

**FILM STUDY GROUP**  
**REPORT ON MICROFILM REEL NO. 20**  
**Prepared by**  
**SHELL DEVELOPMENT COMPANY.**

Shell Development Co.  
Emeryville, California  
December 17, 1945

Report on Roll 20 (Series A) of

J. S. Technical Oil Mission Microfilm

This roll reproduces technical documents seized at the Leuna plant of the Ammoniakwerk Merseburg, GmbH (I. G. Farbenindustrie subsidiary). It contains several items of considerable interest and value. These are:

1) A long report in English on the exchange discussions regarding the Fischer-Tropsch process that were held at Ludwigshafen in 1936. This report and the similar one on Roll 19, also in English, give a complete and detailed account of the process as of that date.

2) Another long report, likewise in English, describing the Ruhrchemie Fischer-Tropsch plant at Holten as of 1936.

3) Minutes of a meeting held by I. G. chemists in 1943 to discuss methods of preparing active alumina for catalysts.

4) A detailed report describing many experiments on the mixing of fluid systems. Novel designs, and methods of quantitative treatment are given. The mixing of plastic materials is also treated.

Other subjects of interest are:

1) Conversion of CO to CO<sub>2</sub> over various catalysts at normal and at elevated pressures.

2) Study of catalysts by the adsorption of gases.

3) Experiments on promoters for ammonia catalyst.

4) Patent applications on catalysts, regeneration methods, fuels, etc.

Abstracts covering Roll 20 follow. With the exception of the section on aluminas, these are quite brief, and are intended only as guides to the information on the film.

- p. 1965-2032 Appendices to exchange report on Fischer-Tropsch described in last abstract of Roll 19.
- p. 2034-2309 Exchange of information on Fischer-Tropsch. (Kellogg, I.G., Shell, Standard of N.J.) A similar report to the one described as the last item of Roll 19. This report on the exchange meeting of 1938 was written by Kellogg and is in English. This report covers the same information as the last item of Roll 19, but it is not an exact duplication.  
Kellogg Company, Laboratory II, February 27, 1939
- p. 2310-2498 Report on: Ruhrchemie Process for the synthesis of hydrocarbons from carbon monoxide and hydrogen. This report contains information obtained at the same exchange meeting mentioned above but confines itself entirely to the Holten plant and to verbal information received from personnel of Ruhrchemie. It was prepared by the Kellogg Company, is in English, and contains detailed information, data, and drawings of equipment as well as flowsheets. Manufacture of synthesis gas and of catalyst are described.  
Kellogg Company, Laboratory II, February 27, 1939
- p. 2499-2509 CO - Conversion to CO<sub>2</sub> Experiments with Kuhlmann Catalyst  
Experiments with a magnesium oxide (46.5%), iron oxide (26%), chromic oxide (3.4%), and alkali carbonate 2.2% K<sub>2</sub>O catalyst, made by Kuhlmann in Paris and used by Bamag in Ruhland at 8 atm. Experiments were carried out at low pressure and at 16 atms. in parallel with experiments using brown oxide catalyst. It was found that the brown oxide catalyst was superior in every respect.  
Ludwigshafen, January 16, 1939
- p. 2510-2525 Investigations on the synthesis of gasoline after Franz Fischer. Use of pure cobalt catalysts without additives. Yields of 135 cc./m<sup>3</sup> liquid product were obtained indicating that the additives only serve as stabilizers. The most active catalysts had a low density and contained 30-60% Co<sub>2</sub>O<sub>4</sub>. The temperature had to be held low, but even so activity decline due to sintering was rapid. No carbide formation was noted with X-ray. The presence of alkali was not found necessary. Oppau, March 18, 1937
- p. 2526-2551 Conversion of CO to CO<sub>2</sub> under pressure over brown oxide catalyst. Experiments were carried out to determine the desirability of converting at 17 atm. It was found that the catalyst remained very stable over a long period of time (148 days with very high throughput). Methane and coke formation were negligible. It was found that it was imperative to keep steam in the reactor when the pressure and temperature were high if gas was present, since otherwise there would be rapid coking. The technique used was to heat and cool in a nitrogen atmosphere, then cut in steam and other gas. Ludwigshafen, April 8, 1936

K. Catalyst Preparation and Properties

- p. 2553-2565 On the adsorption of gases on catalyst carriers and on a hydrogenation catalyst. Surface areas were determined with argon using adsorption isotherms. Substituting ethane and ethylene it was found that the adsorptivity on carbon, silica gel, and catalyst 5058 (metal sulfide), increased greatly, with 5058 increasing at the greatest rate and also being more selective in favor of ethylene. It was noted that 5058 adsorbed more ethylene but less ethane at higher temperatures. It was felt that this might be characteristic of catalytically active catalysts. Reaction rates were measured on 5058 by getting the difference between the rate of hydrogen adsorption on a catalyst free of butylene and one with a layer of butylene. Rates of adsorption on fresh and partially deactivated catalyst were measured.  
Ludwigshafen, April 17, 1939
- p. 2566-2577 Investigation of the catalyst for converting 1,4-butylene glycol to butadiene. It was found that the best catalysts are composed of 60-80% insoluble metaphosphate, 20-30% acid pyrophosphate and 4-7% phosphoric acid on graphite grains. The following catalyst changes during operation had to be avoided: resin deposition, acid transfer, and change of the salt equilibrium. This is accomplished by periodically reversing the flow through the catalyst and by washing the surface to remove aldehyde condensation products.  
Ludwigshafen, May 2, 1939
- p. 2578-2582 Patent application: Preparation of phosphoric acid containing catalysts where the drying is carried out on corrosion resistant surfaces in the presence of a reducing metal such as zinc, aluminum, etc. Ludwigshafen, October 22, 1940
- p. 2583-2587 Patent application: Process for the preparation of shape retaining catalysts or adsorbents where a part of the material (preferably 10-20%) is ground to colloidal dimensions, moistened, mixed with the remainder, formed, and heated.  
Ludwigshafen, October 14, 1941
- p. 2588-2594 Patent application: Air Oxidation of catalyst deposits in a shaft kiln, for regeneration. The kiln is divided into zones of different oxygen concentration, and the catalyst moves into zones of higher oxygen content as it passes through the kiln. Circulation of regeneration gases from one zone to another is also claimed.  
Ludwigshafen, February 11, 1942

p. 2595-2637

Report on exchange of information on the preparation of alumina for catalysts; meeting in Oppau, July 6, 1943. These are minutes of a discussion meeting of I.G. scientists from Leuna and Oppau concerning different methods of preparing alumina. Aluminas were prepared in numerous ways which can be classified according to the following general methods;

- 1) Decomposition of an aluminum salt by heating in air or steam, as for example  $AlCl_3$ ,  $Al(NO_3)_3$ , or basic aluminum acetate (prepared by the action of HOAc on Al).
- 2) Precipitation from an aluminum salt with a base, e.g.,  $Al(NO_3)_3 + NH_4OH$  or  $Al_2(SO_4)_3 + NH_4OH$ .
- 3) Precipitation from sodium aluminate with an acidic material, e.g.  $NaAlO_2 + HNO_3$  or  $NaAlO_2 + NH_4NO_3$ . In the precipitation methods the variables thought to be of importance are concentration of the precipitants, pH at precipitation, and temperature and pH of the wash water.

A new method of precipitation of gelatinous alumina is mentioned which may enable better reproducibility of the active  $\gamma$ - $Al_2O_3$ . This preparation utilizes rapid mixing of the precipitants in a mixing head and continuous removal of the gelatinous precipitate so that it is not contacted by the starting materials.

In the preparation of the active  $\gamma$ - $Al_2O_3$  from the hydrogel, variables that have been studied are pH of the suspension being peptized, peptization agents ( $Al(NO_3)_3$  and  $HNO_3$  mentioned), drying, calcining, washing of the calcined material with ammonia, and pelleting.

For the activated aluminas, various physical properties such as bulk density, apparent density (determined with mercury), true density (determined pycnometrically employing either water or benzene), surface area, pore volume, and particle sizes, have been studied. Use of X-ray and electron diffraction has been made, but they are found lacking in many cases in not being able to distinguish between aluminas prepared by various means and yielding dissimilar results in catalyst tests. An attempt was to be made to find a correlation between heat of solution of the alumina and its activity.

Considerable difficulty was experienced in reproducing aluminas.

It was found that:

- 1) The presence of alkali is generally deleterious to the activity of a catalyst supported on alumina, (e.g.  $Mo/Al_2O_3$  hydroforming catalyst).

- 2) Addition of as little as 5% kaolin to alumina prevents or retards the undesirable  $\gamma$  to  $\alpha$  transformation.
- 3) Alumina is harmed by steam.

An interesting method permits something to be said regarding the size and structure of the electrical fields that surface atoms of a solid body exert on an adsorbed europium atom. The adsorbed europium atom is excited into fluorescence by ultra-violet light and the fluorescence radiation is analyzed spectrographically. R. Tomaschek succeeded by this method in clearly distinguishing differences in samples of MgO which were prepared differently but were identical to the X-ray. (No further details in film)

No good general relationship has been found between test results of alumina or catalysts supported on alumina and the preparative variables. Alumina is used in catalysts employed for dehydration, dehydrogenation, aromatization, amination, high pressure dehydrogenation, and hydroforming.

For use in dehydrogenation of butane it has been found that addition to the alumina of small quantities of alkali,  $H_3PO_4$ ,  $SiO_2$ ,  $H_3BO_3$ , or inorganic non-volatile acids reduces the deposition of coke on the catalyst, increases its life, and increases the conversion to butylene.

The preparation of an alumina from aluminum sulfate and ammonia is described in detail. Methods of preparing microspheres for catalysts are discussed.

Oppau, July, 1943

p. 2638-2641 Patent application: Preparation of catalytically active materials, such as activated alumina, by precipitation where the solution and precipitation agent are mixed at such high velocities that mixing is complete before crystal growth can set in. Ludwigshafen, July 28, 1943

p. 2642-2676 The effect of additives, such as Al, Ca, and K, on the number and energy level of the active centers of the ammonia catalyst. The experimental work is reported and discussed. The following conclusions and results were stated.

- 1) Reaction rates were determined for the combinations: Fe, FeK, FeCa, FeAl, FeAlCa, FeAlK, and FeAlCaK at atmospheric pressure between 300 and 600°C. From these, activation energies, number of active centers and average energy level were calculated.

2) Potassium produces active centers of the highest energy level.

3) If highly active centers are present they, exclusively, are used for reaction and only when they are deactivated will a large number of less active centers partially maintain activity.

4) Potassium appears to facilitate the poisoning of low energy active centers by oxygen.

5) Experiments in the presence of oxygen indicate that the potassium free catalyst is superior at atmospheric pressure while at a pressure of 225 atm. the superiority of the potassium free catalyst is only true in the 300-400°C temperature region.  
Oppau, February 16, 1944

p. 2677-2680 Patent application. Process for the preparation of highly porous materials composed of silicic acid and alumina or magnesium oxide or both. The finely ground solids are mixed with water to form a plastic mass, maintained at that temperature for a while and then shaped and dried.  
Ludwigshafen, March 6, 1945

L. Patent Applications on the Manufacture of Aviation Gasoline

p. 2681-2685 Patent application: Process for the production of motor fuel in which alcohols from Fischer-Tropsch and gasoline from coking coal are mixed and reacted in the presence of hydrogen at 40-70 atm, and at a temperature which gives a partial pressure of 0.5 to 3 atm. for the reactants over a catalyst consisting of sulfide or oxides of metals of the 6th or 8th group, possibly in admixture with metal oxides of the 2nd to 5th group.  
Ludwigshafen, January 13, 1943

p. 2686-2690 Patent application: Preparation of highly aromatic gasoline from highly aromatic gas oils. The gas oil is first freed of oxygen-, sulfur-, nitrogen-, and unsaturated compounds by treating with catalysts such as 1% MoO<sub>3</sub> on alumina at temperatures between 450 and 550°C and pressures between 100 and 700 atm. where the hydrogen partial pressure is above 50 atm. The products heavier than gasoline are treated with a cracking (dealkylation) catalyst, such as 1% MoO<sub>3</sub> on aluminum silicate at temperatures between 350 and 500°C and pressures between 40 and 300 atm.  
Ludwigshafen, October 11, 1943

M. Chemical Engineering Data and Control Equipment

p. 2692-2930 Results of experiments with various mixers. This report covers: the properties of different types of mixers and their field of application; theoretical basis for the calculation of performance requirements; experimental work on energy relationships; and methods of calculation.

It is a very comprehensive report. Work requirements were determined for various types of mixers and vessels. The principles of mixing processes were developed theoretically and the theory was checked by experiments. It was also determined which of the many variables (RPM, shape, baffles, etc.) must be considered when scaling up a mixer from a model. For the case of one type of liquid mixer tables were prepared to permit design from small scale models. Similar development was found possible for the mixing of plastic materials, and enabled the prediction of large scale power and size requirements. Before going into extensive calculation for scaling up mixers, agreement should be reached to standardize on a few types of mixers and certain dimension ratios should then be maintained.

Ludwigshafen, July 31, 1937

SDS-20594

FK:OWB:HHV/jrh