher yields of oil and lower yields of CH_4 in comparison to the 0.98% Ru/ZSM-5 catalyst. Wax is the other hydrocarbon product to be considered, and from the plot, it is observed that the wax production is essentially zero for the 2.88% Ru and 0.98% Ru catalysts. However, for the 7.32% Ru catalyst wax was produced at 260°C but not at the higher temperatures. Above 260°C, the acid sites in the ZSM-5 become effective for the cracking of the high molecular weight hydrocarbons produced by the 7.32% Ru/ZSM-5 catalyst.

The results from the FIA analysis of the oil fractions are plotted in Figure 7. The 0.98% Ru/ZSM-5 catalyst produced significantly more aromatics than the other two catalysts. The 7.32% Ru/ZSM-5 and 2.88% Ru/ZSM-5 samples produced very low yields of aromatics at 260°C and 280°C; however, the production increased at 300°C and 320°C. With the olefin production the trend was the opposite; at 260°C and 280°C, the 7.32% Ru and 2.88% Ru samples produced high yields of olefins which decreased significantly at 300°C and 320°C. However, the overall yield of olefins for the 0.98% Ru/ZSM-5 catalyst was fairly low. Initially, the production of saturates for all three samples was approximately the same. However, at 300°C the percentages of saturates increased for the 7.32% and 2.88% Ru/ZSM-5 catalysts but began to decrease for the 0.98% Ru/ZSM-5 cata-

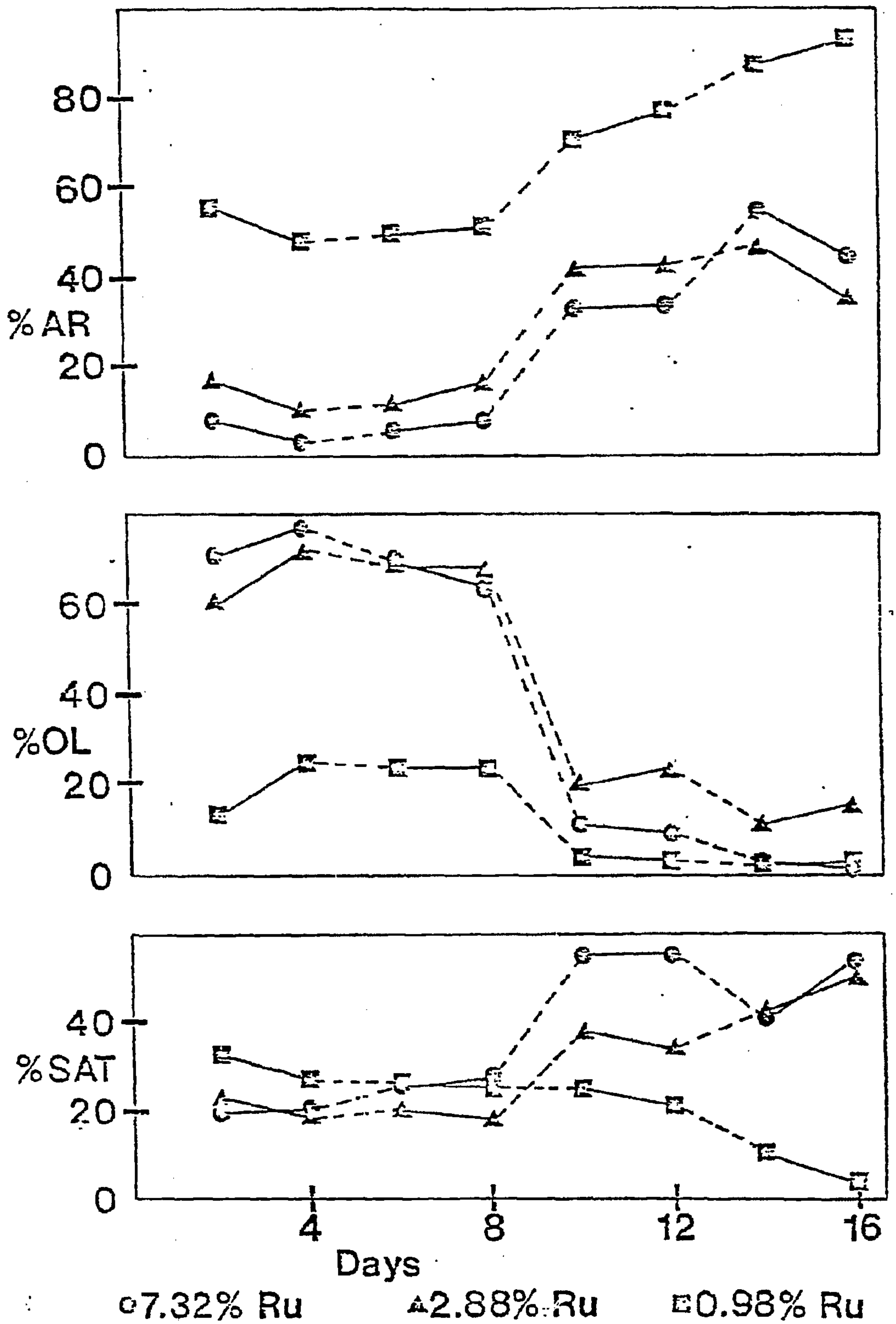

Figure 7. The FIA results obtained on the oil fraction of the Ru/ZSM-5 catalyst products.

lyst. Very high percentages of saturates were never obtained for these samples probably due to the cracking of high molecular weight hydrocarbons by the acid sites in the ZSM-5. These acid sites are also known to aromatize the olefins produced. When the temperature was increased from 280°C to 300°C there was a decrease in the production of gaseous and liquid olefins while the aromatics in the liquid product increased. At or above 300°C, the acid sites aromatize the C_2 to C_{11} olefins producing the high yield of aromatics in the liquid product. The research octane number is known to increase when the aromatics and/or branched olefins in the gasoline sample increases; therefore, the 0.98% Ru/ZSM-5 catalyst would be the sample to study further if a high research octane number is desired.

When adequate oil samples were available, simulated distillation data was also obtained for the catalysts. These results are listed in Table 2, and lower percentages were obtained for the 260°C samples in comparison to the percentages for the other oil samples. The increase in aromatics and decrease in high molecular weight hydrocarbons are probably due to the activity of the acid sites in the ZSM-5 causing a higher percentage of the oil obtained above 280°C to boil below 204°C. Since gasoline hydrocarbons are desired, the oil obtained above 280°C would be preferred.

Table 2: Simulated Distillation Results for the Ru/ZSM-5 Catalysts

% Ru/ZSM-5	TEMPERATURE (°C)	EVALUATION NUMBER	BOILING BELOW 204°C (%)
0.98	280	3	83
	280	4	83
	300	5	84
	300	6	83
2.88	260	1	76
	260	2	74
	280	3	83
	280	4	80
	300	5	85
	300	6	86
	320	7	85
	320	8	86
7.32	260	1	69
	260	2	68
	280	3	82
	280	4	81
	300	5	85
	300	6	84
	320	7	84
	320	8	83

3. Conclusions

The bifunctional catalysts of Ru/ZSM-5 were studied in order to investigate the catalytic activity of the ruthenium and the product selectivity of the ZSM-5. Three ruthenium loadings were studied to indicate the effect of percent metal loading on the activity of the catalyst. The ISS characterization data reported for the three Ru/ZSM-5 catalysts showed that the highest loading of ruthenium still maintained a Ru to Si-Al ratio of over one even after 65 min of sputtering time. However, the ratios for the 0.98% and 2.88% Ru loadings were significantly lower after sputtering. These results indicate that the catalyst of the highest Ru loading contains layering of the metal species over the surface of the support. This layering does not increase the available metal sites for synthesis gas conversion in the 7.32% Ru/ZSM-5 sample in comparison to the 2.88% Ru/ZSM-5 sample which explains the similarity of the catalytic activity of these two samples. Therefore, an increase in the Ru loading above ∿3% does not cause an increase in catalytic activity.

The ZSM-5 plays an important role in this bifunctional catalyst system of Ru/ZSM-5. This zeolite is known to contain acid sites capable of aromatizing olefins and cracking high molecular weight hydrocarbons along with product selectivity due to the size and arrangement of the channel structure. It has been reported that at temperatures below 300°C the inner surface of the H-ZSM-5 channels is not used effectively because higher temperatures are necessary to enable the reactants and products to flow within the channels of the ZSM-5. Therefore, the increase in aromatics and decline in olefins for the

2.88% Ru/ZSM-5 and 7.32% Ru/ZSM-5 samples at 300°C occurred due to the ability of the acid sites with in the ZSM-5 structure above 300°C to aromatize gaseous and liquid olefins produced by the catalysts. The surface acid sites are believed to cause the cracking of the heavier molecular weight products to lighter products since the diffusion of the heavier products into the ZSM-5 structure is severely hindered. For the 7.32% Ru/ZSM-5 catalyst wax was produced at 260°C; however, the acid sites became active in the cracking of high molecular weight hydrocarbons above 260°C. This high loading of Ru probably caused the blockage of some of the surface acid sites at 260°C leading to the wax production.

This study on the three Ru/ZSM-5 catalyst indicated that the desired product can be obtained in relatively high yields when the Ru loading and temperature are selected. The product distribution for the 7.32% and 2.88% Ru/ZSM-5 catalysts are similar; however, the products obtained from the 0.98% catalyst were different from the other two catalysts. The aromatic content for the 0.98% catalyst was consistantly higher than the 2.88% and 7.32% samples. Therefore, if a gasoline high in aromatics is desired the 0.98% Ru/ZSM-5 catalyst would warrant further study. The temperature affected the yield of the oil. The peak oil production occurred around 260°C to 280°C. Thus, if the yield of the oil is the main concern the catalysts should be investigated at these two temperatures.

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Paper Presented

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Degree Requirements Completed

Ph.D. Ketcha J. Mbadcam. Thesis title "H-Mordenite Zeolite and Inorganic Oxide - Supported Metal Catalysts for Synthesis Gas Conversion".

M.S. Robin Y. Eaton. Thesis title "Synthesis Gas Conversion with ZSM-5 Supported Ruthenium Catalysts".