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HIGH-PRESSURE HYDROGENATION OF CARBON MONOXIDE TO ISOPARAFFINIC HYDROCARBONS (ISOSYNTHESIS). PART II. EXPERIMENTS ON MULTICOMPONENT CATALYSTS AND REACTIONS OF DIMETHYL ETHER

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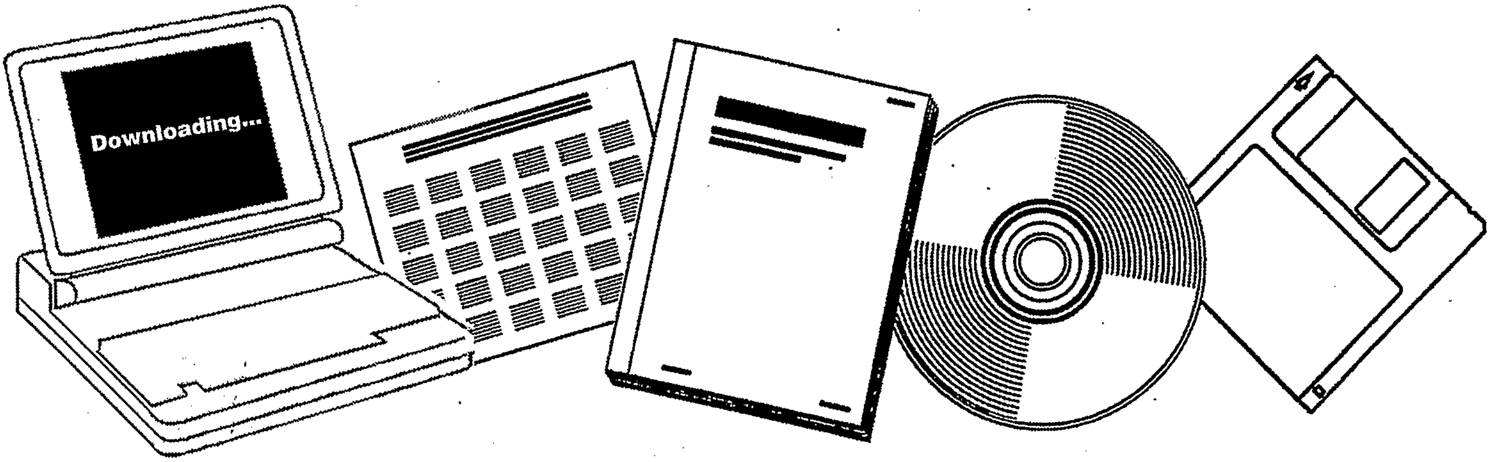

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TRANSLATION

ENGLISH TITLE

High-Pressure Hydrogenation of Carbon Monoxide to Isoparaffinic Hydrocarbons ("Isosynthesis"). Part II: Experiments on Multicomponent Catalysts and Reactions of Dimethyl Ether*

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Über die Hochdruck-Hydrierung von Kohlenoxyd zu vorzugsweise Isoparaffinischen Kohlenwasserstoffen ("Isosynthese"). II. Teil: Versuche an Mehrstoffkatalysatoren und Umsetzungen von Dimethyläther*)

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HIGH-PRESSURE HYDROGENATION OF CARBON MONOXIDE TO ISOPARAFFINIC HYDROCARBONS ("ISOSYNTHESIS"). PART II: EXPERIMENTS ON MULTICOMPONENT CATALYSTS AND REACTIONS OF DIMETHYL ETHER

Initially, we used only single-component catalysts, primarily thorium oxide, for synthesis of isoparaffinic hydrocarbons from carbon monoxide and hydrogen*, but in the following experiments we also used multicomponent catalysts, mainly for two reasons - first, to ascertain which additives might be suitable for improving the catalytic activity of thorium in the desired direction, namely toward greater production of branched hydrocarbons, and secondly to replace the thorium oxide either partially or entirely with suitable combination catalysts (although the activity of none of the other single-component catalysts could approach that of thorium oxide).

For example, to improve the yields of higher hydrocarbons in the synthesis reactions on thorium catalysts, addition of alkali was taken into consideration because it was already known that very small amounts of alkali can have a considerable influence on the conversion in synthesis processes using iron catalysts at a moderate pressure. Alkali suppresses hydrogenation of the intermediate CH_2 radicals and thus inhibits formation of undesired methane and lower homologs thereof while favoring polymerization to long chains. Within the context of synthesis of alcohols from carbon monoxide and hydrogen, addition of alkali to the catalyst suppresses the formation of methanol

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* See "Isosynthesis" Part I, which also includes a detailed listing of the literature: Brenstoff-Chemie, Vol. 30, No. 13, 1949.

in favor of higher alcohols, especially isobutyl alcohol, in a similar way.

There was also some interest in investigating the effects of adding phosphoric acid, since it is known to be capable of conversion of unsaturated hydrocarbons such as propene or n-butene to higher branched hydrocarbons, preferably their dimers, under certain conditions.

In conjunction with the possibility that the hydrocarbons of isosynthesis are formed by way of intermediate alcohols by dehydration, in which case the thorium oxide would be responsible for catalyzing not only the formation of the oxygen-containing compounds but also their dehydration and further conversion of the resulting unsaturated hydrocarbons to saturated products with the same number of carbons or a higher number of carbons, substances which would promote the formation of alcohol were added to thorium in one series of experiments, and in another series of experiments substances were added which would increase the ability of thorium oxide to release water from alcohols. Finally, catalysts were tested which had been produced by combining catalysts that had an alcohol-forming effect and those which had a water-cleaving action (e.g., zinc oxide and aluminum oxide).

Furthermore, other aspects that were investigated included the effects of adding various other substances on the properties of catalysts in isosynthesis, the addition of cerium to thorium and replacement of thorium by dissolved and reprecipitated monozite sand, addition of copper, addition of small and trace amounts of iron, addition of alkaline earth compounds such as magnesium, also manganese, etc.

Many of the additives mentioned above yielded negative results, others did not yield any significant changes in the reaction processes and still others had an especially favorable influence on the reaction process in many regards.

The effects of a number of combination catalysts are discussed below, namely:

1. Thorium oxide + alkali
2. Thorium oxide + phosphoric acid
3. Thorium oxide + aluminum oxide
4. Thorium oxide + aluminum oxide + alkali
5. Thorium oxide + zinc oxide
6. Zinc oxide + aluminum oxide
7. Thorium oxide + zinc oxide + aluminum oxide
8. Aluminum oxide + chromium oxide
9. Thorium oxide + chromium oxide
10. Thorium oxide + iron
11. Thorium oxide + copper
12. Thorium oxide + aluminum oxide + diatomaceous earth

1. Thorium oxide + alkali

The thorium was precipitated by adding soda to a dilute solution of the nitrate and the precipitate was washed on a suction filter until free of alkali (normal catalyst). The thorium carbonate thus obtained was suspended with water in a dish and mixed with certain amounts of potassium carbonate dissolved in water, then heated on a water bath and dried at 110°C and finally at 300°C.

First, comparative experiments were conducted at pressures of 30 atm and various temperatures using catalysts with and without alkali (potassium carbonate contents of 0.5%, 1%, 5% and 25%). The gas throughput in all cases was 10 liters of end gas per hour and per 28 g ThO_2.

Figure 1 shows the influence of the alkali content on the conversion of synthesis gas at 450°C, 475°C and 500°C. The three curves show that larger amounts of added alkali paralyze the activity of the ThO_2 catalysts. This effect is more evident at lower temperatures than at high temperatures. For example, the gas conversion dropped from 13% to almost 0% when the alkali content was increased from 1% to 5% at 450°C, and at 475°C it dropped from 20% to 3%, but at 500°C it dropped from only 28% to 22%. Accordingly, the yield of reaction products was also reduced, specifically the yield of low-boiling products was reduced more rapidly than that of higher hydrocarbons.

When small amounts of alkali are added, the synthesis can be carried out at relatively high temperatures (because of the reduction in activity of the thorium catalyst) without extensive conversion of carbon monoxide and hydrogen to methane under these conditions. It is then possible to work in a temperature range in which the synthesis leads primarily to cyclic hydrocarbons. Thus, with a thorium oxide catalyst which contained 1% potassium carbonate, liquid hydrocarbons consisting of 42% naphthenes and 8% aromatics, primarily toluene, were obtained at 30 atm and 500°C. In addition, 3% phenols were found.

Table I shows the results of an experiment in which the isosynthesis was carried out under favorable pressure and temperature conditions using a thorium catalyst which contained a small amount of alkali that did not substantially reduce the conversion (0.6% K_2CO_3 based on ThO_2), plus a comparative experiment with a thorium catalyst that contained no alkali.

The CO conversion in both cases was 62%. The amount of liquid hydrocarbons increased from 42 g to 65 g as a result of adding the alkali, while the amount of higher alcohols (mostly isobutyl alcohol) increased from 9 to 21 g/m^3 (STP). At the same time, the yield of lower hydrocarbons (C_1-C_4) and methanol dropped.

Although large amounts of alkali had a paralyzing effect on the activity of the thorium catalyst, a small amount of alkali tended to promote the formation of higher-molecular-weight compounds.

2. <u>Thorium oxide + phosphoric acid</u>

Thorium and phosphoric acid in the form of thorium phosphate are completely inactive as catalysts in hydrocarbon synthesis (as is the case with thorium silicate and thorium borate). A powdered thorium oxide catalyst which was produced by precipitation with soda and dried at 300°C, then impregnated with phosphoric acid (100 g ThO_2 with 27 cm^3 89% H_3PO_4, pasted in the cold and sintered at 250°C in a drying cabinet), did however, turn out to be useful for conversion of carbon monoxide and hydrogen to hydrocarbons.

Table II shows the starting gas analysis and end gas analysis for two experiments carried out with the same amount of ThO_2 at 400°C and 150 atm. In experiment 1, the ThO_2 catalyst was impregnated with phosphoric acid and in experiment 2 a normal ThO_2 catalyst was used for comparison purposes.

In experiment 1, contraction amounted to 19%. In addition to 8.5 g iso-C_4 hydrocarbons, 17.4 g liquid hydrocarbons were formed per m^3 (STP), whereas in experiment 2 at a contraction of 27%, 7.3 g iso-C_4 hydrocarbons and 48.7 g liquid hydrocarbons were obtained. The end gas analysis from experiment 1 reveals a greater tendency to formation of gaseous hydrocarbons with a lower number of carbons (2.5% hydrocarbons with 1.3 carbons versus 0.7% hydrocarbons with 2.0 carbons) with a somewhat reduced conversion in comparison with experiment 2.

Addition of phosphoric acid to the ThO_2 catalyst yielded a reduction in the CO-O_2 conversion in isosynthesis and a reduction in yields of liquid hydrocarbons with, at the same time, an increase in the production of methane.

3. Thorium oxide + aluminum oxide

Three fundamentally different types of experiments were conducted here:

a) The ThO_2-Al_2O_3 catalysts were precipitated together.

b) The Al_2O_3 catalyst was produced separately and used after the ThO_2 catalyst.

c) Thorium and aluminum were precipitated separately and the freshly washed but still moist precipitates were mixed thoroughly and dried.

a) Mixed catalysts precipitated together

Experiments were conducted with 0%, 5%, 10% and 20% Al_2O_3 based on ThO_2.

Production of a catalyst with 20% Al_2O_3, for example, would be done as follows: a boiling solution of 167 g soda in 2 liters of water would be poured slowly into a boiling solution of 240 g thorium nitrate and 169 g aluminum nitrate in 2 liters of water, the precipitate would be boiled briefly, filtered, washed 15 times with 400 cm^3 boiling distilled water each time, then dried at 110°C in a drying cabinet and next dried at 300°C in a stream of air.

The gas throughput was 10 liters of reaction gas per hour and per 28 g of thorium oxide, as was the case with the Al_2O_3-free catalyst. The aluminum oxide was thus used in addition.

Tables III and IV show the results of the following experiments. Table III shows the results of experiments with catalysts which contained 0%, 10% and 20% Al_2O_3, based on ThO_2, at a synthesis pressure of 300 atm and a synthesis temperature of 450°C.

Table IV shows the results of experiments conducted under the same conditions as in Table III, but at a temperature of 475°C.

The results of the experiments in Table III can be summarized as follows:

An increase in the amount of Al_2O_3 added does not have a substantial influence on the carbon monoxide conversion, but it does increase the hydrogen consumption. In conjunction with this, the yields of methane and C_4 hydrocarbons are increased at the expense of the liquid hydrocarbons and the alcohols dissolved therein. With an increase in the amount of Al_2O_3 added, there is also a reduction in the amount of C_2 and C_3 hydrocarbons produced, whereas the alcohols dissolved in the reaction water, consisting mostly of methanol, remain at approximately the same level. The size of the C_4 fraction of isohydrocarbons also showed no dependence on the Al_2O_3 content of the catalyst. The numerical results of this series of experiments can be summarized approximately as follows: on a normal ThO_2 catalyst containing no Al_2O_3, 42.2 g liquid hydrocarbons, 8.6 g alcohols in oil (largely isobutyl alcohol), 22.7 g iso-C_4 hydrocarbons and 10.9 g C_3 hydrocarbons were obtained in addition to 11.1 g methane per m^3 (STP) CO-H_2 mixture (1:1). Under conditions that were otherwise the same, but with a corresponding catalyst that contained 20% Al_2O_3, only 21.0 g liquid hydrocarbons and 1.2 g alcohols in the oil were obtained, but 47.2 g iso-C_4 hydrocarbons, 4.8 g C_3 hydrocarbons and 26.9 g methane were obtained.

Table IV shows the results of experiments conducted otherwise under the same conditions as those in Table III, but at a temperature of 475°C. Here again, the amount of iso-C_4 hydrocarbons increases with an increase in the amount of Al_2O_3 added, and the amount of methane also increases, while there is a reduction in yield of liquid hydrocarbons. The alcohol content of the liquid hydrocarbons is lower at 475°C than at 450°C. The maximum yield of iso-C_4 hydrocarbons was 54.8 g/m^3 (STP) of CO-H_2 mixture (1:1) when 20% Al_2O_3.

was added. 92% of this iso-C_4 hydrocarbon yield consisted of isobutane and 8% was isobutene. In accordance with the increased production of gaseous reaction products, the CO-H_2 consumption ratio, which was approximately 1.2:1 at 450°C, was now 1:1.

A last series of experiments was conducted with ThO_2-Al_2O_3 catalysts that had been precipitated together, yielding the results presented in Table V. These experiments were carried out at a temperature of 450°C and pressures of 300, 600 and 1000 atm using catalysts which contained 30% Al_2O_3 based on thorium oxide.

With an increase in operating pressure, the carbon monoxide conversion increased from 64% to 85%, the amount of liquid hydrocarbons produced increased from 21 g to 27 g/m^3 (STP) of the CO-H_2 mixture, and the amount of alcohols contained in the water increased from 11.8 g to 17.5 g. The oily phase contained only small amounts of alcohols. The main reaction product was isobutane which, in addition to a small amount of isobutene, constituted 47.2 g/m^3 (STP) at 300 atm, 15.7 g/m^3 at 600 atm and 54.6 g/m^3 at 1000 atm. In addition, 7.2 g dimethyl ether were also formed at 600 atm, versus 22.1 g dimethyl ether at 1000 atm. The optimum pressure conditions with regard to formation of hydrocarbons are thus in the range of 300-600 atm.

b) Thorium oxide and aluminum oxide in two separate successive beds

In the experiments summarized in section a), it was found that larger amounts of Al_2O_3 in the ThO_2 catalyst increased the iso-C_4 hydrocarbon yields. The question is to be investigated now was whether this would also be the case if the aluminum oxide was used in a separate bed directly after the thorium oxide bed. Both catalysts were produced by precipitation with soda. The operating pressure was 300 atm as in the experiments summarized in Tables III and IV, the operating temperature was 450°C and the amount of aluminum oxide was 20%, based on ThO_2.

The results of such an experiment are summarized in Table VI. When this experiment is compared with those in Tables III and IV, it is evident that the effect of aluminum oxide used in a bed following the thorium oxide catalyst differs considerably from the results when aluminum oxide is used as a constituent of a ThO_2-Al_2O_3 binary catalyst. The results of the two-bed experiment correspond more to those of the Al_2O_3-free ThO_2 catalysts than those with mixed catalysts. This is especially true for the formation of liquid hydrocarbons and isobutane, but not for alcohols, which are further converted on the following aluminum oxide bed to some extent. Nor does this apply to the methane formed in the presence of aluminum oxide.

c) Mixed catalysts precipitated separately

In these experiments, the thorium was precipitated with soda from the nitrate solution, but the aluminum oxide was obtained by precipitation with sulfuric acid from an aluminate solution. The two precipitates were then combined in certain quantity ratios after washing, mixed thoroughly and then dried. A thorium oxide catalyst with 20% aluminum oxide would be produced as follows, for example:

240 g thorium nitrate dissolved in 2 liters of water were heated to the boil, then precipitated at the boiling point with 95 g soda, also dissolved in 2 liters of water, and the precipitate was filtered, then washed 15 times with 400 cm^3 boiling water each time. Separately, 169 g aluminum nitrate were dissolved in one liter of water and mixed while boiling with 77 g sodium hydroxide dissolved in 500 cm^3 water, whereupon the aluminum hydroxide which was first precipitated would be dissolved again except for a slight turbidity. While still boiling, the aluminum hydroxide was precipitated again from the solution of sodium aluminate with 17.2 cm^3 concentrated sulfuric acid in 350 cm^3 distilled water and the precipitate was first suspended 12 times with 1 liter of water each time and then decanted, and after suction filtration washed three more times with 400 cm^3 boiling water each time. The thorium and aluminum precipitates were then suspended in hot water, stirred together and evaporated on a water bath while stirring constantly, and dried first at 110°C and then at 300°C in a stream of air.

Table VII shows that such a catalyst gives especially high yields of isobutane and only small amounts of alcohol at 450 to 475°C and 300 atm. At 400°C, 9 g alcohol and 40 g dimethyl ether were also formed in addition to 19 g liquid hydrocarbons and 17 g iso-C_4 hydrocarbons, but at 475°C only slight amounts of alcohols were formed (0.5 g/m^3 (STP)) and no dimethyl ether, but 69 g iso-C_4 hydrocarbons and 25.9 g liquid hydrocarbons were obtained. The total yield of liquid hydrocarbons and gas oil hydrocarbons in this experiment was 112.7 g/m^3 (STP) CO-H_2 mixture. The composition of the reaction gas in this experiment was as follows: 37.7% CO_2, 0.7% heavy hydrocarbons, 0.1% O_2, 18.2% CO, 17.3% H_2, 12.1% hydrocarbons (C number 2.4) and 14.9% N_2 with a starting gas which contained 42% CO and 48% H_2 plus 7% N_2 and some CO_2.

An experiment carried out with the same catalyst at 600 atm and 450°C yielded 56.4 g liquid hydrocarbons and 61.3 g iso-C_4 hydrocarbons plus 6.5 g n-C_4 hydrocarbons, 5.5 g C_3 hydrocarbons, 5.4 g C_2 hydrocarbons and 17.4 g methane plus small amounts of alcohols per m^3 (STP) CO-H_2 mixture used at an 82% conversion of carbon monoxide and hydrogen.

d) Summary of experiments with ThO_2-Al_2O_3 catalysts produced in various ways

In contrast with pure aluminum oxide (see part I) which has proven to be not very suitable for synthesis of isohydrocarbons, aluminum oxide is especially important as an additive to thorium oxide, especially when working toward maximum isobutane yields. Experiments in which 20% aluminum oxide was added to the thorium oxide yielded the best results. Catalysts produced by separate precipitation of thorium and aluminum and then mixing them together thoroughly after washing proved to be superior to those in which the catalysts were produced by joint precipitation or in which they were arranged in two successive but separate beds, especially with regard to the iso-C_4 yields.

A summary of the most important results with ThO_2-Al_2O_3 catalysts produced in various ways is given in Table VIII.

4. Thorium oxide + aluminum oxide + alkali

Observations in the use of ThO_2-Al_2O_3 catalysts when the aluminum oxide was not completely freed to alkali after precipitation made it seem desirable to investigate more thoroughly the use of ThO_2-Al_2O_3-alkali catalysts. In these experiments, the alkali was not generally added to the freshly precipitated thorium, but instead was added to the aluminum precipitate which had been produced from aluminate separately as described above and first completely freed to alkali by washing.

Table IX shows the results of experiments with 1% and 3% potassium carbonate, based on the aluminum oxide, and for comparison purposes an experiment with an alkali-free ThO_2-Al_2O_3 catalyst (3% K_2CO_3 based on Al_2O_3, corresponds to an amount of 0.6% based on ThO_2, as used in experiment 2 in Table I). The CO conversion was 73% with 0% K_2CO_3 and 78% with 3% K_2CO_3. The amount of liquid hydrocarbons thus formed was approximately the same when 0% or 1% K_2CO_3 was added, but when larger amounts of alkali were added to the aluminum oxide the liquid hydrocarbon production dropped (from 34.1 g/m^3 to 34.9 g/m^3 to 24.4 g/m^3 (STP). In all cases, alcohols were produced only in very small amounts. When 3% Al_2O_3 was added the alcohols amounted to practically 0. No C_3 hydrocarbons were formed, either. Formation of iso-C_4 hydrocarbons was favored in the presence of alkali. The amount increased from 60.5 g/m^3 (STP) with 0% K_2CO_3 to 67.4 g/m^3 with 1% K_2CO_3 to 84.6 g/m^3 with 3% K_2CO_3.

The reaction was especially shifted in the direction of formation of iso-C_4 hydrocarbons in the presence of the alkali-containing ThO_2-Al_2O_3 catalyst. At the same time, larger amounts of isopentane (2-methylbutane) were obtained (30 to 50% of the liquid reaction products), so that approximately 100 g iso-C_4 hydrocarbons and iso-C_5 hydrocarbons were formed in experiment 3 per m^3 (STP) of the CO-H_2 mixture.

Table X presents a summary showing the results with the three components thorium oxide, aluminum oxide and alkali. The aluminum oxide was precipitated separately from aluminate in all cases (see section on thorium oxide + aluminum oxide). The synthesis gas contained 49% carbon monoxide and 41% hydrogen.

Aluminum oxide and similarly also alkalized aluminum oxide yielded unsatisfactory conversions alone (experiments 1 and 2) (the gas throughput in all cases corresponded to 10 liters of end gas per 25 cm^3 catalyst per hour). In these experiments, carbon monoxide conversion was 24% and 25% and 14 g/m^3 and 24 g/m^3 (STP) liquid hydrocarbons and 10 g and

2 g iso-C_4 hydrocarbons were obtained. Alkali as an additive to thorium oxide yields greater production of liquid hydrocarbons at the expense of the gaseous reaction products (experiment 4). However, aluminum oxide + thorium oxide (experiment 5) caused a reduction in yield of liquid products and increased production of isobutane as well as methane. Addition of alkalized aluminum hydroxide to the freshly precipitated thorium precipitate (experiment 6) gave especially high iso-C_4 yields (85 g/m^3 (STP)) whereas a comparative experiment (7) in which the same amount of alkali was added to the washed thorium precipitate before adding the aluminum oxide again resulted in an increase in the yield of liquid hydrocarbons at the expense of the gaseous hydrocarbons.

5. Thorium oxide + zinc oxide

The ThO_2-ZnO catalysts were generally produced by combined precipitation with soda. The type of precipitation, in particular whether the soda solution was poured into the nitrate solution (normal precipitation) or whether the nitrate solution was poured into the soda solution (reverse precipitation) is important for the effectiveness of these catalysts. The reverse type of precipitation led to especially high yields of liquid hydrocarbons.

The gas throughput with the ThO_2-ZnO catalyst was 10 L/hr and end gas per 28 g thorium oxide. With ThO_2-free catalyst the [illegible] 10 liters end gas/hr based on the catalyst volume [illegible].

Table XI summarizes experiments conducted with ThO_2-ZnO catalysts. At the beginning of the list there is a pure ZnO catalyst produced by reverse precipitation which yielded no liquid hydrocarbons nor any mentionable amounts of sio-C_4 hydrocarbons at 300 atm and 450°C, but instead yielded almost exclusively alcohols and methanes.

The last experiment listed in the table, where thorium oxide and zinc oxide were used in a ratio of 3:1, gave the highest yields of liquid hydrocarbons, namely 78.7 g/m^3 (STP) plus 19.3 g iso-C_4 hydrocarbons. The catalyst used in this experiment was produced as follows:

120 g thorium nitrate ($TH(NO_3)_4 \cdot 4H_2O$) and 74 g zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) were dissolved in 2 liters of water and the solution was heated to the boil. Then this solution was poured while stirring into a solution of 86 g sodium carbonate dissolved in 1 liter of water which was also heated to the boil, the precipitate was filtered under suction, washed 15 times with 400 cm^3 water each time and then dried at 110°C. The apparent density of this catalyst was 0.75 with a particle size of 2-4 mm. After drying in a stream of air at 300°C the apparent density was 1.15.

With a second catalyst produced by the same procedure, 67.7 liquid hydrocarbons, 9.1 g alcohols in the oil, 3.3 g alcohols in the water [illegible] g iso-C_4 hydrocarbons, 2.6 g n-C_4 hydrocarbons, 16.3 g [illegible] C_2 hydrocarbons and 14.0 g methane were obtained at a CO conversion of 73% and an H_2 conversion of 69%.

With a catalyst produced from a more dilute solution, e.g., by dissolving 86 g soda in 2 liters of water instead of 1 liter of water, 45.3 g liquid hydrocarbons, 7.3 g alcohols in the oil, 4.3 g alcohols in the water, 33.5 g iso-C_4 hydrocarbons, 25.7 g C_3 hydrocarbons and 13.4 g C_2 hydrocarbons were obtained in addition to 14.0 g methane at a CO conversion of 77% and an H_2 conversion of 73%. Catalysts precipitated from more dilute solutions yielded more gaseous hydrocarbons, while those precipitated from more concentrated solutions yielded more liquid hydrocarbons.

With regard to the constancy in the catalyst activity, it has been found that this is greater as more liquid hydrocarbons are formed in the synthesis.

Experiments 2-8 in Table XI indicate the influence of the type of precipitation, the CO-O_2 ratio in the synthesis gas and the reaction temperature and pressure.

The highest yields of liquid hydrocarbons plus iso-C_4 hydrocarbons (100 g) were obtained with the catalyst mentioned above that was produced by reverse precipitation at a pressure of 300 atm and a temperature of 450°C. The high ThO_2 content of the catalyst is necessary to avoid preferential production of alcohol.

In addition to the increased tendency to form liquid reaction products on the thorium catalysts that contain zinc oxide, it should also be pointed out that these catalysts do not have any tendency to form carbon. Their color remained white to light gray even after lengthy operating times.

6. Zinc oxide + aluminum oxide

Of the single-component catalysts, thorium oxide proved to be the most effective catalyst for the synthesis of branched hydrocarbons (see part I, Tables II and III). Aluminum oxide and zinc oxide used as single-component catalysts were useless for the purposes of isosynthesis. However, these two oxides proved to be suitable additives to thorium oxide to increase its efficacy - in the former case, in the direction of increased production of gaseous hydrocarbons (namely, isobutane) while in the second case, by increasing production of liquid hydrocarbons.

In the search for a possibility of replacing thorium, it was found that a two-component catalyst consisting of aluminum oxide and zinc oxide is capable of catalyzing the synthesis of higher hydrocarbons as well as isobutane. A zinc oxide-aluminum oxide which contained zinc oxide and aluminum oxide in a 1:1 molar ratio, for example, would be produced as follows:

A boiling solution of 117 g Na_2CO_3 in 2 liters of water was poured while stirring (with an agitator) into 187.5 g $Al(NO_3)_3 \cdot 9H_2O$ + 74.5 g $Zn(NO_3)_3 \cdot 6H_2O$ dissolved in 2 liters of boiling water. The entire mixture was boiled again, filtered under suction and washed on the filter 13 times with 400 cm^3 boiling water each time. The precipitate was first dried at 110°C and then aftertreated for 3 hours in a stream of air at 300°C. The final weight was 48 g with an apparent density of 0.84 and a particle size of 2-4 mm.

The hourly gas throughput, which was generally 10 L/hr and end gas per 28 g ThO_2 in the case of the catalysts containing ThO_2, was based on the catalyst volume in the case of the ThO_2-free catalyst. It then amounted to 10 L/hr of end gas per 25 cm^3 catalyst.

Table XII lists the results of 5 experiments with $ZnO-Al_2O_3$ catalysts, specifically 3 experiments carried out at 150 atm with a synthesis gas consisting of 49% CO and 41% H_2 and 2 experiments carried out at 300 atm with a synthesis gas containing carbon monoxide and hydrogen in a 41:49 ratio. High pressures led to high $CO-H_2$ conversions. As experiments 4 and 5 show, however, it is necessary to work with catalysts which contain a large amount of Al_2O_3 to prevent preferential formation of alcohols. Moreover, as in the case of the ThO_2 catalyst, the tendency to form alcohols is greater at low temperatures than at high temperatures (experiments 1 and 2).

A good conversion was achieved in experiment 5, where the catalyst contained 44% ZnO and 56% Al_2O_3, in a reaction at 300 atm and 450°C that yielded 34.5 liquid hydrocarbons, 20.4 g iso-C_4 hydrocarbons, 8.5 g residual gas oil, 9.4 g C_2 hydrocarbons and 19.2 g methane per m^3 (STP) of the $CO-H_2$ mixture. As in the experiments with ThO_2 catalyst, here again, production of dimethyl ether was evident.

The yields in experiments 4 and 5 could be increased even further when using a synthesis gas which contained the two components in the ratio in which they were consumed. The $ZnO-Al_2O_3$ catalyst thus gave yields in g/m^3 (STP) which approached those obtained on single-component ThO_2 catalysts.

With regard to the space-time yields, the ThO_2-containing catalysts were far superior, however. Thus, with a $ThO_2-Al_2O_3$ catalyst (5:1) a throughput of 600 liters of synthesis gas per 1000 cm^3 catalyst volume per hour was achieved and 380 liters of carbon monoxide and hydrogen were converted and 30 g liquid hydrocarbons plus gas oil were formed, whereas with the $ZnO-Al_2O_3$ catalyst (Table XII, experiment 5) a throughput of 340 liters of synthesis gas per 1000 cm^3 catalyst volume and a conversion of 173 liters of carbon monoxide and hydrogen and production of 11.6 g liquid hydrocarbons plus gas oil were obtained.

A comparison of experiments 2 and 3 (150 atm) shows that a reduction in the hourly gas throughput to one-half leads to an increase in yields. However, such a procedure results in a further worsening of the space-time yields.

Following the $ThO_2-Al_2O_3$ experiments, $ZnO-Al_2O_3$ catalysts were also produced by separate precipitation of the components and then mixing the freshly precipitated and washed precipitates. The apparent density of such a catalyst was low, however. A catalyst consisting of 1 mole ZnO and 1 mole Al_2O_3 had an apparent density of 0.32 (instead of 0.84) when produced in this way (both components precipitated with soda). When using such catalysts, the space-time yield would be reduced considerably.

When zinc oxide and aluminum oxide were used not as mixed catalysts but in two separate successive beds, in which case the aluminum oxide came after the zinc oxide, the effect was completely different from that achieved with the combination catalyst (similar to the results obtained with a ThO_2-Al_2O_3 catalyst). Thus, as with a pure ZnO catalyst, the main hydrocarbon formed was only methane.

7. Thorium oxide + zinc oxide + aluminum oxide

Thorium and zinc were precipitated together from the nitrates, aluminum was precipitated from aluminate and the two precipitates were stirred together in various quantity ratios while wet and then dried. The synthesis reaction was carried out at a pressure of 300 atm and a synthesis temperature of 450°C.

A catalyst that contained ThO_2, ZnO and Al_2O_3 in a ratio of 2:1:0.4 yielded the following results per m^3 (STP) of the CO-H_2 mixture (synthesis gas with 51% CO and 39% H_2:

59.2 g liquid hydrocarbons, 31.7 g iso-C_4 hydrocarbons, 4.6 g n-C_4 hydrocarbons, 15.4 g C_3 hydrocarbons, 10.0 g C_2 hydrocarbons, 8.4 g methane, 6.6 g alcohols in the oil, 3.3 g alcohols in the water.

These results are similar to those obtained on Al_2O_3-free ThO_2-ZnO catalyst. In comparison with the ZnO-free catalyst, there is an increased tendency to form alcohols.

8. Aluminum oxide + chromium oxide

An aluminum oxide-chromium oxide catalyst was tested to determine its effectiveness at 30 atm and temperatures up to 500°C. The temperature could be increased up to 500°C owing to the relatively low activity of the catalyst. The absolute yields of liquid hydrocarbons in this experiment were low, amounting to 5 to 10 g/m^3 of synthesis gas. Nevertheless, one experiment carried out with such a catalyst should be pointed out. In this experiment, the liquid hydrocarbons consisted almost exclusively of aromatics (in contrast with the liquid reaction products obtained on other catalysts; the composition of these products will be discussed in detail in Part III of this study).

The refractive index of the total product obtained on Al_2O_3-Cr_2O_3 was n_D^{20} = 1.48-1.50. Figure 2 shows a boiling point analysis thereof. The boiling point curve shows the breaks characteristic of benzene, toluene, xylene and an indication of also mesitylene. The individual fractions had the following refractive indexes: fraction up to 79°C n_D^{20}= 1.4000, 79-83°C fraction n_D^{20} = 1.4795, 83-109°C fraction n_D^{20} = 1.4619, 109-113°C fraction n_D^{20} = 14929, 113-137°C fraction n_D^{20} = 1.489, 1.37-1.47°C fraction n_D^{20} = 1.4960, fraction above 147°C n_D^{20} = 1.4994.

The catalysts used here contain not only aluminum oxide but also 10% chromium oxide. Similar results were also obtained with various other catalysts such as those based on aluminum oxide-molybdenum oxide.

9. Thorium oxide + chromium oxide

The combination of thorium oxide + chromium oxide was also investigated. The catalyst was produced by combined precipitation with soda from the nitrates and subsequent drying at 110°C followed by drying at 300°C. The process was carried out at 300 atm and 450°C (isosynthesis). The starting gas contained 51.6% carbon monoxide and 39.4% hydrogen.

The following results were obtained per m^3 (STP) of the $CO-H_2$ mixture with a 69% conversion and a 64% H_2 conversion:

46.8 g liquid hydrocarbons, 34.2 g iso-C_4 hydrocarbons, 3.0 g n-C_4 hydrocarbons, 18.3 g C_3 hydrocarbons, 11.2 g C_2 hydrocarbons, 11.9 g methane, 6.8 g alcohols in the oil, 2.0 g alcohols in the water.

In comparison with chromium-free ThO_2 catalysts, the isobutane yields were higher but nevertheless substantially lower than the yields obtained on $ThO_2-Al_2O_3$ catalysts. In comparison with them, there is a greater tendency with the catalyst that contains chromium to produce liquid hydrocarbons with a relatively high alcohol content (12.7%).

10. Thorium + iron

As evident from Section 11 in Part I of this study, iron is unsuitable for use as a catalyst in this synthesis reaction. At low temperatures, it catalyzes the production of essentially linear hydrocarbons, whereas under the temperature and pressure conditions of isosynthesis it essentially causes production of methane and carbon.

In the experiments described below, the effects of adding small amounts of Fe to thorium oxide were investigated, as such small amounts could easily enter the catalyst in some way. Thorium and iron were precipitated together with soda for this experiment and otherwise treated as a normal ThO_2 catalyst.

Table XIII presents the results of experiments with such catalysts. With an increase in the iron content from 0% to 1.2%, the yields of liquid hydrocarbons dropped from 42.2 g/m^3 to 18.5 g/m^3 (STP) CO + H_2 and the yields of alcohol dropped from 19.3 g to 9.6 g. The amount of C_3 and C_4 hydrocarbons remained the same while the amount of C_1 and C_2 hydrocarbons (mainly methane) increased from 15.3 g to 68.0 g.

Even a very small iron content in the catalyst is thus harmful for the conversion. It is thus expedient to take measures to assure that iron carbonyls which would decompose on the catalyst at the temperature conditions of isosynthesis cannot be carried into the catalyst space with the synthesis gas, e.g., by passing it first through an autoclave filled with activated carbon.

11. Thorium oxide + copper

The effect of copper was investigated for various reasons - first, because it is the material used to line the reaction tubes, but also because it has a positive influence on the activity of iron catalysts in hydrocarbon synthesis and the catalysts in methanol synthesis. Finally, it was thought that addition of copper could have a hydrogenating and thus stabilizing effect on the unsaturated primary products.

The copper lining of the reaction tubes remained inactive in the synthesis reaction as demonstrated previously (Part I, Section 11).

Experiments in which 1/4% copper was added to thorium oxide and the reaction was carried out at 75 atm and temperatures of 450 and 475°C did not yield any substantially different results from those obtained with a copper-free catalyst. Catalysts containing thorium oxide and copper in a 1:1 ratio (38 atm, 450 and 475°C) yielded hydrocarbon mixtures with lower carbon numbers and an increased to form aqueous reaction products and carbon.

12. Thorium oxide + aluminum oxide + diatomaceous earth

ThO_2-Al_2O_3 catalysts were especially favorable as discussed in the preceding sections. The effect of diatomaceous earth was therefore tested in combination with thorium oxide plus aluminum oxide at 300 atm. The catalyst contained 20% aluminum oxide and 10% diatomaceous earth based on the thorium oxide. It was produced by separate precipitation of thorium and aluminum and then adding diatomaceous earth into the mixture of combined precipitates while still moist. Such a catalyst has an extremely high tendency to form methane, so for this reason it was impossible to work at the reaction temperature of 450°C which was otherwise customary for the catalyst which did not contain any diatomaceous earth. At 425°C and a throughput of 10 L/hr of end gas per 28 g thorium oxide, the CO conversion was 56% and the H_2 conversion was 57% starting gas 51% CO plus 39% H_2). The following yeilds were obtained per m^3 CO-H_2 mixture: 24.6 g liquid hydrocarbons, 17.6 g iso-C_4 hydrocarbons, 8.6 g n-C_4 hydrocarbons, 5.4 g C_3 hydrocarbons, 6.4 g C_2 hydrocarbons, 42.7 g methane, 0.30 g alcohols in the oil, 3.0 g alcohols in the water.

These experimental findings show not only the large production of methane at 425°C, but also increased production of n-C_4 hydrocarbons in comparison with the catalysts that contained no diatomaceous earth (n-C_4 hydrocarbons constituting 1/3 of the total C_4 hydrocarbons).

(Conclusion to follow)

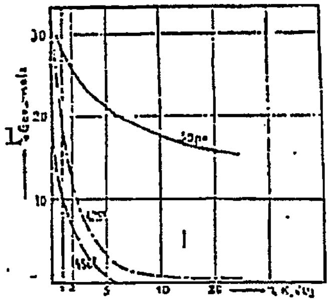


Figure 1. Influence of the alkali content of the ThO_2 catalyst on the $CO-H_2$ conversion at 30 atm.

Key: 1. Gas conversion (%)

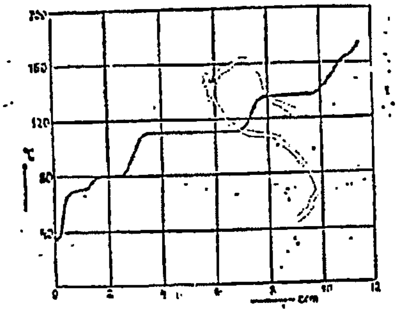
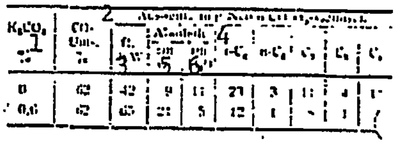


Figure 2. Distillation of the reaction product of the Al_2O_3 + 10% Cr catalyst (30 atm, 500°C).

Table I. Synthesis on a weakly alkalized ThO_2 catalyst (0.6% K_2CO_3, 300 atm, 450°C, 10 L/hr of end gas per 28 g ThO_2).



K_2CO_3 % 1	CO-Um. %	2 [illegible] 3	Alkohole 4 5	6	i-C_4	n-C_4	C_3	C_2	C_1
0	62	42	9	11	27	3	11	4	1
0.6	62	65	23	5	12	1	[illegible]	1	[illegible]

Key: 1. CO conversion (%)
2. Yield in g/m^3 (STP) CO-H_2 mixture
3. Liquid hydrocarbons
4. Alcohols
5. In the oil
6. In the H_2O

Table II. Influence of phosphoric acid on the catalytic properties of a ThO_2 catalyst (400°C, 150 atm).

Nr.	Katalysator	CO_2	sKW	O_2	CO	H_2	KW	CZ	N_2		
1	2		3				4	5			
—	—	3,0	0,0	0,2	48,6	41,0	—	—	7,2	(Anf.-Gas)	8
I	ThO_2 mit 6 H_3PO_4	11,6	1,3	0,2	40,4	35,1	2,5	1,3	8,9	(Endgas)	9
II	ThO_2 ohne 7 H_3PO_4	14,1	1,0	0,0	38,1	36,3	0,7	2,0	9,8	(Endgas)	9

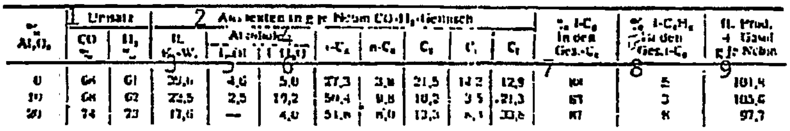
Key:
1. No.
2. Catalyst
3. Heavy hydrocarbons
4. Hydrocarbons
5. No. of carbons
6. With
7. Without
8. Starting gas
9. End gas

Table III. ThO_2 + various Al_2O_3 additives (300 atm, $CO:H_2$ = 45:45), 450°C.

% Al_2O_3	1 Umsatz		2 Ausbeuten in g je Nm³ CO-H_2-Gemisch								% i-C_4 in den Ges.-C_4	% i-C_4H_8 in den Ges.-i-C_4	fl. Prod. + Gasöl g je Nm³
	CO %	H_2 %	fl. KW 3	Alkohole 4 i. Öl 5	Alkohole i. H_2O 6	i-C_4	n-C_4	C_3	C_2	C_1	7	8	9
0	61	47	42,2	8,6	10,7	22,7	3,2	10,9	4,2	11,1	[illegible]	8	98,3
10	59	51	32,8	3,3	12,6	37,0	5,4	5,5	2,7	13,2	87	10	97,2
20	64	60	21,0	1,2	11,6	47,2	6,1	4,8	2,2	20,9	[illegible]	4	92,1

Key:
1. Conversion
2. Yield in g/m³ (STP) CO-H_2 mixture
3. Liquid hydrocarbons
4. Alcohols
5. In the oil
6. In the H_2O
7. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
8. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
9. Liquid products in the gas oil in g/m³ (STP)

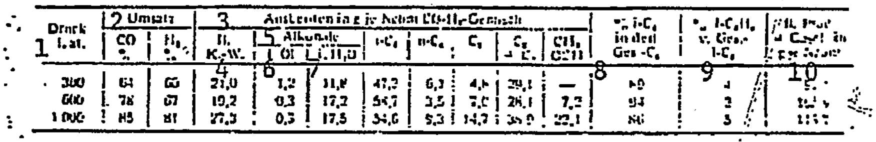
Table VI. ThO_2 + various Al_2O_3 additives (300 atm, $CO:H_2$ = 45:45), 475°C.



% Al_2O_3	1 Umsatz		2 Ausbeuten in g je Ncbm CO-H_2-Gemisch								7 % i-C_4 in den Ges.-C_4	8 % i-C_4H_8 in den Ges.-i-C_4	9 fl. Prod. + Gasöl g je Ncbm
	CO %	H_2 %	3 fl. KW.	4 Alkohole 5 i. Öl	6 i. H_2O	i-C_4	n-C_4	C_3	C_2	C_1			
0	64	61	29,0	4,6	5,0	27,3	3,8	21,5	14,2	12,9	[illegible]	5	101,8
10	68	62	24,5	2,5	17,2	50,4	9,8	10,2	3,5	21,3	[illegible]	3	103,6
20	74	73	17,6	—	4,0	51,8	6,0	13,3	8,1	33,6	87	8	97,7

Key:
1. Conversion
2. Yield in g/m^3 (STP) CO-H_2 mixture
3. Liquid hydrocarbons
4. Alcohols
5. In the oil
6. In the H_2O
7. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
8. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
9. Liquid products plus gas oil, g/m^3 (STP)

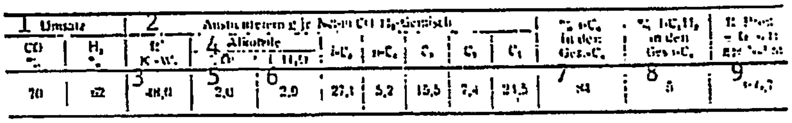
Table V. $ThO_2 + 20\% Al_2O_3$ at 450°C and various pressures ($CO:H_2 = 42:49$).



1 Druck at.	2 Umsatz		3 Ausbeute in g je Nm³ CO-H₂-Gemisch								8 % i-C₄ in den Ges.-C₄	9 % i-C₄H₈ v. Ges. i-C₄	10 fl. Prod. + C₃+C₄ in g pro Nm³
	CO %	H₂ %	4 fl. KW.	5 Alkohole 6 Öl	7 i. H₂O	i-C₄	n-C₄	C₃	C₂ + C₁	CH₃OCH₃			
300	64	65	21,0	1,2	11,8	47,2	6,3	4,6	29,1	—	88	4	[illegible]
600	78	67	19,2	0,3	17,2	54,7	3,5	7,0	26,1	7,2	94	2	[illegible]
1000	85	81	27,3	0,3	17,5	34,6	5,3	14,7	35,0	22,1	86	5	[illegible]

Key:
1. Pressure in atmospheres
2. Conversion
3. Yield in g/m^3 (STP) $CO-H_2$ mixture
4. Liquid hydrocarbons
5. Alcohol
6. In the oil
7. In the water
8. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
9. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
10. Liquid products plus gas oil in g/m^3 (STP)

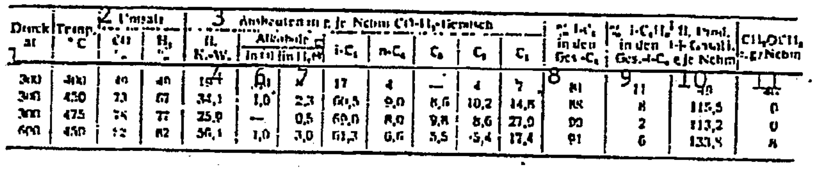
Table VI. $ThO_2 + Al_2O_3$ in two beds. 300 atm, 450°C ($CO:H_2$ = 45:45).



1 Umsatz		2 Ausbeute in g je Nm³ CO-H₂-Gemisch								% i-C₄ in den Ges.-C₄	% i-C₄H₈ in den Ges. i-C₄	g Prod. + [illegible]
CO %	H₂ %	g K.-W.	4 Alkohole i. Öl	i. H₂O	i-C₄	n-C₄	C₃	C₂	C₁			
70	62	3 48,0	5 2,0	6 2,9	27,1	5,2	15,5	7,4	21,5	7 84	8 5	9 64,7

Key: 1. Conversion
2. Yield in g/m³ (STP) $CO-H_2$ mixture
3. Liquid hydrocarbons
4. Alcohols in the oils
6. In H_2O
7. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
8. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
9. Liquid products plus gas oil in g/m³ (STP)

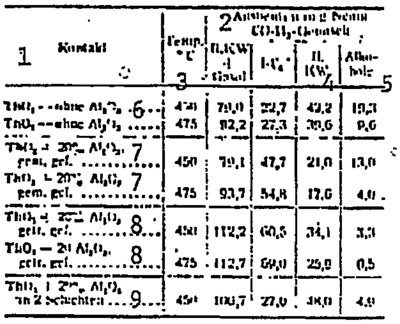
Table VII. ThO_2 + 20% Al_2O_3 (produced separately from aluminate) at various pressures and temperatures ($CO:H_2$ = 49:41).



Druck at 1	Temp. °C	2 Umsatz CO %	Umsatz H_2 %	3 Ausbeuten in g je Nchm CO-H_2-Gemisch fl. K.-W. 4	Alkohole im Öl 6	Alkohole im H_2O 7	i-C_4	n-C_4	C_3	C_2	C_1	% i-C_4 in den Ges.-C_4 8	% i-C_4H_8 in den Ges.-i-C_4 9	fl. Prod. + Gasöl i. g je Nchm 10	CH_3OCH_3 g/Nchm 11
300	400	40	40	19	0,1	[illegible]	17	4	—	4	7	81	11	90	[illegible]
300	450	73	67	34,1	1,0	2,3	60,5	9,0	8,6	10,2	14,8	88	8	115,5	0
300	475	78	77	25,9	—	0,5	69,0	8,0	9,8	8,6	27,0	90	2	113,2	0
600	450	72	82	56,1	1,0	3,0	61,3	6,6	5,5	5,4	17,4	91	6	133,8	8

Key:
1. Pressure (atm)
2. Conversion
3. Yield in g/m^3 (STP) CO-H_2 mixture
4. Liquid hydrocarbons
5. Alcohols
6. In the oil
7. In the H_2O
8. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
9. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
10. Liquid products plus gas oil in g/m^3 (STP)
11. CH_3OCH_3 in g/m^3 (STP)

Table VIII. Summary comparison of a ThO_2-Al_2O_3 experiment (300 atm).



1 Kontakt	Temp. °C	2 Ausbeuten in g/Nm³ CO-H₂-Gemisch fl. KW + Gasöl 3	i-C₄	fl. KW 4	Alkohole 5
ThO₂ ohne Al₂O₃ 6	450	79,0	22,7	42,2	19,3
ThO₂ ohne Al₂O₃	475	92,2	27,3	39,6	9,6
ThO₂ + 20% Al₂O₃, gem. gef. 7	450	79,1	47,7	21,0	13,0
ThO₂ + 20% Al₂O₃, gem. gef. 7	475	93,7	54,8	17,6	4,0
ThO₂ + 20% Al₂O₃, getr. gef. 8	450	112,2	60,5	34,1	3,3
ThO₂ + 20% Al₂O₃, getr. gef. 8	475	112,7	69,0	25,9	0,5
ThO₂ + 20% Al₂O₃ in 2 Schichten 9	450	100,7	27,0	48,0	4,9

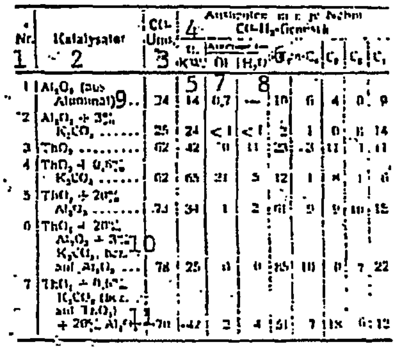
Key:
1. Catalyst
2. Yields in g/m^3 (STP) CO-H_2 mixture
3. Liquid hydrocarbons plus gas oil
4. Liquid hydrocarbons
5. Alcohols
6. Without
7. Precipitated together
8. Precipitated separately
9. In 2 beds

Table IX. Experiments with catalysts containing various amounts of K_2CO_3 in addition to ThO_2 + 20% Al_2O_3 (300 atm, 450°C).

1 % K_2CO_3 bez. auf Al_2O_3	2 Umsatz		3 Ausbeuten in g je Nchm CO-H_2-Gemisch								8 % i-C_4 in Ges.-C_4	9 % C_4H_8 in Ges. n-C_4	10 fl. KW. + Gasol g/Nchm
	CO %	H_2 %	4 fl. KW.	5 Alkohole 6 im Öl	7 i. H_2O	i-C_4	n-C_4	C_3	C_2	C_1			
0	73	67	38,1	1,0	2,3	60,5	9,0	4,6	10,2	14,6	87	8	112,2
1	72	58	34.9	0	1,2	67,4	10,1	0	4,5	15,8	87	8	112,4
3	78	75	25,4	0	0,2	64,6	9,6	0	7,3	21,5	90	5	119,5

Key:
1. % K_2CO_3 based on Al_2O_3
2. Conversion
3. Yields in g/m^3 (STP) CO-H_2 mixture
4. Liquid hydrocarbons
5. Alcohols
6. In the oil
7. In the H_2O
8. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
9. % C_4H_8 in the total C_4 hydrocarbons
10. Liquid carbons + gas oil in g/m^3 (STP)

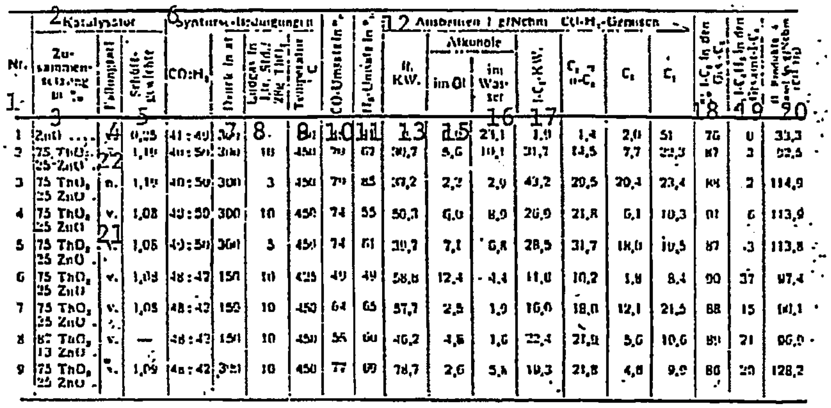
Table X. Catalytic effect of ThO_2, Al_2O_3 and alkali (450°C, 300 atm).



Nr. 1	Katalysator 2	CO-Ums. % 3	Ausbeute in g je Nm³ CO-H_2-Gemisch 4								
			fl. KW 5	Alkohole in Öl 7	Alkohole in H_2O 8	i-C_4 6	n-C_4	C_5	C_6	C_7
1	Al_2O_3 (aus Aluminat) 9	24	14	0,7	—	10	6	4	0	9
2	Al_2O_3 + 3% K_2CO_3	25	24	< 1	< 1	2	1	0	8	14
3	ThO_2	62	42	10	11	23	3	11	1	11
4	ThO_2 + 0,6% K_2CO_3	62	65	21	5	12	1	8	1	6
5	ThO_2 + 20% Al_2O_3	73	34	1	2	61	9	9	10	15
6	ThO_2 + 20% Al_2O_3 + 3% K_2CO_3, bez. auf Al_2O_3 10	78	25	0	0	85	10	0	7	22
7	ThO_2 + 0,6% K_2CO_3 (bez. auf ThO_2) 11 + 20% Al_2O_3	70	47	3	4	51	7	18	6	12

Key:
1. No.
2. Catalyst
3. CO conversion, %
4. Yields in g/m^3 (STP) CO-H_2 mixture
5. Liquid hydrocarbons
6. Alcohols
7. In the oil
8. In the H_2O
9. From aluminate
10. Based on Al_2O_3
11. Based on ThO_2

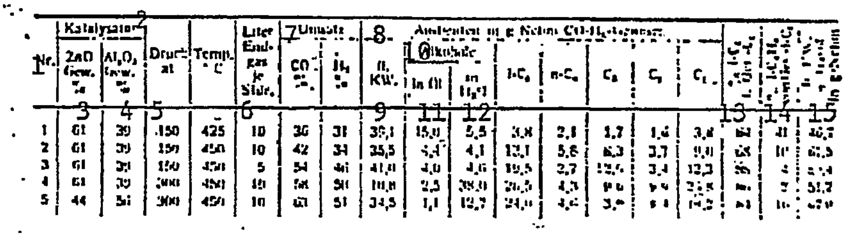
Table XI. Experiments with ThO_2-Zno catalysts.



Nr. 1	2 Katalysator			6 Synthesebedingungen				CO-Umsatz in %	H_2-Umsatz in %	12 Ausbeuten i g/Nchm CO-H_2-Gemisch							i-C_4 in den Ges.-C_4	i-C_4H_8 in den Gesamt-i-C_4	fl. Produkte + Gasöl in g/Nchm CO-H_2
	Zusammensetzung in % 3	Fällungsart 4	Schüttgewicht 5	CO:H_2	Druck in at 7	Endgas in Ltr. Std./28g ThO_2 8	Temperatur °C 9	10	11	fl. KW. 13	Alkohole im Öl 15	Alkohole im Wasser 16	i-C_4-KW. 17	C_3 + n-C_4	C_2	C_1	18	19	20
1	ZnO	4	0,25	41:49	7	8.	9	10	11	13	15	21,1	1,9	1,4	2,0	51	76	0	33,3
2	75 ThO_2 25 ZnO	22	1,19	40:50	300	10	450	70	67	30,7	5,6	10,1	31,7	14,5	7,7	22,3	87	3	92,5
3	75 ThO_2 25 ZnO	n.	1,19	40:50	300	3	450	79	85	37,2	2,2	2,9	43,2	20,5	20,4	23,4	84	2	114,9
4	75 ThO_2 25 ZnO	v.	1,08	40:50	300	10	450	74	55	50,3	6,0	8,9	26,9	21,8	6,1	10,3	91	6	113,9
5	75 ThO_2 25 ZnO	21 v.	1,06	40:50	300	3	450	74	61	39,7	7,1	6,8	28,5	31,7	18,0	10,5	87	3	113,8
6	75 ThO_2 25 ZnO	v.	1,03	48:42	150	10	425	49	49	58,6	12,4	4,4	11,0	10,2	1,8	8,4	90	37	97,4
7	75 ThO_2 25 ZnO	v.	1,05	48:42	150	10	450	64	65	57,7	2,5	1,9	16,0	18,0	12,1	21,5	88	15	101,1
8	87 ThO_2 13 ZnO	v.	—	48:42	150	10	450	55	60	46,2	4,5	1,6	22,4	21,9	5,6	10,6	89	21	96,9
9	75 ThO_2 25 ZnO	v.	1,09	48:42	300	10	450	77	69	78,7	2,6	5,8	19,3	21,8	4,8	9,9	86	20	128,2

Key:
1. No.
2. Catalyst.
3. Composition (in %)
4. Type of precipitation
5. Apparent density
6. Synthesis conditions
7. Pressure in atm
8. End gas L/hr/28 g ThO_2
9. Temperature, °C
10. CO conversion in %
11. H_2 conversion in %
12. Yield in g/m^3 (STP) CO-H_2 mixture
13. Liquid hydrocarbons
14. Alcohols
15. In the oil
16. In the water
17. Iso-C_4 hydrocarbons
18. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
19. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
20. Liquid products + gas oil in g/m^3 (STP) CO-H_2 mixture
21. Reverse
22. Normal

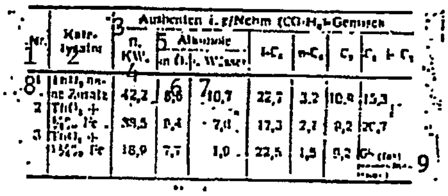
Table XII. Experiments with ZnO-Al_2O_3 catalysts.



Nr. 1	Katalysator 2 ZnO Gew. % 3	Katalysator 2 Al_2O_3 Gew. % 4	Druck at 5	Temp. °C	Liter Endgas je Stde. 6	Umsatz 7 CO %	Umsatz 7 H_2 %	8 fl. KW. 9	Alkohole 10 in Öl 11	Alkohole 10 in H_2O 12	i-C_4	n-C_4	C_3	C_2	C_1	13	14	15
1	61	39	150	425	10	36	31	39,1	15,0	5,5	3,8	2,1	1,7	1,6	3,8	62	41	46,7
2	61	39	150	450	10	42	34	35,5	5,4	4,1	13,1	5,6	6,3	3,7	9,0	68	10	63,5
3	61	39	150	450	5	54	46	41,0	4,0	4,6	19,5	2,7	12,6	3,4	12,3	86	4	[illegible]
4	61	39	300	450	10	58	50	10,8	2,5	38,0	20,5	4,3	[illegible]	[illegible]	21,5	[illegible]	7	51,7
5	44	56	300	450	10	61	51	34,5	1,1	12,7	24,0	4,6	[illegible]	[illegible]	14,2	[illegible]	10	[illegible]

Key:
1. No.
2. Catalyst
3. ZnO (wt%)
4. Al_2O_3 (wt%)
5. Pressure in atm
6. Liters of final gas per hour
7. Conversion
8. Yields in g/m^3 (STP) CO-H_2 mixture
9. Liquid hydrocarbons
10. Alochols
11. In the oil
12. In the H_2O
13. % iso-C_4 hydrocarbons in the total C_4 hydrocarbons
14. % iso-C_4H_8 in the total iso-C_4 hydrocarbons
15. Liquid hydrocarbons + gas oil in g/m^2 (STP)

Table XIII. ThO_2 + Fe catalyst at 300 atm and 450°C.



1 Nr.	2 Katalysator	3 Ausbeuten i. g/Nebm (CO-H_2)-Gemisch						
		4 fl. KW.	5 Alkohole 6 in Öl	7 i. Wasser	i-C_4	n-C_4	C_3	C_1 + C_2
8 1	ThO_2 ohne Zusatz	42,2	6,8	10,7	22,7	3,2	10,9	15,3
2	ThO_2 + ½% Fe	39,5	0,4	7,0	17,3	2,7	9,2	20,7
3	ThO_2 + 1½% Fe	18,9	7,7	1,0	22,5	1,5	9,2	C_1 (fast reines Methan) 9

Key:
1. No.
2. Catalyst
3. Yield in g/m^3 (STP) CO-H_2 mixture
4. Liquid hydrocarbons
5. Alcohols
6. In the oil
7. In the water
8. ThO_2 without additives
9. Almost pure methane

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