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CONTRACT IDENTIFICATION: Micelle-Derived Catalysts for Extended Schulz-Flory	REPORTING PERIOD: 1/1/86 - 3/31/86
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ABSTRACT

The objective of this program is to develop a synthesis gas conversion catalyst selective to gasoline or diesel range fuel via application of a micelle technique for preparing specific size supported ruthenium particles. The current emphasis is to investigate hydrocarbon cutoff principle and to apply it for developing selective catalysts.

During this quarter, micelle technique was further improved and 1 ruthenium particle:1 reverse micelle limit was approached by careful control of catalyst synthesis conditions. Accordingly, it became possible to synthesize supported particles that closely meet the size and composition targets originally set. This improved technique was applied to synthesis of chemically modified ruthenium catalysts. Some of the chemically modified ruthenium catalysts will be evaluated later in the program.

We previously reported that 40-60 Å ruthenium particles prepared on γ -alumina do not result in hydrocarbon cutoff. We could not determine then whether smaller ruthenium particles result in hydrocarbon cutoff because these particles agglomerated via ruthenium carbonyl formation during the course of a 6-10 day test. We have recently evaluated a catalyst with 20-40 Å ruthenium particles prepared on γ -alumina by carefully analyzing products initially made during the test prior to substantial ruthenium agglomeration. We concluded that cutoff is not effected by 20-40 Å ruthenium particles prepared on γ -alumina. In the future, we are going to investigate the occurrence of cutoff principle with <20 Å ruthenium particles prepared on γ -alumina. We are also going to attempt to determine whether some of the literature reports of hydrocarbon cutoff with small ruthenium particles can be attributed to the chain length selective nature of zeolitic supports that were used in those experiments.

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OBJECTIVE

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

INTRODUCTION

Previously (Topical Report for 10/1/1984 - 9/30/1985), we established a micelle procedure for preparing specific size ruthenium particles on γ -alumina. We then investigated occurrence of the hydrocarbon cutoff principle with catalysts containing different size ruthenium particles. No cutoff was observed with 40-60 Å ruthenium particles which made products that obeyed the Anderson-Schulz-Flory distribution up to a carbon number of 250. We could not determine occurrence of cutoff with smaller ruthenium particles because they agglomerated during the course of a 6-10 day test. Ru agglomeration was suppressed but not totally eliminated by increasing the $H_2:CO$ ratio, while maintaining the same total pressure. Lowering the partial pressure of carbon monoxide by lowering the total pressure and maintaining high $H_2:CO$ ratio did not suppress agglomeration and may have even enhanced it, possibly by indirectly lowering the hydrogen partial pressure.

In this quarter, we followed two different approaches to investigate the occurrence of cutoff principle.

The first approach was to improve the stability of small ruthenium particles against agglomeration by chemical modification with another element. Micelle technique was further developed in order to prepare modified ruthenium catalysts.

Second, since agglomeration of small ruthenium particles appeared to occur gradually during the course of the test, products initially obtained during a test were carefully examined to determine whether cutoff occurs prior to ruthenium agglomeration.

RESULTS AND DISCUSSION

Modified Ruthenium Catalysts

Chemically modified ruthenium catalysts can be prepared by utilizing reverse micelles with ruthenium and another modifier dissolved in the water core as precursors for supported ruthenium/modifier particles. Careful control of composition and size of each ruthenium particle on the other hand, requires that a single particle is obtained from a single reverse micelle. Unless catalyst synthesis conditions are very carefully controlled, however, reverse micelles agglomerate to form particles which do not exactly meet composition and size targets originally set. Substantial improvement in catalyst synthesis conditions were recently made in order to approach 1 particle:1 reverse micelle

limit. Chemically modified ruthenium catalysts were made with the improved micelle procedure and characterized. Some of these catalysts are going to be evaluated in the future to determine if stability against agglomeration was improved.

Short Test

A catalyst (4966-76, 0.844 wt.% Ru) previously prepared by a micelle technique had 20-40 Å ruthenium particles on γ - Al_2O_3 according to the STEM analysis. We tested this catalyst at 200°C, 15 atm and 1.5 H_2 :CO ratio (Run 20, Plant 700). Hydrocarbon cutoff at C_{11} was previously reported under these conditions with similar size ruthenium particles encaged in Y-zeolite^{1,2}. The test in Run 20 was kept short in order to analyze products obtained prior to substantial ruthenium agglomeration.

STEM analysis of the used catalyst indicated that for 85% of the alumina particles, no noticeable ruthenium agglomeration was observed. Approximately 15% of the examined alumina particles showed agglomerated ruthenium. The sizes of the agglomerated ruthenium particles were mostly 600-1000 Å. These results indicate that even if the specific activity of agglomerated ruthenium particles is higher than that of 20-40 Å Ru particles, the total exposed metal surface area by these agglomerated particles is too small to have catalytic significance. Therefore, products analyzed in Run 20 can be attributed to 20-40 Å ruthenium particles.

Gaseous products (C_1 - C_5 hydrocarbons and CO_2) were accounted for by analyzing the effluent gas by gas chromatography (GC). No significant amount of products were collected in the product receivers (one at 115°C and 15 atm, the other at 0°C and 4 atm) during the course of the short test. The used catalyst underwent a soxhlet extraction with toluene for recovering the wax and followed by a carbon burn measurement to determine the amount of coke on the used catalyst. The wax recovered from the used catalyst amounted to more than 83% (by wt.) of the hydrocarbons made (calculated based on total CO converted) and showed an Anderson-Schulz-Flory distribution with $\alpha = 0.987$ up to a carbon number of 250. Approximately 14% of hydrocarbons could not be recovered. The hydrocarbons that could not be recovered were in the C_5 - C_{23} range and would normally be recovered in the product receivers in a long test. Nevertheless, since most products, particularly the heavy ones, were accurately analyzed, it was possible to conclude that cutoff is not effected with 20-40 Å ruthenium particles supported on γ - Al_2O_3 .

¹H. H. Nijs, P. A. Jacobs and J. B. Uytterhoeven, J. Chemical Society, Chemical Communications, p. 180, 1979.

²H. H. Nijs, P. A. Jacobs, J. J. Verdonck and J. B. Uytterhoeven, Proceedings of Fifth International Conference on Zeolites, p. 633, 1980.

FUTURE PLAN

We will evaluate a catalyst with $<20 \text{ \AA}$ ruthenium particles prepared on $\gamma\text{-Al}_2\text{O}_3$ in the future in a short test to determine whether cutoff occurs prior to substantial ruthenium agglomeration. Chemical modification of ruthenium will be considered if ruthenium agglomeration is significant with $<20 \text{ \AA}$ particles even during the course of a short run. Also, we will attempt preparing 20-40 $\text{\AA}$ ruthenium particles encaged in Y-zeolite as reported in the literature. We would like to determine whether some of the literature reports of hydrocarbon cutoff with small ruthenium particles can be attributed to the chain length selective nature of zeolitic supports used in those experiments.

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