Metallic Phases and Activities of Nickel-Tin-Silica Catalysts

Dehydrogenation of Cyclohexanone, Cyclohexanol, and Cyclohexane

HAROLD E. SWIFT AND JOHN E. BOZIK

From the Process Research Division, Gulf Research & Development Company,
Pittsburgh, Pennsylvania 15230

Addition of tin to a nickel-silica catalyst greatly promotes the activity and gives a longer catalyst life for the dehydrogenation of cyclohexanone and/or cyclohexanol to phenol. Outstanding results are obtained with a catalyst having a nickel-to-tin molar ratio of 2.5:1. Reduction of the nickel-to-tin molar ratio to 0.9:1 gives very little dehydrogenation of cyclohexanone; however, a new reaction takes place, which is the aldolization of cyclohexanone to 2-(1-cyclohexenyl)cyclohexanone. An explanation of the promoting effect of tin and the change in reaction selectivity with nickel-to-tin ratio is given.

An investigation of the reduced nickel-tin-silica catalysts by X-ray diffraction has revealed the presence of a supported nickel-tin alloy phase.

I. INTRODUCTION

With supported metal catalysts, the majority of the work reported in the journal literature has been carried out on single metal systems rather than bimetallic or multimetallic catalysts. This is understandable because of the complexity involved even with single metal systems. For example, a metal can exist in different physical and chemical forms (1–9) depending on the support.

We have been examining the state of metallic phases in reduced bimetallic catalysts. In an earlier paper, (10) it was reported that a reduced impregnated nickel-copper silica-alumina catalyst contained nickel-copper alloy phases, as determined by X-ray diffraction. It was also found that the combination of the metals on a support can have a tremendous effect on the reaction selectivity.

This area of research has been extended to the nickel-tin silica system where it has been found that hydrogen reduction results in the formation of nickel-tin alloy phases on the silica support. This catalyst system has been used to study the dehydrogenation of cyclohexanone, cyclohexanol, and cyclohexane. Complete changes in reaction selectivity have been observed as catalysts with various nickel–tin molar ratios were used.

II. EXPERIMENTAL

Five catalysts were prepared by impregnating Davison Grade 70 silica gel (10–20 mesh) with an aqueous solution or dispersion of the metal salts to the point of incipient wetness. The reagents used were Fisher Certified nickel nitrate hexahydrate and Mallinkrodt stannous chloride dihydrate. Dispersions were obtained because of the precipitation of $Sn(OH)Cl$ upon adding stannous chloride to water. The compositions of the catalysts are given in Table 1.

Catalysts 2, 3, and 4 were prepared by keeping the nickel concentration constant and varying the tin concentration. All catalysts were dried for 16 hr at 110°C and calcined in air at 500°C for 20 hr. The surface areas of the calcined catalysts were obtained by the BET method using a nitrogen adsorbate.

TABLE 1

COMPOSITION OF NICKEL-TIN-SILICA CATALYSTS

Catalyst	Ni (wt %)	Sn (wt %)	Ni:Sn molar ratio[a]	BET area (m²/g)
1	12	0	∝	246.7
2	8.3	3.7	4.5	237.7
3	8.7	7.1	2.5	242.7
4	6.6	14.1	0.9	209.4
5	0	10	0	253.9
SiO₂	—	—	—	261.4

[a] Determined by X-ray fluorescence.

The X-ray diffraction patterns of the reduced catalysts were obtained with a Norelco diffractometer using nickel-filtered Cu $K\alpha$ radiation. A gas proportional counter detector was used in conjunction with a pulse-height analyzer, the window of which was set to discriminate somewhat against fluorescent Ni radiation, and the diffraction patterns were obtained as strip chart recordings of the output of a counting rate meter. Film patterns were prepared by placing the catalysts in thin-walled capillary glass tubes. The diffraction films were obtained using Cu $K\alpha$ radiation, a Ni filter, and a camera having a radius of 57.3 mm. The sample was exposed to radiation for approximately 4 hr.

Metallic nickel was removed from the nickel-silica and nickel-tin-silica catalysts by the Mond process. The samples were reduced with hydrogen for 4 hr at 500°C; and carbon monoxide (Matheson CP), which had been dried by passing it through a molecular sieve column, was passed over the catalyst at 80°C and a space velocity of 300 hr⁻¹ for 6 hr. The volatile nickel carbonyl which was formed was swept out of the sample tube and decomposed to metallic nickel and carbon monoxide at 250°C in another tube. The amount of nickel removed from the catalyst was determined by weighing the sample tube in which the nickel had deposited.

The catalysts were tested in an atmospheric pressure, bench-scale reactor. The reactor was constructed of 20-mm OD Pyrex glass tubing 50 cm long, with a porous glass disc positioned midway in the reactor as a support for the catalyst bed. The catalyst was diluted with 4-mm diameter perforated glass beads obtained from Fisher Scientific Company. The temperature of the furnace was controlled with a Variac in conjunction with a Foxboro Model 4036 Potentiometer Controller. The parts of the reactor which were out of the furnace were wrapped with heating tape and were kept at a temperature sufficient to keep the products in the vapor phase until they reached the collection system. Purified cyclohexanone and technical cyclohexanol were obtained from the Fisher Scientific Company, and cyclohexane was Phillips Pure Grade. All were chromatographed before using to detect any impurities. The reactant was introduced into the system by means of a constant-drive syringe infusion pump (Harvard Apparatus Company Model 600-000) and was vaporized in a flash zone before being carried over the catalyst in a stream of hydrogen. The hydrogen carrier flow was maintained at 40 cc/min. Condensable components in the reactor effluent were trapped out in a spiral trap immersed in ice water.

Reaction and catalyst pretreatment conditions are given in Table 2.

Quantitative analysis of the products was made with an F&M Model 700 programmed-temperature gas chromatograph equipped with a disc integrator and utilizing a ¼-inch OD stainless steel column, 10 ft long, packed with 20% Carbowax 20M on Fluoropak. For the dehydrogenation runs, the temperature was programmed from 70° to 200°C at a rate of 10°C/min. For the condensation experiments, the column was operated isothermally at 200°C in order to shorten the retention time of heavier condensation products.

III. RESULTS

Of the reactions studied, the dehydrogenation of cyclohexanone and cyclohexanol to phenol were of the most interest. These reactions are well known and have been investigated by several workers in the past (11–17). The catalyst variation studies reported in this paper were carried out under conditions to obtain high yields

TABLE 2
REACTION CONDITIONS

| | Dehydrogenation | | Condensation |
	Cyclohexanone and cyclohexanol	Cyclohexane	Cyclohexanone
Catalyst reduction temp. (°C)	375°	375°	375°
Catalyst reduction time (hr)	3	3	3
Reaction temp. (°C)	375	300	250
Reaction time (hr)	1–7	1	1–7
LHSV (hr⁻¹)	0.5–2.5	2.3	0.5–2.5
Carrier flow (H₂) (cc/min)	40	32	40
Catalyst weight (g)	2	1	6
Reactor bed volume (cc)	12	12	15

of phenol. The formation of phenol by dehydrogenation of cyclohexanone and cyclohexanol is a reversible reaction.

$$(1)$$
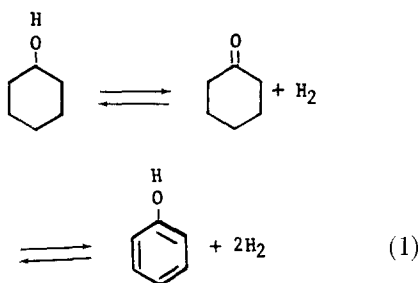
The ratio of the amounts of cyclohexanone, cyclohexanol, and phenol present at equilibrium will depend on the temperature and concentration. The equilibrium for cyclohexanone, phenol, and hydrogen can be expressed by

$$K = \frac{P(\text{phenol}) \times P(\text{hydrogen})^2}{P(\text{cyclohexanone})} \quad (2)$$

where $P(\text{phenol})$, $P(\text{hydrogen})$, and $P(\text{cyclohexanone})$ are the partial pressures of phenol, hydrogen, and cyclohexanone, respectively (16–17). A temperature around 350°C is required to obtain a high yield of phenol. This was shown by a study of the variation in equilibrium concentrations of cyclohexanone, cyclohexanol, and phenol with temperature by Cubberley and Mueller (18).

IV. CATALYST ACTIVITY STUDIES

One of the most interesting finds reported in this paper is that the addition of tin to a nickel-silica catalyst greatly promotes the dehydrogenation of cyclohexa-

none and cyclohexanol to phenol. This promoting effect is shown by the data in Tables 3 and 4. Not only does the tin promote the initial activity, but it also gives a catalyst of longer life with high selectivity to phenol. This is especially evident from the data obtained using the 2.5:1 nickel-tin catalyst and using a cyclohexanone feed. The yield of phenol per pass is lower when a cyclohexanol feed is used instead of cyclohexanone. This is because the cyclohexanol has to be converted first to cyclohexanone.

With Catalyst 4 (nickel-to-tin ratio = 0.9) very little phenol was formed from cyclohexanone. However, a new product was formed. This compound was 2-(1-cyclohexenyl)cyclohexanone, which is formed via an aldol condensation reaction (3). By increasing the space velocity a higher yield of this compound

$$(3)$$
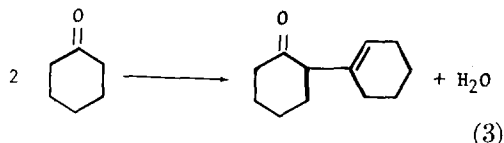
was obtained as shown by the data in Table 3. No condensation product or phenol was formed when cyclohexanol was passed over this catalyst. The products formed were cyclohexene and cyclohexanone. Cyclohexene is formed by a dehydration reaction (4).
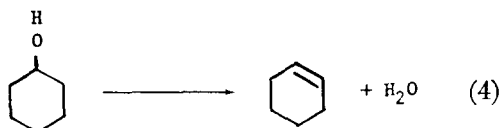

$$(4)$$

TABLE 3
Dehydrogenation of Cyclohexanone to Phenol

Catalyst	Nickel tin molar ratio	Time (hr)	% Cyclohexanone converted, ±3%	% Selectivity to phenol	Cyclohexenes	Benzene	Cyclohexanone	Cyclohexanol	Phenol	Dimer
				$LHSV = 0.5\ hr^{-1}$						
1	∞	1	34.9	77.8	0.99	0.52	65.32	1.12	27.36	—
		2	16.2	58.7	0.93	0.24	84.22	0.52	9.39	—
		5	10.9	41.9	0.55	0.15	88.85	0.31	4.60	—
2	4.5:1	1	97.9	96.1	0.04	1.19	2.02	0.06	94.10	—
		3	83.0	94.6	0.24	1.55	16.57	0.83	78.81	—
		5	70.0	93.0	0.45	1.22	29.97	1.50	84.84	—
3	2.5:1	1	98.3	93.4	—	1.05	1.23	—	96.40	—
		3	96.0	95.7	—	0.98	3.74	0.23	93.65	—
		4	94.7	95.5	0.04	0.92	5.51	0.33	91.81	—
		5	91.6	95.6	—	0.87	8.43	0.63	88.00	—
		6	89.0	86.0	0.06	0.87	12.96	0.71	86.51	—
4	1:1	1	31.3	4.0	8.2	—	78.1	2.3	1.6	4.2
		2	34.3	3.3	7.6	—	78.0	2.4	1.4	4.0
		4	24.1	7.1	4.8	—	83.4	1.2	1.9	4.9
				$LHSV = 2.5\ hr^{-1}$						
4	1:1	1	15.7	8.8	1.34	—	85.50	—	1.32	8.99

[a] GLC analysis values in weight percent.

TABLE 4

DEHYDROGENATION OF CYCLOHEXANOL TO PHENOL

Catalyst	Ni:Sn ratio	Time (hr)	% Cyclohexanol converted ±3%	% Selectivity to phenol	Cyclohexene[a]	Benzene	Cyclohexanone	Cyclohexanol	Phenol	Dimer
					$LHSV = 0.5\ hr^{-1}$					
1	∞	1	82.5	24.3	3.31	3.54	26.94	13.42	24.40	0
		2	71.7	21.2	7.06	3.82	35.73	31.59	16.87	0
		3	65.7	19.0	7.07	3.38	34.17	36.71	13.59	0
		4	61.5	15.0	7.23	3.10	31.82	42.69	10.50	0
2	4.5:1	1	99.7	90	0	2.03	2.74	0.52	91.47	0
		2	99.2	77.5	0.16	1.09	6.62	0.61	83.31	0
		3	98.8	86.0	0.38	1.19	11.45	0.97	84.65	0
		4	99.0	81.8	0.23	0.95	15.59	1.14	80.86	0
3	2.5:1	1	99.3	73.3	0.16	1.75	8.31	0.78	87.08	0
		2	99.3	82.1	0.09	0.87	5.87	0.58	91.79	0
		3	98.9	71.7	0.26	1.76	13.94	1.43	81.04	0
		4	98.3	74.7	0.24	0.99	14.90	1.73	81.07	0
4	0.9:1	1	72.5	0	25.24	0	28.56	33.05	0	0
		2	65.3	0	23.39	0	32.43	38.68	0	0
		3	64.5	0	23.47	0	32.03	39.42	0	0
		4	66.1	0	20.72	0	36.82	37.59	0	0
					$LHSV = 2.5\ hr^{-1}$					
3	2.5:1	1	92.0	—	1.1	0.6	36.5	8.4	51.1	1.9
		3	92.0	—	0.3	0.4	49.7	9.0	40.4	0

[a] GLC analysis values in weight percent.

A further investigation revealed that the aldol reaction, which forms 2-(1-cyclohexenyl)cyclohexanone is also catalyzed by a tin-silica and silica catalyst as shown by the data in Table 5.

TABLE 5

CONDENSATION OF CYCLOHEXANONE WITH TIN-SILICA AND SILICA GEL CATALYSTS

Catalyst	% Conversion	% Selectivity[a]
SiO₂	10.8	92.0
1% Sn-SiO₂	15.0	87.7
5% Sn-SiO₂	29.8	72.0
10% Sn-SiO₂	27.5	93.9

[a] To 2-(1-cyclohexenyl)cyclohexanone.

A chromatographic analysis of the product showed cyclohexene to be the only other major component, amounting to about 4 wt % of the sample. A very small amount of another material which had a long retention time was formed. Positive identification of this component was not made, but it may be a condensation product of 3 moles of cyclohexanone.

The dehydrogenation of cyclohexane to benzene with nickel and nickel-tin catalysts was also studied. The results obtained are summarized in Table 6. The data show

TABLE 6

DEHYDROGENATION OF CYCLOHEXANE TO BENZENE

Catalyst	% Conversion	% Selectivity
1	12.0	100
2	9.2	100
3	9.5	100
4	0	—

that the nickel is the most active catalyst for this reaction, and the addition of tin poisons the reaction. The nickel-tin catalyst with a mole ratio of 0.9:1 was completely inactive for the reaction even at 450°C.

No trouble was encountered in reproducing catalyst preparations providing that exact calcining and pretreatment conditions were used.

A. *X-Ray Diffraction Analyses*

The X-ray diffraction patterns of the reduced nickel and nickel-tin catalysts are

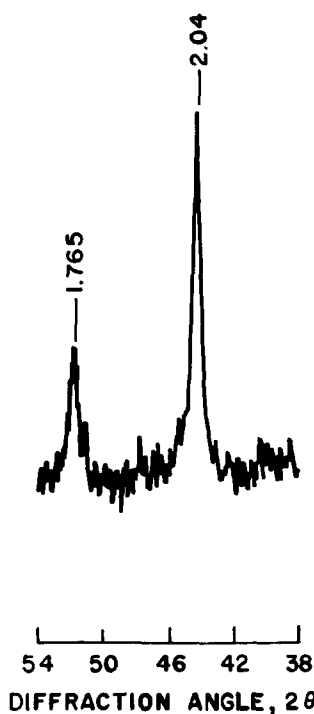FIG. 1. Portion of the X-ray diffraction pattern of reduced nickel-silica catalyst (1).

shown in Figs. 1 through 4. All of these catalysts contain the same number of gram atoms of nickel. The X-ray pattern of Catalyst 1 exhibited intense lines due to metallic nickel. The addition of tin to this
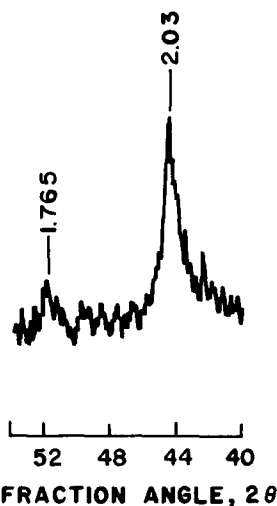

FIG. 2. Portion of the X-ray diffraction pattern of reduced nickel-tin-silica catalyst (2); nickel-tin molar ratio, 4.5.
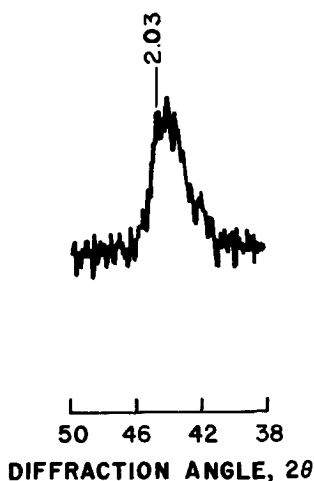
FIG. 3. Portion of the X-ray diffraction pattern of reduced nickel-tin-silica catalyst (3); nickel-tin molar ratio, 2.5.

catalyst had a marked effect on reducing the intensity of the diffraction lines, as is evident from Figs. 2 and 3. This decrease in intensity is probably due to the combining of some nickel to form alloy phases of small crystallite size or which are amorphous to X-rays. Catalyst (4) with a nickel-to-tin ratio of 0.9 exhibits a diffrac-
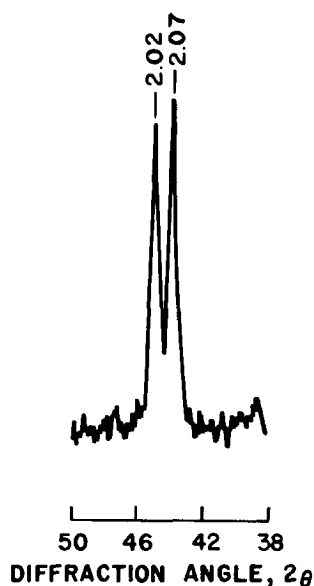
FIG. 4. Portion of the X-ray diffraction pattern of reduced nickel-tin-silica catalyst (4); nickel-tin molar ratio, 0.9.

tion pattern of only a highly crystalline nickel-tin alloy phase (see Fig. 4). All of the diffraction patterns were obtained under identical conditions.

TABLE 7

X-RAY DIFFRACTION LINES OF THE REDUCED NICKEL-TIN-SILICA CATALYST (3)

Observed		Reported Card (3-1004)[a] Nickel-tin alloy		Reported Card (4-0850)[a] Nickel	
d (Å)	I	d (Å)	I	d (Å)	I
2.92	M	2.92	80	—	—
2.59	W	2.61	10	—	—
2.29	VW	—	—	—	—
2.16	W	—	—	—	—
2.10	M	2.09	100	—	—
2.03	M	2.03	100	2.034	100
1.866	VW	—	—	—	—
1.765	W	—	—	1.762	42
1.672	VW	1.67	50	—	—
1.610	VW	1.60	50	—	—
1.552	VW	1.55	50	—	—
1.467	W	1.46	60	—	—
1.281	VW	1.29	50	—	—
1.246	W	—	—	1.246	21
1.191	VW	1.19	70	—	—
1.167	VW	1.18	40	—	—
1.098	VW	1.09	80	—	—
1.064	W	—	—	1.062	20

[a] ASTM Card File. M, medium; VW, very weak; W, weak; I, intensity.

With Catalysts 2 and 3, both metallic nickel and nickel-tin alloy phases are present, as verified by X-ray diffraction films. Table 7 shows the data obtained from Catalyst 3.

The calcined tin-silica Catalyst 5 was examined by X-ray diffraction, and it was found that the tin was present as SnO_2. After reduction with hydrogen for 3 hr at 375°C the catalyst turned black, probably due to the formation of β-tin which was observed by X-ray diffraction.

B. *Removal of Nickel by Carbon Monoxide from Reduced Impregnated Catalysts*

Treatment of reduced nickel and nickel-tin-silica catalysts with carbon monoxide resulted in the removal of metallic nickel in the form of nickel carbonyl. Table 8 gives the results obtained from carbon

TABLE 8
PERCENT OF THE TOTAL NICKEL REMOVED
WITH CARBON MONOXIDE

Catalyst	Nickel (%)	Tin (%)	% of the nickel removed, ±2%
1	12.0	0	100
2	8.3	3.7	29
3	8.7	7.1	15
4	6.6	14.2	0

monoxide extraction experiments on catalysts containing various nickel-to-tin ratios.

Almost quantitative removal of nickel from the nickel-silica catalyst was obtained after a 6-hr period. As tin was added, less nickel could be removed; and for Catalyst 4, no nickel was removed. The fact that no nickel was removed with carbon monoxide from this catalyst is interesting, since in another study it was found that nickel could be removed from unsupported and supported nickel-copper alloys (10).

V. DISCUSSION

The experimental results show that nickel-tin alloy phases will form upon reduction of impregnated nickel-tin silica
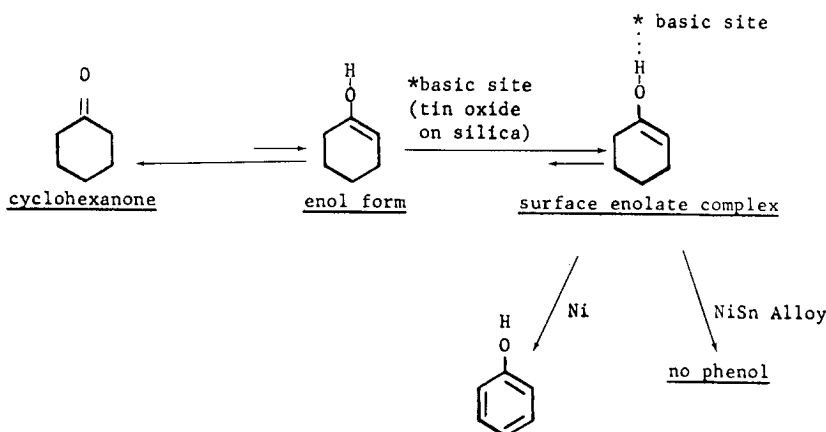
catalysts. The evidence for this alloy formation is provided by the X-ray diffraction results. Also, the carbon monoxide extraction data indicate that nickel is combining with the tin so that as the tin content is increased, less nickel can be removed as nickel carbonyl.

Few reports of supported alloys have been made. Endter (19) reported that platinum-aluminum alloys were formed during the preparation of a platinum-alumina catalyst used in the synthesis of hydrogen cyanide and several reports of supported nickel-copper alloys have been made (20–22). Alloys of Pt-Rh, Pd-Rh, Pt-Ru, and Os-Pt on impregnated alumina catalysts have also been reported (23). However, the existence and nature of these alloys were definitely not established.

A possible explanation of the promoting effect of tin on nickel-silica for the dehydrogenation of cyclohexanone to phenol is that tin oxide dispersed on a silica surface acts as a "basic site" which promotes enolization. The enol form is stabilized, to a certain degree, by bonding between the acidic enol hydrogen with oxygen of the tin oxide. Since the enol form has its ring partially dehydrogenated, the metallic nickel which is known to be present from the X-ray and carbon monoxide extraction data easily further dehydrogenates the ring. The surface aromatic complex then desorbs as phenol. The proposed mechanism is illustrated on page 13.

According to X-ray diffraction and carbon monoxide extraction data, Catalyst 4 with a nickel-tin molar ratio of 0.9 contains no free metallic nickel. This catalyst produced very little phenol, suggesting that the nickel-tin alloy phase is a weak dehydrogenation catalyst. This conclusion is supported by the fact that no benzene was formed when cyclohexane was passed over the catalyst at temperatures as high as 450°C. However, this catalyst did catalyze the dehydrogenation of cyclohexanol to cyclohexanone. The major product formed by Catalyst 4 with cyclohexanone was 2-(1-cyclohexenyl) cyclohexanone. This product is formed by a vapor-phase aldol condensation reaction. A further investiga-

tion revealed that the silica gel also catalyzed this reaction to some extent; however, the addition of tin greatly enhanced the activity. What complex is catalyzing this condensation reaction is not known. Surface species of the type Si–O–Na have been proposed (24) to be present on sodium hydroxide-treated silica gels. These sites supposedly act as active basic centers which catalyze vapor-phase aldol condensation reactions. It is possible that tin could form similar type surface complexes or that tin oxide dispersed on silica is the active species. Bulk SnO_2 did not catalyze the condensation reaction under the conditions reported for the tin-silica catalyst. However, the area of the bulk SnO_2 was very low, approximately 5 m²/g. Since the tin was added as $SnCl_2 \cdot 2H_2O$ there was concern that the condensation reaction was promoted by a form of chloride on the silica surface. The chloride content of the silica gel was less than 0.01 wt %. After adding $SnCl_2 \cdot 2H_2O$ to give 10 wt % tin on silica, and calcining at 500°C for 16 hr, the chloride content was 0.06 wt %. Since there was an increase in the chloride concentration, the possibility existed that the chloride was in some way responsible for promoting the condensation reaction. Because of this a chloride-free tin-silica catalyst was prepared and tested. This catalyst was prepared by dispersing a hydrated tin oxide, prepared by reacting tin metal with dilute nitric acid, onto the silica. This catalyst gave almost identical activity as one prepared from $SnCl_2 \cdot 2H_2O$. Therefore, it is

believed that a form of tin is responsible for the promoting of the condensation reaction. This subject will be discussed in more detail in a subsequent paper. The fact that very little 2-(1-cyclohexenyl) cyclohexanone was formed with Catalysts 2 and 3 suggests that the rate of the dehydrogenation reaction is faster than the condensation reaction. With Catalyst 4 the nickel is all tied up in an alloy which is not active for phenol formation, thus permitting the condensation reaction to proceed over the basic sites.

According to the electron band theory, the catalytic activity of transition metals for hydrogen transfer-type reactions, such as hydrogenation–dehydrogenation, is due to the partially empty d bands of the metal. Adding various amounts of hyperelectronic metals, (25) such as copper and tin, results in the donation of electrons to the base metal with the gradual filling of the d-band vacancies. This filling of the d band usually results in a corresponding decrease in catalytic activity. The results of the cyclohexane dehydrogenation studies over the nickel-tin catalysts, where the addition of tin to nickel reduced the activity, could be explained by this theory. Similar results were previously obtained using nickel-copper silica-alumina catalysts for the same reaction (10).

The results presented in this paper serve as an excellent example of how the reaction selectivity can be completely changed as the metal ratio is varied in a bimetallic catalyst system.

REFERENCES

1. TAYLOR, W. F., YATES, D. J. E., AND SINFELT, J. H., *J. Phys. Chem.* **68,** 2962 (1964).
2. BEUTHER, H., AND LARSON, O., *Ind. Eng. Chem.* **4,** 177 (1965).
3. SWIFT, H. E., LUTINSKI, F. E., AND TOBIN, H. H., *J. Catalysis* **5,** 285 (1966).
4. HILL, F., AND SELWOOD, P., *J. Am. Chem. Soc.* **71,** 2522 (1949).
5. HIGHTOWER, J. W., AND KEMBALL, C., *J. Catalysis* **4,** 363 (1965).
6. HIROTA, K., AND UEDA, T., *Bull. Chem. Soc. Japan* **35,** 228 (1962).
7. CARTER, J. L., CUSUMANO, J. A., AND SINFELT, J. H., *J. Phys. Chem.* **70,** 2257 (1966).
8. CARTER, J. L., AND SINFELT, J. H., *J. Phys. Chem.* **70,** 3003 (1966).
9. TAYLOR, W. F., SINFELT, J. H., AND YATES, D. J. C., *J. Phys. Chem.* **69,** 3857 (1965).
10. SWIFT, H. E., LUTINSKI, F. E., AND KEHL, W. L., *J. Phys. Chem.* **69,** 3268 (1965).
11. SABATIER, P., *Chem. Ber.* **44,** 1984 (1911).
12. SABATIER, P., AND GAUDION, C., *Compt. Rend.* **168,** 670 (1919).
13. SKITA, A., AND RITTER, H., *Chem. Ber.* **44,** 668 (1911).
14. BARTLETT, E. P., AND FIELD, E., U. S. Patent 2,291,585 (1942).
15. LODER, D. J., U. S. Patent 2,321,551 (1943).
16. CHITWOOD, H. C., FITZPATRICK, J. T., FOWLER, G. W., AND FREURE, B. T., U. S. Patent 2,588,359 (1952).
17. CHITWOOD, H. C., FITZPATRICK, J. T., FOWLER, G. W., AND FREURE, B. T., *Eng. & Proc. Develop.* **44,** 1696 (1952).
18. CUBBERLEY, A. H., AND MUELLER, M. B., *J. Am. Chem. Soc.* **69,** 1535 (1947).
19. ENDTER, F., presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pennsylvania, April 5–10, 1964.
20. REINACKER, G., AND BURMANN, R., *J. Prakt. Chem.* **158,** 95 (1941).
21. FUDERER-LEUTIC, P., AND BRIHTA, I., *Croat. Chem. Acta* **31,** 75 (1959).
22. REYNOLDS, P. W., *J. Chem. Soc.,* p. 242 (1950).
23. GRAY, T. J., MASSE, N. G., AND OSWIN, H. G., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2,** 1697 (1961).
24. MALINOWSKI, S., BASINSKI, S., AND SZCZEPANSKA, S., *Intern. Chem. Eng.* **5,** 426 (1965).
25. PAULING, L., "The Nature of the Chemical Bond." p. 432. Cornell Univ. Press, Ithaca, New York, 1960.