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TECHNICAL PROGRESS REPORT

ABSTRACT

The objective of this program is to develop a synthesis gas conversion catalyst with higher selectivity to liquid fuels, while maintaining catalytic activity and stability at least equivalent relative to state-of-the-art precipitated iron catalysts.

During this quarter, the emphasis in the program has been the investigation of the hydrocarbon cutoff hypothesis with supported ruthenium catalysts.

An alumina-supported catalyst with smaller than 20Å ruthenium particles was tested under conditions of maximal water gas shift activity. During this test more than 90% of the water made in the Fischer-Tropsch synthesis reaction was converted to H₂. However, the extent of ruthenium metal agglomeration was not reduced. Accordingly, it was not possible to conclude whether hydrocarbon cutoff occurs with smaller than 20Å ruthenium particles on γ-alumina.

A ruthenium catalyst prepared on Y-type zeolite had 20Å or smaller ruthenium particles according to STEM examination and a 15Å average ruthenium metal particle size according to EXAFS examination. The ruthenium metal particle size was stable during the test with this catalyst. The hydrocarbon product distribution was Anderson-Schulz-Flory with no cutoff up to a carbon number of 160.

A well-dispersed titania-supported ruthenium catalyst is going to be evaluated during the next quarter in order to determine whether hydrocarbon cutoff occurs.

OBJECTIVE

The objective of this program is to develop a synthesis gas conversion catalyst with higher selectivity to liquid fuels, while maintaining catalytic activity and stability at least equivalent relative to state-of-the-art precipitated iron catalysts.

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INTRODUCTION

During this quarter, the emphasis in the program has been the investigation of the hydrocarbon cutoff hypothesis with supported ruthenium catalysts.

Previously, we concluded that cutoff was not effected with 40-60Å and 20-40Å ruthenium particles prepared on γ -alumina (Topical Report for 10/1/84-9/30/85 and Technical Progress Report for 1/1/86-3/31/86). Ruthenium particles smaller than 20Å underwent extensive agglomeration on γ -alumina. A possible metal agglomeration mechanism was determined to be via formation of the volatile ruthenium carbonyl species.

Agglomeration of smaller than 20Å ruthenium particles on γ -alumina could not be eliminated by increasing the $H_2:CO$ ratio from 0.9 to 3.0 at 34 atm total pressure or by lowering the total pressure from 34 atm to 10 atm at a $H_2:CO$ ratio of 3.0 (Technical Progress Reports for 1/1/86-3/31/86 and for 4/1/86-6/30/86).

New test conditions and a new support material were investigated this year in order to stabilize and evaluate smaller than 20Å ruthenium particles.

RESULTS AND DISCUSSION

Test of Well-Dispersed Alumina-Supported Ruthenium Catalyst Under Maximum Water Gas Shift Conditions

A catalyst (4966-72; 1.04 wt.% Ru) with smaller than 20Å ruthenium particles on γ -alumina was tested at 208°C, 34 atm, 2.5 $H_2:1CO$ feed ratio and 136 GHSV (Run 25, Plant 700).

The selectivity of CO to CO_2 was 40-45% during Run 25. Since the theoretical maximum selectivity to CO_2 is approximately 50%, more than 90% of the water made during Fischer-Tropsch should have been converted via the water gas shift reaction. STEM examination indicated that most of the alumina particles contained agglomerated ruthenium.

These results indicate that the steam partial pressure did not have a major effect on ruthenium agglomeration.

Test of Y-Type Zeolite Supported Ruthenium Catalyst

A ruthenium catalyst (4966-114; 6.3% Ru) was prepared on Y-type zeolite according to the recipe given in the literature (J. J. Verdonck, P. A. Jacobs, et al., J. C. S. Faraday I, 76, 403, 1980). According to STEM examination ruthenium was in the form of 20-30Å or smaller particles. EXAFS examination indicated the average ruthenium particle size to be narrow, around 15Å. Temperature programmed oxidation experiment showed that all of the ruthenium in the reduced catalyst could be oxidized at room temperature. This result, according to the discussion in the literature (H. H. Nijs, P. A. Jacobs, et al., Proceedings of Fifth Int. Conf. on Zeolites, 1980) is an indication that the ruthenium may be inside the zeolite.

The ruthenium catalyst prepared on Y-type zeolite was tested for 24 hours under conditions (200°C, 14 atm, 1.5 H₂:CO feed ratio and ~30% CO conversion) at which cutoff at C₁₁ was reported in the literature with such a catalyst (H. H. Nijs, P. A. Jacobs, et al., Proceedings of Fifth Int. Conf. on Zeolites, 1980). Test duration was kept short to minimize ruthenium agglomeration. The ruthenium particle size was stable during the test according to SIEM examination.

This result indicates that ruthenium metal agglomeration was substantially suppressed on Y-type zeolite relative to on alumina.

Products in the C₁₀-C₂₃ range apparently were not fully recovered in the product receivers because of the short duration of the test. Nevertheless, 30% of the hydrocarbon products accumulated as wax on the catalyst, showed Anderson-Schulz-Flory distribution up to a carbon number of 160, and therefore it was possible to conclude that cutoff did not occur with 15Å ruthenium particles on Y-type zeolite.

FUTURE PLAN

A catalyst with small ruthenium particles is going to be prepared on titania and is going to be evaluated in order to further investigate the hydrocarbon cutoff hypothesis.

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