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ABSTRACT

The objective of this program is to develop a synthesis gas conversion catalyst with improved selectivity to gasoline or diesel range fuel via application of a micelle technique for preparing novel supported catalysts with specific size ruthenium particles.

The major emphasis is to investigate hydrocarbon cutoff principle and to apply it for developing selective catalysts. We previously reported that cutoff is not effected with 40-60 Å and 20-40 Å ruthenium particles on γ - Al_2O_3 . We recently tested a catalyst with <20 Å ruthenium particles. Well dispersed ruthenium in that catalyst extensively agglomerated to larger particles even during the course of a short test despite the high H_2 :CO ratio used. Therefore, we could not conclude whether cutoff is effected with <20 Å ruthenium particles.

We are going to continue to evaluate the effect of operational conditions and also evaluate the effect of modifiers on ruthenium agglomeration. A catalyst with <20 Å ruthenium particles will be evaluated to investigate occurrence of cutoff, after no agglomeration conditions are identified.

We are now proposing to conduct, parallel to the main approach, a second research approach which will aim at developing a ruthenium catalyst with substantially lower light ends selectivity while maintaining at least similar activity and stability relative to state-of-the-art precipitated iron catalysts. Under this approach, preliminary experiments indicated that a catalyst (1.12 wt.% Ru or γ - Al_2O_3) with 30-70 Å ruthenium particles shows initially ~10% lower carbon atom selectivity to light ends (C_1 - C_4) and is approximately 4X less active relative to precipitated iron catalyst used in the Sarol Arge reactor. It now appears that future research efforts should be aimed at establishing stability and lowering further the light ends selectivity and improving activity by optimizing the ruthenium particle size and by increasing the ruthenium loading. We would like to determine, clearly, by the end of the current program, developmental needs for such a new ruthenium catalyst.

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OBJECTIVE

The objective of this program is to develop a synthesis gas conversion catalyst with improved selectivity to gasoline or diesel fuel via application of a micelle technique for preparing specific size supported ruthenium particles.

INTRODUCTION

The current emphasis in the program is to investigate the occurrence of the hydrocarbon cutoff principle and to apply it for the development of selective catalysts.

Previously, we concluded that cutoff was not effected with 40-60 Å and 20-40 Å ruthenium particles prepared on γ -alumina. Since 20-40 Å or smaller ruthenium particles agglomerated to larger particles during the course of a six to 10 day test, products initially obtained during the test, prior to substantial ruthenium agglomeration, had to be carefully examined in order to investigate occurrence of cutoff. During this last quarter <20 Å ruthenium particles prepared on γ -alumina were evaluated in a short test to investigate occurrence of cutoff.

In order to meet the objective of the program we would like to initiate a second research approach which we propose to conduct parallel to the main program approach discussed above. This new approach will be to develop a ruthenium catalyst with substantially lower light ends selectivity while maintaining at least similar activity and stability relative to state-of-the-art precipitated iron catalysts.

One of the key findings in our current program so far has been to establish that for synthesis gas conversion catalytic activity, stability and selectivity are very sensitively influenced by ruthenium particle size. 40-60 Å ruthenium particles prepared on γ -alumina, for instance, compared to other size ruthenium particles tested, proved to be most active and most stable against ruthenium agglomeration and also showed minimum light ends selectivity, much lower than that obtained with the precipitated iron catalyst used in Sasol-Argo reactor. By optimizing ruthenium particle size further, it should therefore be possible to develop an improved catalyst with minimal light ends selectivity. This kind of a high- α -catalyst may be geared to operate at the first stage of a two-stage process in which first stage wax is hydrocracked to gasoline or diesel fuel in a second stage, and result in very high overall yields to desired products compared to alternate two-stage processes.

Under this second approach we are proposing to identify, by the end of the current program, developmental needs for such a new ruthenium catalyst.

RESULTS AND DISCUSSION

A catalyst (4966-72, 1.05 wt.% Ru) with ruthenium particles less than 20 Å was tested to determine if cutoff would occur. High $H_2:CO$ ratio was used in this run (Run 21, Plant 700) in order to minimize ruthenium agglomeration via ruthenium carbonyl formation. Cutoff was not observed. Analysis of the used catalyst with STEM, however, indicated that most of the ruthenium agglomerated to 20-50 Å size during the course of the 12-hour-test. Therefore, we were not able to determine if cutoff is effected by <20 Å ruthenium particles. This unexpected result indicates that an additional factor plays an important role in ruthenium agglomeration. It now appears that relatively high water partial pressures caused by the absence of significant water gas shift reaction at high $H_2:CO$ ratio may have enhanced ruthenium agglomeration.

A micelle-derived ruthenium catalyst (4966-96-1, 1.12 wt.% Ru) had 30-70 Å ruthenium particles according to the STEM examination. This catalyst was tested with $2H_2:1CO$ feed gas, similar to that used in the Sasol Arge reactor, and at various temperatures, pressures, and space velocities (Runs 22-24, Plant 700). Preliminary results indicate that this ruthenium catalyst has initially ~10% lower carbon atom selectivity to light ends (C_1-C_4) (based on total CO converted) and is approximately four times less active relative to precipitated iron catalyst used in the Sasol Arge reactor.

One key finding of recent tests with ruthenium catalysts at different space velocities has been to establish that light ends selectivity, particularly selectivity to methane increases sensitively with a decrease in the conversion level at the same $H_2:CO$ ratio. The effect of conversion on selectivity is not clearly discussed in the literature, and the results obtained here may indicate that, at relatively high conversions, adsorbed hydrocarbons may favorably compete with H_2 for adsorption sites, and therefore indirectly increase the chain growth probability.

FUTURE PLAN

We are going to continue to evaluate the effect of operational conditions and also evaluate the effect of modifiers on ruthenium agglomeration. A catalyst with <20 Å ruthenium particles will be evaluated to investigate occurrence of cutoff, after no agglomeration conditions are identified.

Under the second research approach, we propose future research efforts be aimed at establishing catalytic stability, at lowering further the light ends selectivity and improving activity by optimizing the ruthenium particle size and by increasing the ruthenium loading.

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