APPENDIX A

CATALYST SYNTHESIS

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Over the past year, the emphasis of both catalyst synthesis and testing has shifted from Task 1 to Task 2. Much has been learned about the importance of various catalyst properties to Task 1 performance. Some excellent Task 1 catalysts were investigated. UCC-108, which will be discussed later in this report, is the best catalyst tested for propylene oligomerization. UCC-104 and ZSM-5 are also excellent catalysts. The liquid yield from UCC-104 was superior to that from ZSM-5. Some of what was learned from the Task 1 testing has been useful in the formulation of Task 2 catalysts. Since the ultimate purpose of this contract is to develop superior Task 2 catalysts, the emphasis is now to that end with a large cutback in Task 1 activities.

The only Task 1 catalyst prepared this quarter was from UCC-109. It was formed in the usual way as 20% alumina bonded extrudate. The result of Task 1 testing of this catalyst along with 6 other previously synthesized catalysts are presented in Appendix C. It is anticipated that new materials will still be brought into the program. These new materials will not necessarily be tested for Task 1 activity but may be used directly under Task 2, particularly if quantities are very limited.

The preparation of Task 2 catalysts has followed fairly standard procedures established earlier in the contract. While iron was still the dominant metal component used in the catalysts, the use of cobalt continued to grow significantly. The promotion of cobalt with thorium began this quarter. Two modes of metal loading were employed in the quarter, physical mixture for iron catalysts and precipitation for both iron and cobalt catalysts. The effects of these different modes of metal loading, particularly the effects of the promoter are discussed with the individual catalysts in Appendix C.

One physical mixture catalyst was prepared using potassium promoted iron and UCC-109. The preparation was slightly different then previous physical mixtures. The tablets of the physical mixture would not hold together, probably because the UCC-109 particle size was less than normal for molecular sieves. The catalyst was bonded using 15% silica binder. In this process, there was a possibility that some of the potassium promoter was transferred from the metal component to the molecular sieve. As is discussed in the section of Appendix C dealing with a test of promoted iron precipitated on UCC-101, Run 10011-11, this can be disastrous to the molecular sieve's ability to alter the F-T product. The test results with this catalyst will be reported next quarter.

Iron was precipitated on LZ-105 to give a 20% metal loaded catalyst. This catalyst was potassium promoted and formed into pellets as usual. A similar catalyst was prepared using UCC-108 instead of LZ-105. There was nothing unusual about the preparation of this catalyst. As is discussed in Appendix C, this catalyst was completely inactive for syngas conversion. The reason for this poisoning of metal component activity is unknown.

Precipitation was also used this quarter to metal load molecular sieves with cobalt. The precipitation is done with sodium carbonate instead of ammonia and it is done at room temperature but washed with hot distilled water. Two catalysts were prepared using this method. One used LZ-105 as the molecular sieve, the other used UCC-101.

The new procedure used this quarter was promotion with thorium. Since thorium is radioactive, an α-emitter, every effort has been taken to minimize the solutions and materials with which the thorium comes in contact. This is to prevent radioactive contamination of the lab. The cobalt loaded molecular sieve is impregnated with thorium nitrate solution dried at 100°C and formed into pellets. The thorium is not precipitated with the cobalt because of the excess wash water that would have to be disposed of.

The catalysts reported in the testing section of this report, Appendix C, are summarized in Table 1.

TABLE 1

CATALYSTS REPORTED IN APPENDIX C

TASK 1

ZSM-5	A medium pore molecular sieve synthesized at Tarrytown based on procedures described by Mobile Oil, with SiO_2/Al_2O_3 ratios of 35 and 85.
UCC-108	A new proprietary Union Carbide Molecular Sieves; a more active modification of UCC-104.
UCC-109	A new large pore proprietary Union Carbide Molecular Sieve.
$AlPO_4$-11	A new Union Carbide Aluminophosphate Molecular Sieve with a pore size of 6Å and undetermined structure (U.S. Patent 4,310,440).
LZ-Y-82	The steam-stabilized acid form of Y zeolite.
97% H-Y-62	A form of unstabilized Y-zeolite synthesized by extensive ammonium ion exchange of NaY followed by calcination.

TASK 2

Physical Mixture Fe/K+α-Al_2O_3	Potassium promoted $Fe_2O_3 \cdot XH_2O$ powder physically mixed with 1μ particle size α-Al_2O_3 and pressed into pellets.
Physical Mixture Fe/K+UCC-104	Similar to the above catalyst except with UCC-104 replacing the α-Al_2O_3.
Fe/K on UCC-101	Iron precipitated on UCC-101, followed by potassium promotion and pressing into tablets.
Fe/K on UCC-108	Similar to the above except with UCC-1 replacing UCC-101.
Co on SiO_2/Al_2O_3	20% Al_2O_3 bonded extrudate of Aerocat 8020, pore-filled with cobalt nitrate solution and calcined.
Co on UCC-101	Similar to the above except with UCC-1 extrudate replacing the silica alumina extrudate.