has been used.

Weigh 2.0-2.5 ± 0.001 g of the detergent and dissolve (warming is usually necessary) in ca. 250 ml of water. Cool and dilute to one liter. Remove a 2 ml aliquot to a test tube and add 0.1 ml of the phenol solution. Mix well, then add 6 ml of concentrated sulfuric acid solution. Again mix, then allow the solution to stand for 10 min. Measure the absorbance of the sample solution versus a blank (made by using 2 ml of water) at 490 mμ. The CMC level in the sample is obtained from a standard curve plotting absorbance versus grams of CMC. The optimum range for CMC in the test solution was found to lie between 6×10^{-5} and 16×10^{-5} g.

Table I shows data obtained by replicate determinations on the same sample. Table II shows recoveries obtained by adding known amounts of CMC to a typical household detergent product. This particular product handled the least satisfactorily of any that we tested by this procedure and also had the lowest CMC content.

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[Received June 24, 1971]

Selective Hydrogenation of Soybean Oil. VI. Copper-on-Silica Gel Catalysts

ABSTRACT

The preparation of copper-on-silica gel catalysts containing 15% and 20% copper is described. These catalysts can be reused three times without appreciable loss of activity. Their activity compares favorably with the highly active 5% copper-on-silica gel catalyst previously reported. Higher copper catalysts are somewhat less selective for the reduction of linolenate in soybean oil than 5% copper-on-silica gel, but these copper catalysts have greater activity, better reuse characteristics, and selectivity comparable to commercial copper-chromite catalysts.

It has been well established that copper catalysts are the most selective for the reduction of linolenate in soybean oil. The activity of copper catalysts is often influenced by the choice of support and by the method of preparation (1,2). Although copper chemisorbed on silica gel was active and selective (2), the amount chemisorbed was only 5%, so that increasing this percentage should have economic advantages. Catalysts containing 15% and 20% copper have now been prepared. Furthermore these higher copper-on-silica gel catalysts were also prepared from copper sulfate, which is less expensive than copper nitrate previously used (2).

Enough 30% ammonium hydroxide (1.2 ml) was added to 25 ml of an aqueous solution containing 1 g of copper nitrate trihydrate to redissolve the copper hydroxide precipitate. About 2.5 g of silica gel (MS-GEL: microspheroidal particles with average size 54 to 65 μ, surface area = 600 sq M/g, pore volume = 1 cc/g, average pore diameter = 67 Å, supplied by Davison Chemical Division, W.R. Grace & Co.) was added to the copper-complex solution. Part of the blue copper ions was adsorbed on the surface of the gel instantly. The remainder of the copper was precipitated on the gel when the volume was made (while swirling the flask) up to 200 ml with distilled water. After the colorless supernatant was poured off, another batch of copper complex solution (1 g copper nitrate + 1.2 ml ammonium hydroxide in 25 ml) was added. While swirling the flask the volume was made up to 400 ml with

TABLE I

Hydrogenation of Soybean Oil with Copper-on-Silica Gel Catalysts[a]

	Catalyst	Reaction time, min	IV drop	Linolenate (alkali isomerization), %	*Trans*, %	Selectivity (K_{Le}/K_{Lo})
A.	15% Copper-on-silica gel					
	(copper sulfate)	14	13	1.1	9	11
	Reuse 1	14	14	1.3	9	9
	Reuse 2	15	14	0.9	8	11
	Reuse 3	18	14	1.4	8	9
B.	15% Copper-on-silica gel					
	(copper nitrate)	15.5	13	1.0	9	12
	Reuse 1	11.5	13	1.4	8	10
	Reuse 2	13	13	1.4	10	9
	Reuse 3	13	14	1.4	9	9
C.	20% Copper-on-silica gel					
	(copper sulfate)	17	12	1.2	9	11
	Reuse 1	10	13	1.5	8	9
	Reuse 2	14	13	1.7	8	8
	Reuse 3	16	13	1.7	8	8

[a] Total of 300 ml oil at 170 C and 30 psig; catalyst 0.3 g copper oxide.

distilled water. The copper-on-silica gel catalyst (B, Table I) was separated from the pale blue supernatant by filtration and dried at 110 C to yield 3.04 g. Analysis by atomic absorption (3) showed that this catalyst contained 15% copper. A copper-on-silica gel catalyst was similarly prepared with copper sulfate (Catalyst A, Table I) except the catalyst was thoroughly washed with distilled water to ensure complete removal of sulfate ions.

A 20% copper-on-silica gel catalyst (C, Table I) was prepared as follows: Enough 30% ammonium hydroxide (3.6 ml) was added to 3 g copper sulfate pentahydrate in 15 ml water to redissolve the copper hydroxide. About 2.5 g of silica gel was added. The volume was then gradually made up while swirling the flask to 1 liter with distilled water. Catalyst C was separated from the blue supernatant by filtration, washed thoroughly with distilled water and dried at 110 C to yield 3.3 g. Analysis by atomic absorption (3) indicated that Catalyst C contained 20% copper.

After these catalysts were calcined at 350 C for 2 hr, they were evaluated for the selective hydrogenation of soybean oil (Table I). Hydrogenation procedure and methods of analysis were the same as described previously (1,2). All catalysts at a concentration of 0.1% as copper oxide are much more active than 0.5% commercial copper-chromite catalysts (4) under similar conditions of temperature and pressure. The activity and reuse properties of these catalysts compare favorably with the chemisorbed catalyst (2). The activity of catalysts prepared from copper sulfate was somewhat diminished during third reuse. No significant differences in the amount of *trans* isomers were found. In general the selectivity ratios obtained with these catalysts are lower than those obtained with the previously reported catalyst (2); after an IV drop of 13-14 units the amount of linolenate in the product was 0.9-1.7% with the present catalysts while it was below 1% with chemisorbed catalyst (2). Selectivity for the reduction of linolenate decreased during reuse possibly due to poisoning of the catalyst. The selectivity ratios of 8-12 achieved with the present catalysts compare favorably with those obtained with commercial copper-chromite catalysts (4).

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ACKNOWLEDGMENT

Atomic absorption analyses were performed by G. List.

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[Received August 13, 1971]

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Trace Phosphate Analysis in Silicate-Containing Detergents

ABSTRACT

A colorimetric method has been developed, suitable for determining low levels (10-200 ppm) of phosphorous in detergent formulations containing large amounts of silicate. Samples are ashed to remove organic matter, hydrolyzed to convert all phosphates to ortho-phosphate, and centrifuged to remove any SiO_2, carbon or other solids. Phosphomolybdic acid is formed and extracted into an organic solvent, where it is reduced to the classic molybdenum blue color by stannous chloride. The procedure yields accurate and reproducible results, with reliability at the 25 ppm phosphorous level of ±3 ppm.

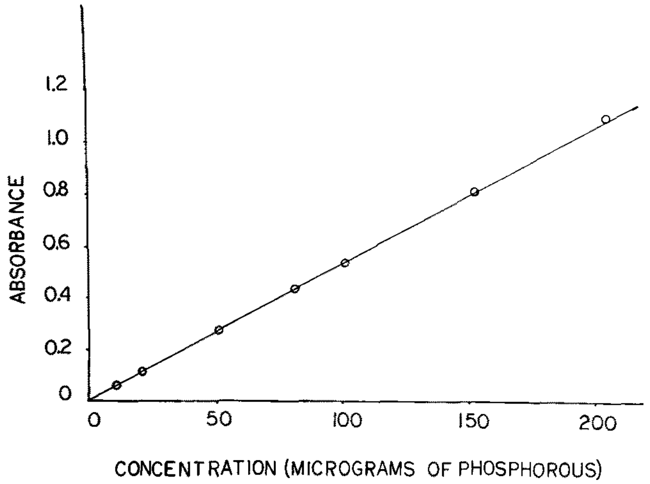

FIG. 1. Calibration curve; phosphorous concentration vs. absorbance.

Interference problems, inherent in analyzing current detergent formulations by existing standard methods, have been pinpointed (1,2). We have developed a simple colorimetric method capable of analyzing silicate-containing detergents for phosphate, at the 10-200 ppm level of phosphorous. The method is based, after ashing and removal of silicate, on the formation of phosphomolybdic acid, which is extracted into benzene-isobutanol and reduced to molybdenum blue by stannous chloride. The method as written calls for sample sizes of 1 g. If lower limits of phosphate detection are required, larger sample sizes may be used. The procedure is as follows: A 1.00 g sample is placed in a porcelain crucible and ashed overnight in a muffle furnace at 450-650 C. If any carbon remains, it will be removed in a later step. The cooled residue is transferred, with the aid of 40 ml of water and 8 ml of 8 N sulfuric acid, to a 250 ml beaker, and heated on a steam bath for 1 hr. Beakers are not covered. The final volume, after heating, will be about 20 ml. The hydrolyzed sample is transferred to a 40 ml centrifuge tube using several small portions of water to assist in the transfer. The sample is centrifuged at about 2000 rpm for ten min, or until all solids settle to the bottom of the tube. This centrifugation effectively removes silicate, now present as SiO_2, and any carbon which may have remained from the ashing. The clear solution is carefully decanted into a 100 ml extraction cylinder. It is not necessary to wash the precipitate. The solution is diluted with water to 48 ml, and 50 ml of benzene-isobutanol 1:1, followed by 8 ml of 10% ammonium molybdate solution, is added. The stoppered cylinder is shaken vigorously for a minimum of 15 sec to extract the