

The composition and method of preparation was obtained for all catalysts that had been manufactured or used at Leuna for the preparation of fuels, oils, etc. Since many of the senior officials had left the district, most of the personnel interrogated were of the second or lower ratings, and were not familiar with all the details of the processes in question. In particular, Dr. Emil Schich had replaced Dr. S. Schneider as Works Manager. In addition, the time available, before the Russians moved into the area, was insufficient for a thorough analysis of the methods of manufacture of catalysts and there was no opportunity to make a study of the catalyst plant and its equipment. It is believed, however, that the information on composition and preparation of catalysts is adequate and that the catalysts could be prepared after only the usual amount of experimentation. The information on the methods of manufacture was obtained from Dr. Kurt Hill.

Purchase of chemicals for catalyst manufacture was not made on the basis of specifications, as is the general rule. The principal metal oxides and salts were purchased by "mark", and were in all instances the technically pure grade. Distilled water or condensate was used throughout for making solutions and for washing. Condensate was usually freed from oil by use of a charcoal filter.

The numbering of catalysts at Leuna has not been systematic; the only certain information conveyed by the numbering is the chronological order in which they were produced commercially. For the principal catalysts, estimated productions at the peak of manufacture have been given.

Catalyst 616

Use: Methanol synthesis, from carbon monoxide and hydrogen.

Composition:	Cr ₂ O ₃	33%
	ZnO	60%
	Graphite	4%
	Water and Impurities	6%

Preparation:

Sixty kilograms of chromic acid anhydride is run in a chaser for thirty minutes; 100 kg. of zinc white is added and the mixing continued for 20 minutes. Thirty litres of water is next added, and ten minutes later 1 kg. of graphite (natural). Mixing is continued until all components are well blended. The chaser is then emptied, the charge is passed through a drum sifter (coarse pieces are returned to the chaser), and the mixture is

pressed into 9 mm. pellets.

Quantity: 30 tons per month.

Catalyst: 1132:

Use: Isobutanol synthesis, from carbon monoxide and hydrogen.

Composition:

Cr ₂ O ₃	33%
ZnO	60%
Graphite (natural)	1%
K ₂ O	1%
Water and impurities	5%

Preparation:

Procedure is the same as for catalyst 616, except that K₂O is introduced by adding potassium hydroxide or potassium carbonate along with the zinc white. Good mixing and fine grinding are again important factors.

Quantity: 60 tons per month.

Samples: Nos. 17 and 18

Catalyst 1750: A mild hydrogenation catalyst.

Use: After-hydrogenation of higher alcohols (same as No.1930).

Composition:

Cu	1.25 mol
Cr ₂ O ₃	0.50
ZnO	1.00

Preparation:

125 kgs. of copper sulphate (CuSO₄.5H₂O) is dissolved in 1400 litres of water. 50 kgs. of Chromic acid anhydride is dissolved in 300 litres of water and reduced with SO₂. After mixing the two solutions, a solution of 200 kg. of sodium carbonate in 500 litres of water is added with constant stirring. When the precipitation is finished, 15.1 kg. of zinc white is added while stirring. The whole is heated to 78°C and held at this temperature for 24 hours (alcohol bath). The contents are withdrawn into a filter, washed, dried and pressed into pellets.

The time spent in mixing, heating, etc, was said not to be critical.

Sample: No.73.

Catalyst 2493:

Use: Dehydrogenation of alcohols to aldehydes.

Composition:

ZnS	25%
Pumice (Italian)	75%

Preparation:

The pumice is broken into 4-7 mm granules, sifted and washed. Ten kg. of wet pumice is run in a pill-coating apparatus until the pieces are uniformly coated with the 3 kg. of zinc sulphide (Menn) that is added. The grains are put in shallow metal pans, dried for 12 hours at 80-90°C and sifted to remove fines.

(Note made for last 4 years).

Catalyst 2730:

Use: Polymerisation of isobutylene to iso-octylene (used for relatively pure isobutylene).

Composition:	H ₃ PO ₄	35%
	Activated carbon	60%
	Water	5%

Preparation:

Eight kgs. of activated carbon, 4 litres of water and 5.12 kg. of phosphoric acid are run in the mixer until all the liquid is absorbed. The mass is then dried for 24 hours at 80-100°C.

Catalyst 3076:

Use: Hydrogenation of di-isobutylene to iso-octane. Also hydrogenation of Kogasin.

Composition:	NiS	2 moles
	WS ₂	1 mol

Preparation:

Fifty kgs. of nickel powder is dissolved in 250 litres of 60% HNO₃. The nickel is then precipitated by adding a solution containing 90 kg. of sodium carbonate (volume said not to be highly important). The precipitate is filtered, washed free from nitrates and dried. The dried material is ground and analysed. For each 25 kg. of nickel found by analysis, there is added to the metal precipitate in a kettle, 50 kg. of WO₃.H₂O in 25 litres of water. The contents are mixed continuously and evaporated to a thick paste. The mass is then put into shallow metal pans, dried for 12 hours, recovered from the pans, treated at 400°C with H₂S, ground, mixed with 1% of graphite and pelleted. These pellets are ground and reformed into 10 mm. pellets.

Quantity: 1 ton per month.

Sample : No. 9.

Catalyst 3390:

Use: Strong hydrogenation catalyst, for example, hydrogenation of phenol to cyclohexanol.

Composition:

Ni	3 mols
Al ₂ O ₃	1 mol

Preparation:

Nickel powder (70.6 kg) is dissolved in the stoichiometric amount of strong nitric acid in a small agitator; 21.56 kg. of sheet aluminium is dissolved in a second small agitator with caustic soda solution (stoichiometric quantity of NaOH, concentration not important). The small agitators are then filled up with water, and the two solutions simultaneously run into a large agitator which originally contains about 1 M³ of water. The filling operation takes about half an hour, but time is not critical. Caustic soda solution is added for precipitation. The precipitate is separated in a filter press and washed well with water. The filter cake is removed and dried for about 8 hours at 200°C in a drying oven, then ground and pressed into 5 mm. pellets.

Quantity: 1 ton per month.

Sample: No.70.

Catalyst 3510: (Not made since 1935/1936; replaced by catalyst 5058)

Use: Vapour phase hydrogenation of middle oil to gasoline.

Composition:

MoO ₃	1 mole
ZnO	1 mole
MgO	1 mole

Preparation:

The three materials are pasted with water, spread on a metal plate, cut into cubes and dried.

Catalyst 4577:

Use: Preparation of stearylamine from stearic acid and methylamine.

Composition:

NiS	1 mole
MoS ₂	1 mole

Preparation:

Two solutions are prepared separately:

(a) 45.36 kg. molybdic acid anhydride (MoO₃) in 100 litres of 50% caustic soda, and

(b) 91.67 kg. nickel nitrate (Ni(NO₃)₂·6H₂O) in 100 litres

of water. The solutions are run simultaneously and slowly (24 hours) into an agitator. The precipitate is removed and washed on a filter press. The filter cake is then dried at 100°C and is formed into tablets in a hydraulic press. The tablets are broken by hand into 4-6 mm granules and converted into the sulphide as described above under catalyst 3076.

(Note: There is a large loss of K_2O_3 due to incomplete precipitation).

Quantity: 100 kgs. per year.

Catalyst 4788:

Use: Hydrogenation of acetylene to ethylene (ethylene purification for lubricating oil manufacture).

Composition:

Cr_2O_3 approx. 95%
Ni " 5%

Preparation:

50 kg. of chromic acid anhydride (CrO_3) in 20 litres water are mixed with 9.24 kg. of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) in a stainless steel (V_2A) mixer. The slurry is evaporated with continuous stirring (by hand, with special spades) until no more nitrogen oxides are given off. The material is then heated in a muffle furnace for 12 hours at 300°C before breaking into 8-10 mm granules. The granules are reduced by heating for 12 hours at 400°C in a stream of hydrogen (high space velocity no recycle of H_2). The product is cooled under a stream of nitrogen and stored under nitrogen.

Sample: No. 20

Catalyst 4821:

Use: Polymerisation of isobutylene to iso-octylene. (For gases low in isobutylene concentration (20-30%)).

Composition:

Asbestos (serpentine, long fibre Canadian, unwashed; later Russian or Finnish). Approx. 25%
 P_2O_5 Approx. 75%
Water 4-5%

Preparation:

16 litres of phosphoric acid is heated at 260°C for 3 hours and then mixed with 8 kg. of asbestos. The mixture is hand-formed into 1-cm. cubes, which are dried for 60 hours at 150°C. The resulting catalyst is very hard.

Samples: Nos. 34 and 35.

Catalyst 5058:

Use: Vapour-phase hydrogenation of middle oil to gasoline.

Composition:

WS₂

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Preparation:

Tungstic acid (WO₃.H₂O) is dissolved in the mother liquor from a previous preparation by gassing with NH₃ at a temperature below 60°C. The solution is precipitated with H₂S, cooled, and the (NH₄)₂ WS₄ filtered under vacuum. The crystals are dried in a nitrogen stream on the filter at room temperature, and then converted to WS₂, NH₃ and H₂S by heating at 450°C in a stream of hydrogen in a scroll-type furnace. The resulting WS₂ is ground in a mill and pressed into 10 mm pellets under a nitrogen atmosphere.

Quantity: Made up to May 1, 1944 - 25 tons per month.

Samples: Nos. 30, 31, 32, and 33.

Catalyst 5436: (identical with Catalyst 5931 except that caustic is from a different source. No. 5939 uses the same Al₂O₃ as 5436 with only 5% MoO₃)

Use: Conversion of paraffinic gasoline into aromatic and isoparaffinic hydrocarbons - HF or DHD processes.

Composition:

Al ₂ O ₃	90%
MoO ₃	10%

Preparation:

Catalyst 5780 (see below) in cubical form is soaked once with ammonium molybdate solution, then dried. The solution is so prepared that the above composition of catalyst results.

Note: For 5436 or 5931, use about 20% MoO₃ in 25% NH₄ OH.
For 5939, dilute with water.

Quantity: 10 tons per month.

Sample: No. 44 - Catalyst 5931.

Catalyst 5623:

Use: Toluene synthesis from benzene and methanol.

Composition:

P ₂ O ₅	60%
ZnO	6%
Acid-treated clay (Montmorillonite type)	3%
Kieselguhr (Hanover No. 12OR fused with NaCl and washed with HCl)	25%
Water	Balance

(any ignited kieselguhr can be used).

Preparation:

44.1 kg. of kieselguhr, 9.0 kg. ZnO, 4.5 kg. clay and about

130 litres of 85% phosphoric acid are mixed in a kneader for about 40 minutes, placed on trays, dried for about 10 hours at 300°C, broken up and finally screened.

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Quantity: 150 tons per month.

Sample: No. 19

Catalyst 5633:

Use: Conversion of paraffinic hydrocarbons to aromatics and iso-paraffins (HF and DH Processes).

Composition:

Al ₂ O ₃	95%
MoO ₃	5%
Na ₂ O	up to 0.7%

Preparation:

Technical alumina is plasticized in a kneader with a little nitric acid and water, then extruded and rolled into balls. These are dried and later ignited at 450°C. The balls are then soaked in an ammonium molybdate solution, controlled so as to give 5% MoO₃ in the catalyst on subsequent drying.

Catalyst 5780: (also prepared at Ludwigshafen as No. 695A)

Use: Dehydration of alcohols.

Intermediate product in the preparation of other catalysts.

Composition:

Al₂O₃ Gamma-form.
Na₂O (usually 0.03-0.04%) - less than 0.1%
Water - 1%

Preparation:

400 kg. of technical alumina (65% Al₂O₃) is dissolved in 470 litres of 50% caustic soda at 110-120°C and diluted with 600 litres of water to 1.35 sp.gr. The solution is cooled and precipitated with nitric acid at a pH of 6.5, then filtered, washed, resuspended, brought back to a pH of 6.5 with NH₃, washed and dried at 100°C. (This intermediate product is known as 5780 Z-100). This product is ground, peptized with 1% nitric acid in a kneader, spread on a sheet, cut into cubes and dried stepwise at temperatures from 60 to 180°C (slow drying, 2-3 days). It is finally ignited at 450°C in air until nitrate-free.

Laboratory tests of catalyst activity are based on (1) absorption of propane, (2) dehydration of isobutyl alcohol at 350°C.

Quantity: 100 tons per month.

Catalyst 6067:

Use: Amine synthesis (very small amounts used). Catalyst 6069 is preferred.

Composition:

Al ₂ O ₃	50%
Kaolin	50%

Preparation:

See No. 6069.

Catalyst 6069:**Use:** Preparation of methylamine from methanol and ammonia.**Composition:**

Al ₂ O ₃	90%
Kaolin (flotation to remove excess SiO ₂ by a Siemens electro-osmosis machine)	10%

Preparation:

150 kg. catalyst 5780 Z 100 (ground) are mixed with about 140 litres of water and 225 cc. of 52% HNO₃ and 11 kg. of kaolin then added. The mixture is kneaded for 2 hours, spread on trays, cut into cubes, air dried for 24 hours, dried 12-15 hours at 120°C and finally ignited for 4-6 hours at 450°C.

Quantity: 10 tons per month.

Catalyst 6448:**Use:** Dehydrogenation of n-butane to butenes.**Composition:**

Al ₂ O ₃ (use ordinary alumina for iso-butane dehydrogenation)	90%
K ₂ O	2%
Cr ₂ O ₃	8%

Preparation:

22.5 kg. catalyst 5780 (finely ground), 2 kg. catalyst 5780 Z 100 (as peptizer-binder), 1.53 kg. KOH, 1.63 kg. CrO₃, 2.7 litres HNO₃ (62%) and about 7-9 litres water are mixed for about 40 minutes in a kneader, then formed into balls or cubes, dried at 150°C for about 16 hours, and finally ignited at 450°C for 4 hours.

Quantity: 100 tons per month.

Samples: Nos. 68 and 69.

Catalyst 6523**Use:** Hydrogenation of phenol to cyclohexanol.**Preparation:**

Catalyst No. 3390 is reduced for 8 hours at 300°C with hydrogen (in situ; high space velocity, 400-600 cu.m./hr/500 litres catalyst) and purged with nitrogen.

Catalyst 6853: (Arobin Catalyst)

Use: Conversion of high boiling aromatic middle oil into lower boiling aromatic hydrocarbons. Conversion of higher alkyl benzenes to lower homologues.

Composition:

Catalyst 7187 plus 1% MoO_3

Preparation:

Catalyst 7187 is soaked in dilute ammonium molybdate solution so made that the product after drying contains 1% of MoO_3 .

Sample: No. 11.

Catalyst 7187:

Use: Catalytic cracking (atmospheric pressure conversion of middle oils into isoparaffinic gasoline.)

Composition:

SiO_2	85.1%
Al_2O_3	14.9%

Preparation:

Kieselguhr (with 70% SiO_2) and activated alumina (70% Al_2O_3 , catalyst 5780 Z 100) are mixed to a stiff paste in a kneader with a little water and the addition of a small amount of nitric acid (sufficient stoichiometrically to convert 1% of the Al_2O_3 to $\text{Al}(\text{NO}_3)_3$). This mass is allowed to stand 24 hours at 60-70°C to "ripen". It is then further kneaded, extruded and formed into 6 mm. balls, dried at 100°C and ignited at 400° until nitrate-free. There is no humidity control during the drying.

Quantity: Planned to make 100 tons per month.

Samples: Nos. 36 and 37.

Catalyst 10927:

Use: Liquid-phase hydrogenation of tars.

Composition: 5% Fe on Winkler generator coke.

Preparation:

Winkler generator fines are soaked with iron sulphate solution and then with an equivalent amount of osustic soda solution, the concentrations being adjusted so that the final dried product contains 5% of Fe.

Ammonia-Catalyst: (No number).

Use: Ammonia synthesis from hydrogen and nitrogen.

Synal catalyst (manufacture of alcohols from CO and H_2)

Composition:

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Fe_2O_3	75%
FeO	20%
Al_2O_3	1.9%
K_2O	1.1%

Preparation:

Five tons of pig iron is melted by a direct blast of oxygen. A cake containing a mixture of 200 kg. of crude alumina, 50 kg. of aluminium nitrate and 25 kg. of concentrated nitric acid is introduced into the molten iron with continued blowing with O_2 . The melt is allowed to cool and is broken up and screened to the desired size. Oxygen consumption: 7000 cubic metres.

Sample: No.23 - Synol Catalyst.