Test Procedure for Evaluation of Catalysts for Nitrile Reduction

F.E. Friedli and **R.M. Gilbert**
Sherex Chemical Company, Dublin, Ohio

A procedure was developed that examines the effectiveness of nickel catalysts for the hydrogenation of fatty nitriles to amines. Rates of reaction, selectivity, and olefinic reduction were the parameters studied. The procedure can be used for new catalyst screening and is ideally suited for quality assurance testing of production catalysts. It involves the reduction of nitriles to amines at 410°F (210°C) and 500 psig using a .2% Ni loading level. A mixture of primary and secondary amines is obtained which is characteristic of the catalyst's selectivity. Both sponge and supported nickel catalysts were tested using tallow nitriles as the feedstock.

Catalytic hydrogenation of nitriles to amines is the primary mode of preparation of many cationic surfactants. The rate of reaction and selectivity of a particular catalyst are critical parameters in determining whether a catalyst will economically produce an acceptable product. Surprisingly, few test procedures for catalysts have been published. Methods exist (1) for testing for surface area, porosity, and other parameters needed to physically characterize a catalyst, but accepted protocols for evaluating a catalyst for nitrile reduction have not been defined. The AOCS activity test of oil hardening catalysts (2) and Papers by Alcorn (3) and Chaudhari (4) are examples of evaluations of hydrogenation catalysts.

Oleochemical companies that makes amines have methods to examine catalysts for nitrile reduction. Since these usually mimic a production process, they are kept as trade secrets. Catalyst manufacturers control the quality of their materials by testing them using their own nitrile reduction procedures or, more often, by an unrelated hydrogenation. Reductions of nitrobenzene, sorbitol, or soybean oil have been used as quality assurance tests on nickel catalysts regardless of the industry the products serve.

A method of catalyst evaluation for batch reduction of nitriles to amines is needed and is presented here.

EXPERIMENTAL

The nitriles used for the study were distilled tallow nitriles from standard production at Sherex. A sponge nickel and three supported nickel catalysts were evaluated by the procedure. The catalysts used were commercial materials from Grace, Hoechst, United Catalyst, and Englehard (Harshaw), provided as free samples.

All reductions were carried out using the outlined procedure (Table 1) or only slight variations. The temperature rise was controlled by addition of small amounts of water through the cooling coils of the reactor. The feedstock nitrile was analyzed for acid value (5) and % amide (6-8). Product analyses were by standard AOCS tests (9) for Total Amine Value (TAV), Secondary & Tertiary Amine Value (II + III AV), Tertiary Amine Value (III AV), and Iodine Value (IV). Conversion was checked by infrared (IR) analysis on a Perkin-Elmer 1420 spectrometer; the characteristic nitrile and imine absorbances at 2200 cm-1 and 1650 cm-1, respectively were measured.

From the amine values using equations 1, 2, and 3, % primary, % secondary, and % tertiary amine were calculated.

$$\%\ \text{primary} = \frac{(\text{TAV}) - (\text{II} + \text{III AV})}{217} \qquad (1)$$

$$\%\ \text{secondary} = \frac{(\text{II} + \text{III AV}) - (\text{III AV})}{113} \qquad (2)$$

$$\%\ \text{tertiary} = \frac{\text{III AV}}{75} \qquad (3)$$

TABLE 1

Proposed Method for Catalyst Evaluation for Batch Reduction of Nitriles to Amines

Apparatus:

Parr SS autoclave (2-L, cooling coil, agitator, temperature controller, and pressure gauge).

Reagents:

500 g distilled soft tallow nitrile	(Acid Value = .1 max., *optional* % amide = .3 max.)
about 2 g nickel catalyst	(sufficient to provide 1.00 g nickel metal)

Operating Steps:

1. Charge the nitrile and catalyst to reactor, close, and start the agitator.
2. Pull vacuum (25 mm Hg or less) on the reactor and heat-up to 400°F.
3. At 400 - 405°F, break the vacuum with hydrogen.
4. Pressure to 500 psig and maintain pressure between 400 - 500 psig and control the exotherm to maintain 410°F (210°C). ± 5°F.
5. When hydrogen uptake ceases, sample and analyze for amine and iodine values.
6. Thirty minutes later, sample for amine and iodine values and stop the hydrogenation.

RESULTS AND DISCUSSION

Two types of products are desired from the hydrogenation of long-chain nitriles — primary amines and dialkyl secondary amines (equations 4 & 5). The former are useful as mining flotation reagents, asphalt emulsifiers, corrosion inhibitors, and as chemical intermediates to other surfactants. The latter are usually further derivatized to quaternary salts for use in organoclay complexes, sugar refining, personal care, and laundry products. Catalyst selectivity to give the desired amine is most important. Other significant parameters are the rate of conversion to product and the rate of decrease in IV.

$$\mathrm{RCN} \xrightarrow[\text{cat.}]{2H_2} \mathrm{R\text{-}CH_2\,NH_2} \qquad (4)$$

$$2\,\mathrm{RCN} \xrightarrow[\text{cat.}]{4H_2} \mathrm{(R\text{-}CH_2)_2NH + NH_3} \qquad (5)$$

The chosen procedure (see Table 1) involved a "deadheaded" reactor with a partial pressure of hydrogen only. By design, this method gave a mixture of primary and secondary amines and ammonia which was consistent from batch to batch for a catalyst and indicative of its inherent selectivity. The strongly exothermic nature of the nitrile hydrogenation posed a temperature control problem that was the largest source of error in batch consistency.

Table 2 shows data obtained at various conditions. A balance between reasonable reaction rate, correct product distribution, and controllable temperature is necessary. Reductions at 500-600 psig and 410°F were too fast to consistently control the temperature to + 5°F but at 400 - 500 psig they were slower and more manageable. Incomplete conversion, as measured by both amine values (88% after 300 min) and IR, occurred at 200 psig, probably due to build up of ammonia concentration. Since our goal was a 1 to 2 hour test that produced a significant and characteristic level of secondary amines, the rate at 330°F was

TABLE 2

Effect of Pressure & Temperature (Catalyst — sponge nickel)

TAV	II+ IIIAV	III AV	Primary Amine %	Secondary Amine %	Tertiary Amine %	IV	Time (min)	Remarks
Conditions: 410°F		500-600 psig						
192	28	2.1	75	23	2	nd*	40	
191	30	2.0	74	24	2	nd	60	
189	35	3.2	69	29	3	17	90	no H_2 uptake
186	36	2.4	68	30	3	15	120	final
Conditions: 410°F		400-500 psig						
88	6	nd	38	5	nd	nd	20	
122	9	nd	52	8	nd	nd	30	
161	8	nd	71	8	nd	nd	40	
187	14	nd	80	13	nd	nd	50	uptake slower
190	21	nd	78	18	nd	nd	60	
188	34	1.1	71	28	1	30	90	no H_2 uptake
187	34	1.2	71	28	1	25	120	final
Conditions: 380°F		400-500 psig						
125	nd	nd	58	nd	nd	nd	20	
162	nd	nd	75	nd	nd	nd	30	
182	6.1	1.5	81	4	1	nd	40	
197	11.3	1.2	86	9	1	21	60	
197	22	1.1	80	19	1	12	100	final
Conditions: 380°F		200 psig						
90	nd	nd	41	nd	nd	nd	60	
136	nd	nd	63	nd	nd	nd	120	
163	nd	nd	75	nd	nd	nd	180	
176	nd	1.2	81	nd	1	nd	240	
182	7	1.1	81	6	1	18	300	final
Conditions: 330°F		400-500 psig						
69	nd	nd	32	nd	nd	nd	20	
119	nd	nd	55	nd	nd	nd	40	
156	nd	nd	72	nd	nd	nd	60	
181	nd	1.0	83	nd	1	nd	80	
193	13	1.1	83	11	1	37	110	final

*nd = not determined.

TABLE 3

Results of Reductions Comparing the Different Catalysts

Catalyst Used	TAV	II+ IIIAV	III AV	Primary Amine %	Secondary Amine %	Tertiary Amine %	IV	Time (min)	Remarks
Conditions:	410°F	400-500 psig							
Sponge	188	34	1.1	71	28	1	30	90	no H_2 uptake
Nickel	187	34	1.2	71	28	1	25	120	final
Supported	148	79	5.6	31	63	6	24	30	no H_2 uptake
Catalyst A	143	80	5.2	29	65	6	24	60	final
Supported	160	66	1.1	43	56	1	23	30	no H_2 uptake
Catalyst B	150	78	2.1	33	65	2	22	60	final
Supported	174	50	1.1	57	42	1	28	20	no H_2 uptake
Catalyst C	158	64	1.2	43	56	1	13	50	final

deemed to be too slow because it produced only 11% secondary amines in 110 min. Reaction at 410°F was chosen as the optimum.

The heat-up from room temperature to 410°F takes 30-60 minutes. During this time, the reactor can be under hydrogen pressure, nitrogen pressure, or vacuum. Using hydrogen keeps the catalyst active but the exact start of the reaction is not controllable. The presence of nitrogen may alter the activity of the catalyst and/or allow dehydrogenation-type side reactions, and requires the reactor to be vented just prior to pressuring with hydrogen. Keeping it under vacuum also runs the risk of changing the activity of the catalyst and promoting side reactions, but the start of the reaction is easily defined. Considering all of these parameters, we decided to heat up under vacuum and break this with hydrogen at reaction temperature. Previous work in our laboratory has shown no adverse effects from this approach.

The proposed procedure takes a sample when the hydrogen uptake has ceased or is very slow. No residual nitrile or Imine was observed at this time. Then the reaction is continued another thirty minutes, at which time a final sample is taken. The additional thirty minutes is to allow time for an equilibrium mixture of amines to be established and determine if there has been further reduction in IV.

Table 3 shows the results of catalyst comparisons using the proposed procedure. Sponge nickel is known to be a good catalyst for preparation of primary amines (10). It gave the highest Total Amine Value and the lowest Secondary and Tertiary Amine Values or about a 71/28 ratio of primary/secondary amines. Supported Catalyst A had the highest rate of preparing secondary amines, while Supported Catalyst B produced less tertiary amines. Supported Catalyst C caused the highest rate of hydrogen uptake and seemed best for IV reduction.

Ideally, a catalyst good for primary amines will have a high ratio of primary/secondary amines, retain the IV (many primaries sold are unsaturated), and have fast conversion. Sponge nickel is the best choice for primaries. A good secondary amine catalyst will have a high ratio of secondary/primary, harden the IV (most secondary amines are saturated), give a low percentage of tertiary amine, and also have fast conversion. the data supports Catalyst B as the best for secondaries. Repeat experiments gave amine and iodine values within 4 units of each other.

Handling of the feedstock nitrile is another concern when comparing a new catalyst to a standard catalyst. Tallow nitrile is not a pure substance. It contains several chain lengths and some unsaturation. Small amounts of fatty acid and amide are also present. Since the nitrile was derived from a natural fat, trace amounts of phospholipids, beta-carotenes, and other natural substances can occur. Each lot of nitrile is thus somewhat unique. It is also not totally stable, being subject to air oxidation.

For exploratory catalyst evaluation, our laboratory prefers to always run a standard catalyst against a new catalyst using a fresh batch of nitrile as the feedstock. For quality assurance of manufactured catalyst, it is recommended that only the new catalyst be run using a lot of nitrile stored in a freezer in batch size jars. This frozen nitrile is probably good for over a year.

The proposed procedure is simple and can be finished in 1 to 3 hours. It is ideal for quality assurance testing since each batch of catalyst should give consistent ratios of amines' unsaturation levels. It is also a quick initial test of a new catalyst. Based upon the data generated in the initial evaluation, a prospective catalyst can then be tried with the appropriate proprietary amine procedure.

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