aldehyde peak. In that case, 19.4% of Δ_{12} (on the basis of A and AE) was found, which made the agreement even better.

We always obtained good agreement between the experimental and real composition of mixtures of positional isomers (2). Table III shows some experimental data on Δ_6, Δ_9, and Δ_{12} isomers. In contrast with the findings of Lanser, et al., we did not observe a shortage of degradation products with a short chain for the positional isomers mentioned. K'', derived from well resolved and reliable peaks, was independent of the position of the double bond, but it truly depended on GLC conditions, for unknown reasons (2). When, for instance, a column was replaced by another with the same immobile phase and support, the K'' values changed under the same operational conditions. We also observed a change in K'' values during the lifetime of a column. It may be that the differences between the FID and GDB data reported by Lanser, et al., also were due to differences in GLC conditions and types of column.

Our conclusion is that for a good evaluation of differences between these detection systems on the basis of the degradation products mentioned, application of the same GLC conditions/columns may play a major role.

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TABLE III

Measured Peak Areas of Aldehydes (A), Aldehydic Esters (AE), and Their Molar Ratios (K'') After Correction for Ionizable Carbon Atoms

Sample		Double bond position	Measured peak areas		K''
			A	AE	
1[a]	cis	6	1571	589	1.21
	cis	9	1158	982	1.18
2[b]	cis	9	250	231	1.08
	cis	12	117	239	1.09
	trans	9	76	67	1.13
	trans	12	46	96	1.07
3[b]	cis	9	116	103	1.13
	cis	12	54	108	1.11
	trans	9	255	237	1.08
	trans	12	152	296	1.13

[a]Sample 1 is a 50:50 mixture of methyl oleate and methyl petroselinate.

[b]Isolated fractions from partially hydrogenated methyl linoleate.

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Net Hydrogenation Activity: A Rational Index

ABSTRACT

In a fixed regime of temperature, agitation, and hydrogen pressure, regression analysis yields a rational technique for indexing the activity of hydrogenation catalysts. Refractive index measurements as a function of time were analyzed to produce a family of rate constants. These, in turn, were analyzed via polynomial regression to yield a quantitative activity index.

INTRODUCTION

In a nickel hydrogenation catalyst development program, the quickest methods of activity comparison, dead end, fixed time hydrogenation, produced highly scattered data despite relative stability of raw stock, in this case refined soybean oil. A quantitative method for comparing the activities of nonselectively used catalysts was required. The character of the refractive index versus log time relationship suggested that a regression analysis correlation would yield an efficient means for quantifying activities.

EXPERIMENTAL PROCEDURES

All hydrogenations were conducted in a Parr Equipment Company 2-liter converter with internal cooling loop and catalyst dropping device. All conversions were done at 40 psig hydrogen pressure using 640 rpm agitation and temperature stabilization at 210 ± 2 C. Vacuum purge was used throughout the heating process, and hydrogen at the reaction pressure was purged through the charge for 1-2 min at an intermediate temperature (∿110 C). Vacuum purging was re-established, and conversion began 5 min after stabilization of the temperature at 210 C.

A specific catalyst was chosen to be a standard of comparison. In this case, a commercially available material, Girdler G-53, was selected. Hydrogenation experiments were done, at least in duplicate, at a series of nickel concentrations varying from 0.0104% Ni to ∿0.176% Ni. Refractive index [N_D(70 C)] measurements were made as a function of hydrogenation time. This hydrogenation regime yielded an extensive region of linearity when N_D(70 C) was plotted as a function of log time. Typical data for 3 different hydrogenation reactions are shown in Figure 1. The linear regions of each are indicated. Conversions initially were measured by iodine value methods (1). A large number of these analyses, ranging in iodine value (IV) from

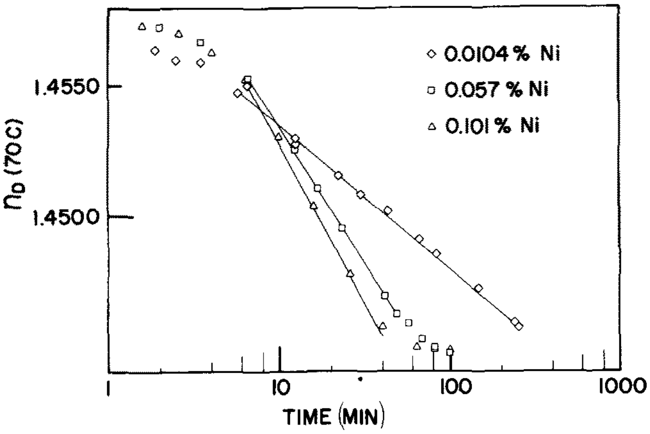

FIG. 1. Typical hydrogenation data for standard catalyst. All experiments were conducted at hydrogen pressure = 40 psig, agitation 640 rpm, and temperature = 210 ± 2 C.

TABLE I

Nickel Concentrations, Slopes and Linearity Values

Ni (%)	Slope X10^3	F ($\leqslant$0.005)	F critical	Sum of Squares
0.0104	-2.353	5900	11.75	0.129×10^{-3}
0.0174	-2.945	3100	12.83	0.171×10^{-3}
0.0577	-4.546	9600	31.33	0.593×10^{-4}
0.101	-5.253	1500	55.55	0.592×10^{-4}
0.172	-6.077	440	98.50	0.459×10^{-4}

0.2 to 137 were subjected to regression analysis yielding a correlation of excellent linearity, (F_{crit} (0.005) $\sim$9.2; F(0.005) = 4800; sum of squares = 53,760). Careful plotting of IVs as a function of refractive index at 70 C showed a slight curvature, but the line was everywhere well-behaved and monotonic, and this curvature in no way vitiated the usefulness of the developed activity correlation. Mattil (2) has pointed out that refractive index measurements can indicate the IV to within 1-2 units or less. Therefore, for the purposes of this investigation, we relied on refractive index measurements to follow the degree of conversion.

RESULTS

All hydrogenation data from experiments with G-53 were plotted on semilog paper and the linear part of each curve was subjected to polynomial regression analysis. In every case, linearity was excellent, as indicated in Table I. The regressions yielded a family of pseudo-rate equations of the form

$$N_D(70\ C) = m\ \ln t + N_D^0(70\ C) \qquad (I)$$

where N_D^0 is the zero-time intercept of the linear portion of the hydrogenation curve, and m is an overall rate constant that corresponds to a given Ni concentration.

The percent Ni for the body of data then was plotted as a function of the rate constants in Equation I. A logarithmic correlation appeared, and log percent Ni versus m then was subjected to a polynomial regression analysis, yielding a straight line with the formula

$$\log(\%\mathrm{Ni}) = -755.1\ m - 6.3031 \qquad (II)$$

and possessing excellent linearity (F value$\sim$2600). A semilog plot of percent Ni versus -10^3m was linear and divided the plane into 2 regions; results for catalysts with superior activity and those whose activities were inferior to the standard.

For this specific comparative method, the index plot is shown in Figure 2. The index has been used on development catalysts and on other commercially available hydrogenation catalysts. Their placement on the indexing plane is indicated in Figure 2.

DISCUSSION

For developmental purposes, the correlation cited has been quite useful. It permits strict numerical quantification of the net activity of experimentally manufactured hydrogenation catalysts as they are developed, and has allowed us to make appropriate pilot plant processing decisions.

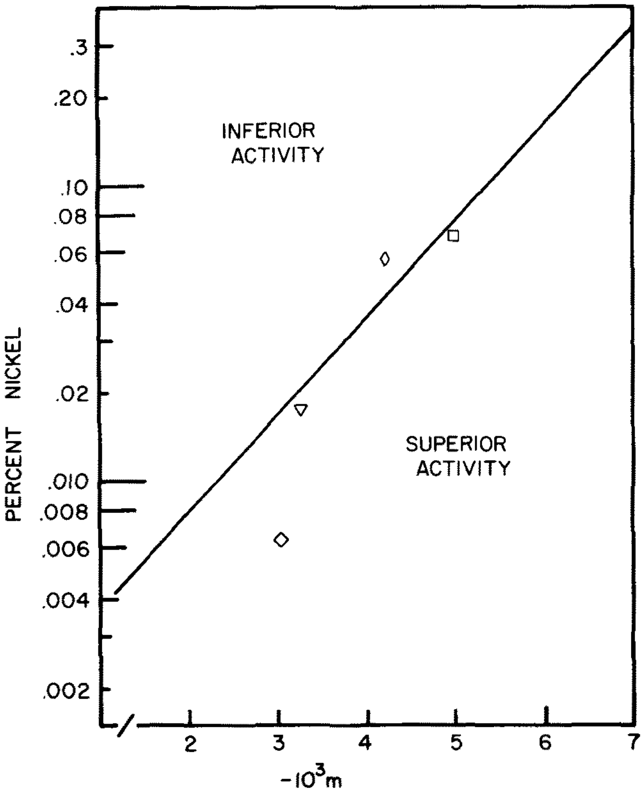

FIG. 2. Diagram of activity index. This line is the result of regression analyses of activity testing. □, ◇, and ▽ represent experimentally prepared catalysts; ◇ is a commercial catalyst for selective hydrogenation. All experiments carried out at 40 spig H_2 pressure and 640 rpm agitation at 210 C.

Orthogonal distance from the line (Fig. 2) indicates the divergence from the selected activity standard. Two experimental catalysts indicated in Figure 2 were reduced at differing hydrogen stoichiometries. The more active catalyst was reduced at a hydrogen stoichiometry more than twice that of the other catalyst. Both reductions were done at the same temperature.

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