TECHNICAL PROGRESS REPORT

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ABSTRACT

Our objective is to develop a catalyst for making gasoline or diesel range fuel selectively from synthesis gas. Our catalyst development approach is to provide a cut-off for the higher end of the hydrocarbon distribution by limiting the size of the active metal particle. We are using a micelle technique for preparing specific size ruthenium particles supported on γ -alumina.

Hydrocarbon cut-off was not observed with 40-60 Å ruthenium particles on γ -alumina. We could not determine whether smaller ruthenium particles would provide cut-off since they agglomerated during the test, apparently through the formation of ruthenium carbonyl. In order to determine whether ruthenium migration can be eliminated under a new set of testing conditions, we evaluated the effect of $H_2:CO$ feed gas ratio and the effect of total pressure on ruthenium migration.

Ruthenium migration was significantly suppressed but not totally eliminated by increasing the $H_2:CO$ feed gas ratio from 0.9 to 3.0. At the same $H_2:CO$ feed gas ratio, lowering the total pressure from 500 psig to 150 psig enhanced ruthenium migration.

During the next quarter, the use of high pressure in conjunction with high $H_2:CO$ feed gas ratio will be evaluated to eliminate ruthenium migration. In case agglomeration of small ruthenium particles cannot be totally eliminated, products initially obtained during a test will be carefully examined to determine whether cut-off occurs prior to ruthenium agglomeration.

OBJECTIVE

Our objective is to develop a catalyst for making gasoline or diesel range fuel selectively from synthesis gas. Our catalyst development approach is to provide a cut-off for the higher end of the hydrocarbon distribution by limiting the size of the active metal particle. We are using a micelle technique for preparing specific size ruthenium particles supported on γ -alumina.

INTRODUCTION

Early in the program we used the C-73-1-101 iron reference catalyst to establish the testing and analytical procedures (Runs 1-8, 10, Plant 700).

We later showed that hydrocarbon products obtained with 40-60 Å ruthenium particles prepared on γ -alumina obeyed the Anderson-Schulz-Flory distribution, with no cut-off up to a carbon number of 90. We could not determine whether hydrocarbon cut-off would occur with smaller ruthenium particles. Ruthenium particles which were 20-40 Å or smaller in size were not stable on γ -alumina. For smaller particles, ruthenium migration apparently through ruthenium carbonyl formation caused ruthenium agglomeration and ruthenium loss from the catalyst (Runs 9, 11-17).

These two sets of results have been summarized in the first topical report which will be issued shortly.

Since determining whether hydrocarbon cut-off occurs with 20-40 Å or smaller ruthenium particles requires that small ruthenium particles are stable on γ -alumina, we considered two different approaches to improve the stability of small ruthenium particles.

The first approach was to determine whether ruthenium migration via ruthenium carbonyl formation can be eliminated by lowering the partial pressure of carbon monoxide. Work done under this approach is currently being summarized in a second topical work and will be briefly discussed in this report (Runs 18, 19).

The second approach involves improving the stability of small ruthenium particles by chemical modification with a new element. Work under this approach has recently been initiated, and results will be reported later.

RESULTS AND DISCUSSION

We prepared a conventional ruthenium catalyst (4966-72; 1.05 wt.% Ru) by using an aqueous impregnation technique. Catalyst 4966-72 had very well dispersed ruthenium, $\leq 20 \text{ \AA}$, according to the STEM examination and was tested in Run 18 at a $\text{H}_2:\text{CO}$ ratio of 3.0, instead of the 0.9 which was used in Run 16 with a similar conventional catalyst (4956-86; 1.09 wt.% Ru) with very well dispersed ruthenium. Other conditions were 208°C , 500 psig, 60 GHSV, and 152 hours.

Catalyst 4956-86 had lost 43% of ruthenium, presumably in the form of the volatile carbonyl during Run 16, at a $\text{H}_2:\text{CO}$ ratio of 0.9. Chemical analysis of catalyst 4966-72 tested in Run 18 for the same amount of time at a $\text{H}_2:\text{CO}$ ratio of 3.0 showed no overall ruthenium loss from the catalyst. However, separate analysis of the bottom portion of the catalyst bed showed 22% higher concentration of ruthenium relative to the top catalyst bed portion, indicating that ruthenium migration still occurred. STEM analysis of the catalyst used in Run 18 also indicated that ruthenium agglomeration indeed occurred, although apparently most of the ruthenium, particularly in the bottom bed portion, still remained well dispersed. These results indicate that ruthenium migration was

significantly suppressed but not totally eliminated by increasing the $H_2:CO$ feed ratio.

In order to gain further insight on the effect of test conditions on ruthenium migration, we tested a micelle-derived catalyst (4966-76; 0.844 wt.% Ru) with 20-40 Å ruthenium particles at 150 psig; other conditions were 3.0 $H_2:CO$ ratio, 208°C, 60 GHSV, 100 hours (Run 19). Analysis of catalyst used in Run 19 indicated that 21% of the ruthenium was lost from the catalyst. Since larger ruthenium particles should have lesser tendency for ruthenium migration, the lower total pressure used in Run 19 with 20-40 Å ruthenium particles should have enhanced ruthenium migration relative to that observed with <20 Å ruthenium particles tested at higher pressure in Run 18. One possible explanation is that at the same $H_2:CO$ feed gas ratio the relative surface coverage of H_2 with respect to CO may decrease with a decrease in total pressure, and thereby enhance formation of the volatile carbonyl.

Analysis of the run average overall product distributions obtained with catalysts showing initially 20-40 Å or smaller ruthenium particles (Runs 16-19) shows a relatively low chain growth probability in the C_1-C_{20} carbon number range and a higher chain growth probability at larger carbon numbers. Ruthenium particles (catalyst 4956-76; 0.926 wt.% Ru) which had remained 40-60 Å during the test (Run 15) did not show such a dramatic variation in the chain growth probability. Our interpretation is that ruthenium which did not agglomerate during Runs 16-19 was responsible for the relatively low chain growth probability observed at C_1-C_{20} , whereas agglomerated ruthenium was responsible for the relatively high chain growth probability observed at higher carbon numbers. The overall run average product distribution seems to be the superimposition of products obtained on two different size ruthenium particles. Since hydrocarbon synthesis activity should increase as ruthenium particles agglomerate during the

run, even under mild agglomeration conditions, agglomerated ruthenium may be responsible for a significant fraction of the overall hydrocarbon products collected. The fraction of products made by agglomerated ruthenium may be large enough to mask any possible hydrocarbon cut-off that the non-agglomerated particles may provide.

FUTURE PLAN

Since stability of small ruthenium particles was adversely affected by lowering the total pressure while maintaining the same $H_2:CO$ feed gas ratio, desired stability may possibly be achieved by using high total pressure in conjunction with high $H_2:CO$ feed gas ratio. This approach is going to be evaluated during the next quarter. In case agglomeration of small ruthenium particles cannot be totally eliminated under new test conditions, products initially obtained during a test will be carefully examined to determine whether cut-off occurs prior to ruthenium agglomeration. Improving the stability of ruthenium particles by chemical modification will be emphasized if hydrocarbon cut-off is observed initially during the test prior to ruthenium agglomeration.

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