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The Activity of Nickel on Sodium-Neutralized Silica–Alumina

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A series of 8% Ni/SiO_2–Al_2O_3 catalysts was prepared with increasing amounts of preimpregnated sodium up to 2.37 wt%. Magnetic susceptibility and hydrogen adsorption showed the dispersion of the nickel relatively unaffected by the sodium and insignificant poisoning of the metal surface. Cumene dealkylation, benzene hydrogenation, ethane hydrogenolysis, and cyclopropane hydrogenation/hydrogenolysis were studied with a pulse reactor. These experiments indicate that (i) the acidity of the support decreased with Na neutralization, (ii) benzene hydrogenation and ethane hydrogenolysis were not affected, and (iii) cyclopropane conversion and selectivity to hydrogenation decreased considerably with increasing Na content. Poisoning titration with H_2S showed moderate changes in the site concentration and revealed isomerization on the support. The pattern of cyclopropane activity was attributed partly to a dual-functional effect and partly to the possible formation of an active overlay.

INTRODUCTION

Metal-support effects have for many years been recognized in catalysis, yet the experimental evidence always introduces secondary complications that hinder a clear understanding of the phenomenon. For example, Richardson (*1*), following the lead of others (*2, 3*), reported that the intrinsic activity of nickel for benzene hydrogenation and ethane hydrogenolysis decreased over many orders of magnitude as the acidity of the support increased. The hydrogenation–dehydrogenation function in *n*-hexane isomerization paralleled this behavior. Several possible explanations were postulated (*1*). Among these were electron transfer from electronegative centers on the support and metal surface poisoning either from acid hydroxyl groups or cracked residues. However, the supports used varied from silica to faujasites so that other factors such as crystallite morphology and size distribution could not be ruled out.

In an attempt to resolve some of these uncertainties, we have made similar measurements on a series of nickel on silica–alumina samples whose only difference is the acidity of the support. This was done by progressively neutralizing the support with alakli prior to impregnation. Possible modification of the metal by the alkali must, however, be considered.

The use of these catalysts for carbon monoxide methanation was reported in another communication (*4*). It was concluded that alkali poisoning on the metal was not significant but that its presence on the support affected both the pre-exponential factor and activation energy of the rate-determining step in such a way that the turnover number passed through a maximum at 0.3 wt% of Na.

In this paper we present our results on the measurements of ethane hydrogenolysis

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TABLE 1

Characteristics of Sodium-Neutralized $Ni/SiO_2-Al_2O_3$ Catalysts

Na (wt%)	BET surface area ($\times 10^{-5}$) (m^2/kg)	Ni (wt%)	d_{Ni} (nm)	S_H[a]	S_H/S_M[b]
0	1.74	7.6	8.8	7.23	0.94
0.12	1.82	6.3	7.6	7.20	0.97
0.44	1.78	8.0	8.8	8.42	1.04
0.73	1.68	8.0	8.8	7.43	0.91
2.37	1.52	8.0	9.0	6.65	0.84

[a] Site concentration from H_2 adsorption, (sites per kilogram of catalyst) $\times 10^{-22}$.

[b] S_M calculated from d_{Ni}.

and benzene hydrogenation as examples of single reactions, and of cyclopropane hydrogenation/hydrogenolysis as typical of parallel reactions. This last reaction has received considerable attention in the past (*5–9*). For instance Sinfelt and co-workers have shown that the intrinsic activity of nickel increases by two orders of magnitude when the support is changed from silica–alumina to less acidic silica (*6–8*).

EXPERIMENTAL

Catalyst preparation. Extrudates of Davison Chemical SMR-7-3598 silica–alumina (25% Al_2O_3) were crushed to 100–120 mesh and divided into 0.060-kg portions. Each sample of silica–alumina was treated for 2 days with 100 cm^3 of H_2O containing increasing amounts of NaCl. They were then dried in an oven at 413 K for an additional day and calcined at 723 K in flowing air for 3 hr. This procedure was found by Maatman *et al.* to be effective in removing all of the chloride ions with a deposition of Na on the catalyst surface (*10*).

Portions (0.030 kg) of each sample were further treated with 50 cm^3 of H_2O containing 0.015 kg of $Ni(NO_3)_2 \cdot 6H_2O$. These were contacted for 1 week, dried at 373 K for 1 day, crushed to 48–60 mesh, and stored for use. Prior to each subsequent experiment, each catalyst was reduced at 623 K for 16 hr in flowing hydrogen as a standard procedure.

Catalyst characterization. Characterizations of these catalysts were described in another communication (*4*). Magnetic susceptibility was used to measure the amount of reduced nickel and the average crystallite size, nitrogen adsorption was used to measure the BET surface area, and hydrogen adsorption was used to measure the dispersion of the nickel. Results are summarized in Table 1.

From these data we concluded that the catalysts contain approximately the same amount of reduced nickel with equivalent crystallite sizes and exhibit similar concentrations of surface nickel atoms. The close agreement between the number of sites (nickel atoms) calculated from the hydrogen adsorption, S_H, and the crystallite sizes, S_M, indicates very little surface poisoning of the metal by sodium atoms. Some may be present in the 2.36% Na sample, which has the lowest value.

Kinetic measurements. Figure 1 shows the microreactor used in the reactivity measurements. The catalyst charge of 2×10^{-4} kg was equally mixed with inert α-Al_2O_3 in a 6-mm stainless-steel tube. The nickel was reduced at 623 K for 16 hr in hydrogen. Pulses of reactants were injected into the reactor by either the pulsing valve (for ethane and cyclopropane) or the injection port (for cumene and benzene). The product was analyzed with an appropriate column

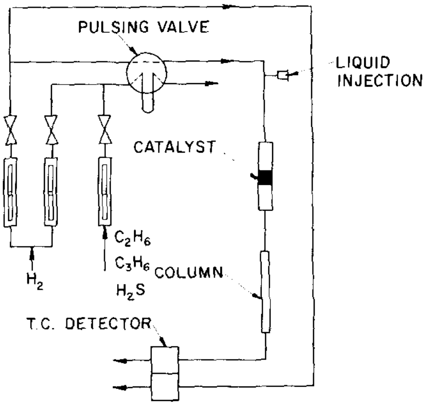

FIG. 1. Pulse microreactor for activity measurements.

TABLE 2

Experimental Conditions in the Pulse Microreactor

Reaction	Pulse size	Carrier gas	Temperature (K)	Flow rate (cm^3/s)	Column
Cumene dealkylation	3 mm^3	Helium (100 kPa)	673	1.0	1 m × 6 mm DC 200 373 K
Benzene hydrogenation	3 mm^3	Hydrogen (100 kPa)	573	1.0	1 m × 6 mm ODPN Chromosorb 373 K
Ethane hydrogenolysis	20% C_2H_6/H_2 4.31 cm^3	Hydrogen (100 kPa)	623	0.5	1 m × 6 mm Silica gel 273 K
Cyclopropane hydrogenation/ hydrogenolysis	25% C_3H_6/H_2 4.31 cm^3	Hydrogen (100 kPa)	273–523	0.08–2.00	30 cm × 6 mm Silica gel 273 K

as shown in Table 2. Other conditions are also given.

Cumene dealkylation, benzene hydrogenation, and ethane hydrogenolysis measurements were made to characterize the acidity and metal activities of the various catalysts. Kinetic studies were not carried out so that conversions at fixed conditions are reported. Successive pulses were followed to check for deactivation.

More detailed kinetic measurements were made on cyclopropane hydrogenation/hydrogenolysis by varying the flow rates and temperatures. Concentration of the feed was maintained at a constant value. Checks for deactivation were made during these experiments by returning to standard conditions.

Hydrogen sulfide poisoning. Titration by dosing with catalyst poisons is a convenient method for determining site heterogeneity and concentration (*1*). We used pulses of 2% H_2S in H_2 alternated between pulses of cyclopropane. Since care must be taken that the poison is uniformly distributed throughout the catalyst bed, the poisoning was carried out at room temperature. Under these conditions adsorption is slow and zoning in the bed minimized. The chromotographic column was bypassed so that the amount of H_2S adsorbed could be found from analysis of the effluent peak. The temperature was raised to reaction temperature following each poisoning pulse. Desorption is very slow under these conditions (*11*), and very little loss of accumulated poison occurred.

RESULTS AND DISCUSSION

Cumene dealkylation to benzene and propylene is a measure of the support acidity. Results, shown in Table 3, show that the sodium does indeed poison the Brønsted sites of the silica–alumina in agreement with Maatman (*10*). Further quantification of the acidity loss was not made.

Ethane hydrogenolysis has been used as a model reaction for saturated carbon–carbon bond hydrogenolysis. Both kinetics and mechanisms have been studied (*3*, *12–15*). The reaction proceeds through the formation of CH_x fragments and only involves the metal, although these species may polymerize on the acid sites of the support. The effect of support acidity on the intrinsic activity may originate from

TABLE 3

Cumene Conversion at 673 K and 100 kPa

Na (wt%)	Conversion (mol%)
0	31
0.12	29
0.44	25
0.73	7
2.37	0

the poisoning effect of carbonaceous residues. Measurements reported previously (*1*, *3*) were made with continuous flow microreactors, where this effect is significant. Pulse measurements provide the possibility of extrapolating back to the "clean" catalyst.

Our results are given in Table 4. Conversions at standard conditions were used to calculate the average rate within the pulse, without recourse to the kinetics within the pulse. The average turnover numbers of Table 4 were calculated by using the values of S_H from Table 1.

The results indicate that Na neutralization up to 0.44 wt% does not change the activity and that the initial rate is maintained for up to 12 pulses. We infer that the amount of metal poisoning through carbonaceous residues produced by the acid sites is insignificant for ethane hydrogenolysis. For the last two samples, with higher sodium content and lower acidities, the rate decreases but remains constant for succeeding pulses. Sinfelt and co-workers have studied this reaction extensively. Their data extrapolated to the conditions of Table 4 give values of 52 min^{-1} for Ni/SiO$_2$–Al$_2$O$_3$ (*14*) and 1.7 × 10^3 min^{-1} for Ni/SiO$_2$ (*15*). In view of the large degree of extrapolation involved, their value of 52 min^{-1} for Ni/SiO$_2$–Al$_2$O$_3$ compares reasonably with our value of 11 min^{-1} for the 0% Na sample. However, the increase by a factor of 30 for the less acidic silica support is not consistent with the small decrease for the higher sodium samples. Factors other than acidity must be responsible. In Sinfelt's experiments these may be structural or morphological effects. For our samples, with opposite trends, the cause is most probably related to the presence of sodium at the higher levels.

A possible explanation may be found in the data of Table 1, which gives a S_H/S_M ratio of 0.84 for the 2.37-wt% Na sample. If the decrease is due to the adsorption of sodium randomly over the nickel surface, the amount of two-point adsorption of ethane will also decrease. Rideal (*16*) has shown how statistically the number of "paired" nickel atoms decreases by a factor of θ^2, where θ is the fraction of surface unpoisoned. This leads to a prediction of 9 and 7 min^{-1} for the 0.73- and for the 2.37-wt% Na samples, respectively, which is in the direction observed.

Similar trends are found in the data for benzene hydrogenation in Table 5, except that deactivation within the first 12 pulses occurs for the more acidic catalysts. Deactivation decreases with increasing sodium content. This is not surprising since aromatics are much more active coke pre-

TABLE 4

Ethan Hydrogenolysis at 623 K and 100 kPa

Pulse number	Turnover number (min^{-1})				
	Weight percent of sodium				
	0	0.12	0.44	0.73	2.37
1	11	12	12	8	4
2	11	12	13	8	4
3	11	12	12	8	4
4	11	12	13	9	4
5	11	12	13	9	4
6	11	12	13	8	4
7	12	12	13	10	5
8	12	12	12	9	5
9	11	12	13	8	5
10	12	12	12	10	5
11	11	12	12	10	8
12	11	12	13	10	5

cursors than paraffins. The decreasing deactivation implies that the decrease in acidity is much faster than indicated by the cumene conversion alone.

Taylor and Staffin reported rates for various silica- and silica–alumina-supported nickel catalysts (*2*). For 5% Ni, their data extrapolated to the condition in Table 5 give turnover numbers of 32 and 9 for SiO_2 and SiO_2–Al_2O_3, respectively. In view of the extrapolation, these are in reasonable agreement with the values in Table 5, although the large difference between different supports is not evident. Aben *et al.* (*17*) also reported no differences due to support.

We conclude that, for our samples, the sodium neutralization results in no change in initial benzene hydrogenation although further poisoning by carbonaceous residues does result in small differences. The decrease for the 2.36-wt% Na sample may again be attributed to statistical factors in which, for six-point adsorption of the benzene molecule, the indicated surface poisoning leads to a predicted rate of 10.6 compared to 12.1 min^{-1}.

TABLE 5

Benzene Hydrogenation at 473 K

Pulse number	Turnover number (min^{-1})				
	Weight percent of Na				
	0	0.12	0.44	0.73	2.37
1	30	38	42	39	12
2	27	27	36	36	12
3	25	24	31	38	12
4	25	25	29	35	12
5	23	25	26	35	12
6	22	24	25	33	12
7	22	22	25	35	12
8	20	21	28	32	11
9	19	19	28	32	11
10	20	20	28	31	11
11	19	19	28	31	12
12	18	17	29	31	11

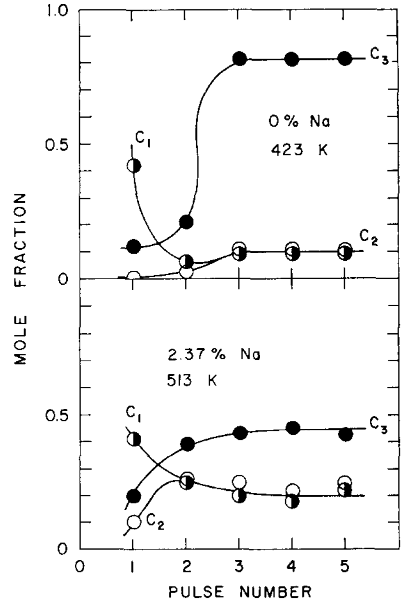

FIG. 2. Product distribution in subsequent pulses.

From these findings, we conclude that acidity has no direct influence on the activity of nickel for benzene hydrogenation and ethane hydrogenolysis and that previous results (*1*, *3*) for these reactions must be due to other factors.

Cyclopropane hydrogenation/hydrogenolysis is a model reaction for the simultaneous study of the reactions

$$C_3H_6 + H_2 \rightarrow C_3H_8 \qquad (1)$$

and

$$C_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \qquad (2)$$

Comparisons with propane hydrogenolysis show that reactions (1) and (2) are simultaneous and not consecutive. Reaction (1), termed hydrogenation, is similar to olefin hydrogenation. On the other hand, reaction (2), hydrogenolysis, suggests the behavior of paraffins.

These reactions have been studied by many investigators (*18–27*). Preferred mechanisms suggest a weakly π-adsorbed cyclic species which dissociates with a common 1,3 deadsorbed mode followed by rapid conversion via the two paths. Schlatter and Boudart (*28*) and Compagnon

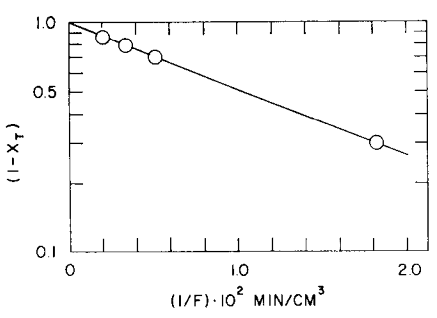

FIG. 3. First-order kinetics of total cyclopropane conversion.

et al. (*29*) found evidence for a dual-functional path for hydrogenation on Pt/SiO_2–Al_2O_3. They postulated that cyclopropane isomerizes to propylene on the acid sites of the carrier and then passes through the vapor phase to metal hydrogenation sites.

In our experiments, the pulse method was used in order to avoid self-poisoning effects. However, with cyclopropane there was an induction period before activity reached a steady state. Figure 2 shows typical results for two samples.

In the case of the sodium-free catalyst, activity was low in the first pulse and the major product was methane. Presumably this resulted from complete hydrogenolysis on very active sites. Carbonaceous residues from this reaction poisoned these active sites so that in the second pulse, formation of methane decreased but the activity for hydrogenolysis and hydrogenation increased. Finally, after the third pulse the conversion products satisfied the stoichiometry for the two reactions and reached a steady state.

Other samples in the series showed similar effects. In all cases the initial amount of methane was approximately the same, and activity increased to a steady state after the third pulse.

No loss of hydrocarbon could be detected in the product pulse, so that retention of carbon must be less than experimental error, which was 5%. Nevertheless, in three pulses this is sufficient to cover all surface nickel atoms. This uncertainty complicates the interpretation since hydrogen adsorption was measured on the clean sample, and the concentration of exposed nickel sites is unknown. Furthermore, this conditioning may involve the formation of an "overlay" as suggested by Blakely and Somerjai (*30*). Steady-state compositions remained constant for many pulses and were independent of time between pulses, thus indicating a permanent effect.

The influence of the sodium neutralization on these steady-state values will now be considered in greater detail. Figure 3 shows typical data plotted to demonstrate pseudo-first-order behavior.

Figure 4 shows the product distribution to be in accordance with the parallel path mechanism.

From these data we calculated the turnover numbers N_P and N_E for hydrogenation and hydrogenolysis, respectively, using the values of S_H from Table 1. This procedure neglects the poisoning of the surface during the first two or three pulses. Figure 5 shows these values at 443 K.

Both N_P and N_E decrease rapidly with increasing sodium concentration, but N_P is more sensitive so that the selectivity N_P/N_E decreases. The data of Sinfelt and co-workers may be used for comparison purposes (*6–8*). For Ni/SiO_2–Al_2O_3, their results give values for N_P and N_E of 32

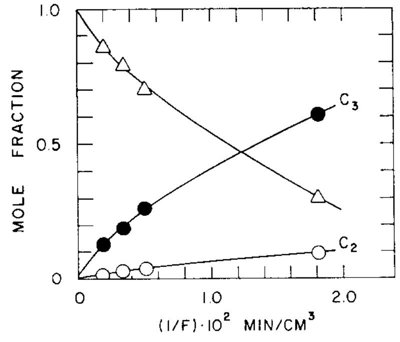

FIG. 4. Product distribution of the parallel formation of propane and ethane (plus methane).

and 5 min^{-1} under the conditions of Figure 5. These compare favorably with our values of 63 and 7 min^{-1}, respectively. For Ni/SiO$_2$, however, Sinfelt's data calculate as 5.9 $\times 10^3$ and 6.1 $\times$ 10^3 for N_P and N_E. For the less acidic support, the selectivity decreases but total activity increases by a factor of about 30.

A completely opposite trend in activity is observed in Fig. 5, although selectivity follows the same decrease. Clearly the concept of acidity-induced electron transfer or surface contamination cannot be invoked. The decrease is too pronounced to be due to sodium surface blocking shown in Table 1. Indeed, the greatest decrease occurs in the region from 0 to 0.5 wt% of Na where benzene hydrogenation and ethane hydrogenolysis are constant.

The activation energies of both reactions are the same with differences only in the pre-exponential factors. The activation energies for the series are also relatively constant with values from 80 to 96 kJ/mol.

Hydrogen sulfide titration measurements led to further information on the site concentrations. Typical results are shown in Fig. 6.

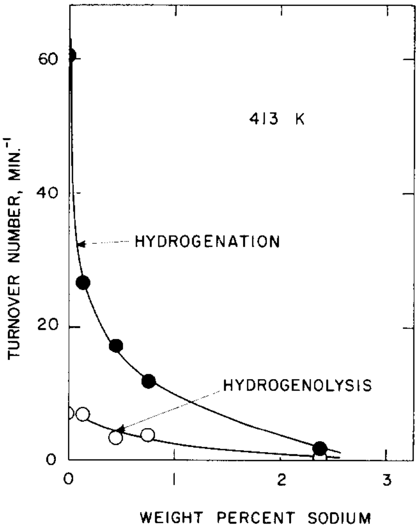

Fig. 5. Turnover numbers for hydrogenation and hydrogenolysis.

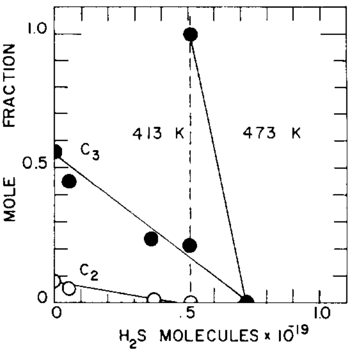

Fig. 6. Hydrogen sulfide titration.

Sulfur poisoning produced a linear decrease in conversion with the hydrogenolysis activity disappearing first. This was confirmed by raising the temperature, which increased the hydrogenation rate but showed no further hydrogenolysis. Great care was taken to avoid zoning which would give a linear poisoning curve. It is reasonable to assume that poisoning is uniform. In fact, if it were not, then both activities would disappear at the same poison level.

The titration of the hydrogenolysis sites implies that either sites of higher energy [edge, step, or kinks (30)] are involved in this reaction or that groups of sites (e.g., on assembly of three adjacent nickel atoms) are responsible. This last effect is more probable since a common intermediate has been postulated and the diadsorbed species could require three-point adsorption before C–C bond rupture occurs.

Results of titration experiments on all samples are given in Table 6.

These data show that the ratio of hydrogenolysis to hydrogenation sites is relatively constant in the range of 0.67 to 0.78 and that the ratio of hydrogenation to hydrogen adsorption sites increases with sodium content. Rostrup-Nielsen has shown that for a wide variety of nickel catalysts the ratio of adsorbed sulfur to adsorbed hydrogen atoms is about 0.8 (*11*) and not altered by the presence of sodium (*31*).

TABLE 6

H_2S Titration of Sodium-Neutralized Samples

Na (wt%)	Concentration[a] of H_2S to poison		N_{SE}/N_{SP}	N_{SP}/S_H
	N_{SP} hydrogenation	N_{SE} hydrogenolysis		
0	3.63	2.56	0.71	0.50
0.12	4.70	3.29	0.70	0.65
0.44	5.38	3.63	0.67	0.64
0.73	6.33	4.31	0.68	0.85
2.37	5.51	4.31	0.78	0.82

[a] Molecules of H_2S/per kilogram of catalyst × 10^{-22}.

The last two samples in Table 6 fall within experimental error of this value so that all surface nickel atoms may be considered to be exposed and unpoisoned by the carbonaceous residues in initial pulses. Similarly, the first sample has only about 60% of the surface exposed. These conclusions are in agreement with the qualitative trends showing decreased conditioning as the sodium content increases.

The turnover numbers in Fig. 5 were calculated assuming surface atomic concentrations from hydrogen adsorption measurements. Results from Table 6 may now be used to give corrected values for the turnover number. These are given in Table 7.

The hydrogenation activity decreases even more rapidly but the sodium-free value is still less than Sinfelt's silica-supported sample by a factor of about 60.

TABLE 7

Corrected Turnover Numbers for Sodium-Containing Samples at 443 K

Catalyst	Turnover number (min^{-1})	
	N_P	N_E
0	137	22
0.12	70	26
0.44	53	15
0.73	30	9
2.37	2	1

Again, as with ethane hydrogenolysis and benzene hydrogenation, enhancement on the less acidic support must involve effects other than acidity or acid-induced poisoning.

When all hydrogenation/hydrogenolysis activity disappeared due to sulfur poisoning, isomerization of cyclopropane to propylene was detected. The conversion for the sodium-free sample was 20%, but increasingly higher temperatures were necessary in order to reach this level with the remainder of the series. This implies that the isomerization activity decreased as the sodium level increased.

Acid-induced reactions on sulfided nickel are known to occur (*22*, *32*). However, the 2.4% sample contains the maximum amount of sulfur yet requires the highest temperature (550 K) to produce propylene. This suggests that the isomerization of the cyclopropane occurs on the acid sites of the support and not on the metal–sulfur surface. In support of this conclusion, Hall and co-workers (*34*, *35*) have shown that cyclopropane isomerizes over silica–alumina with measurable conversions as low as 373 K depending upon the hydrogen content of the catalyst.

Wallace and Hayes (*36*) found that propylene is rapidly hydrogenated to only propane over nickel so that with propylene produced on the acid sites of the support, a dual functional path to cyclopropane hydrogenation may exist. This path is presumably parallel to hydrogenation on the

TABLE 8

Effect of Additional Acidity on Cyclopropane Conversion at 443 K

	Conversion (mol%)		
	x_P	x_E	x_P/x_E
0.73 wt% of Na (0.2 g)	0.31	0.08	4
0.73 wt% of Na (0.2 g) + silica–alumina (0.2 g)	0.63	0.03	21

nickel surface itself and accounts for the higher selectivity to propane found for more acidic catalysts in Sinfelt's and our experiments.

This was confirmed by adding a charge of the original (sodium-free) silica–alumina to the front of a bed of nickel-containing fresh 0.73-wt% Na catalyst. A comparison of the results before and after the addition is shown in Table 8.

With the increase of the acidic function, total conversion increased from 0.39 to 0.66, propane formation doubled, and ethane dropped slightly. The selectivity to hydrogenation increased from 4 to 21.

The physical separation between the acidic and the hydrogenation parts of the bed further confirm that the dual-functionality is trivial with propylene transport through the gas phase. Activation energy for isomerization has been reported as 71 kJ/mol (*35*) which is close enough to those for nickel-induced hydrogenation and hydrogenolysis to account for the constant values found in our experiments.

The alternate dual-functional path to hydrogenation must account for a considerable amount of the activity if the selectivity of the neutralized catalyst is typical of the metal alone. Here the selectivity is close to that observed by Sinfelt *et al.* in the silica support, i.e., about 1 (*6*). However, even if we assume that the intermediate propylene does not lead to hydrogenolysis [as concluded by Wallace and Hays (*36*)] and subtract the dual-functional contribution from the hydrogenation activity, both activities decrease with sodium content. We have shown that the sodium has no effect on related functions such as benzene hydrogenation and ethane hydrogenolysis. Since decreasing support acidity results in greater not less activity for nickel or silica we conclude that acidic effects do not occur. Other factors must be considered in attempting to explain the differences between the behavior of cyclopropane and the other molecules. One possibility may be the presence of an overlay formed from the initial pulses resulting in a catalytically active surface. The lower sodium samples contain more of this residue and would be expected to give higher activities. Blakely and Somorjai postulated such an effect for cyclohexene dehydrogenation (*30*). This speculation, however, requires further study before acceptance as an explanation for the observed trends.

CONCLUSIONS

We began this investigation in an attempt to discover the possible role of support acidity in the decrease of ethane hydrogenolysis, benzene hydrogenation, and cyclopropane hydrogenation/hydrogenolysis as the support changes from silica to silica–alumina. From our results we conclude that there is no significant effect. Our conclusions are based upon (i) the similarity between our initial activities and those reported in the literature and (ii) the unchanging or decreasing activity as support acidity decreases.

Cyclopropane selectivities are complicated by a dual-functional path and by the possibility of the development of an active overlay during initial exposure.

Activity enhancement for silica (and alumina) supports must be caused by other factors. Future research should consider crystallite morphology and metal–support compound formation.

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REFERENCES

1. Richardson, J. T., *J. Catal.* **21**, 122 (1971).
2. Taylor, W. F., and Staffin, H. K., *Trans. Faraday Soc.* **63**, 2309 (1967).
3. Carter, J. L., and Sinfelt, J. H., *J. Phys. Chem.* **70**, 3033 (1966).
4. Huang, C. P., and Richardson, J. T., *J. Catal.* **51**, 1 (1978).
5. Merta, R., and Ponec, V., *in* "Fourth International Congress on Catalysis Moscow, 1968"

(B. A. Kazansky, Ed.), Paper No. 50. Adler, New York, 1968.

6. Sinfelt, J. H., Yates, D. J. C., and Taylor, W. F., *J. Phys. Chem.* **69**, 1877 (1965).

7. Taylor, W. F., Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **4**, 347 (1965).

8. Dalla Betta, R. A., Cusamano, J. A., and Sinfelt, J. H., *J. Catal.* **19**, 343 (1970).

9. Sridhar, T. S., and Ruthven, D. M., *J. Catal.* **16**, 363 (1970).

10. Maatman, R. W., Leenstra, D. L., and Leenstra, A., *J. Catal.* **7**, 1 (1967).

11. Rostrup-Nielsen, J. R., *J. Catal.* **11**, 220 (1968).

12. Sinfelt, J. H., *Catal. Rev.* **3**, 175 (1969).

13. Sinfelt, J. H., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 23. Academic Press, New York, 1973.

14. Sinfelt, J. H., *J. Phys. Chem.* **68**, 2962 (1964).

15. Sinfelt, J. H., *J. Amer. Chem. Sci.* **86**, 2996 (1964).

16. Rideal, E. K., "Concepts in Catalysis." Academic Press, New York, 1973.

17. Aben, P. C., Platteenw, J. C., and Southamer, B., *in* "Fourth International Congress on Catalysis, Moscow, 1968" (B. A. Kazansky, Ed.), Paper No. 31. Adler, New York, 1968.

18. Bond, G. C., and Sheridan, J., *Trans. Faraday Soc.* **48**, 713 (1952).

19. Bond, G. C., and Turkevich, J., *Trans. Faraday Soc.* **50**, 1335 (1954).

20. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 368, 377, 383, 388 (1957).

21. Benson, J. E., and Kwan, T., *J. Phys. Chem.* **60**, 1601 (1957).

22. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56**, 1501 (1960).

23. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6**, 92 (1966).

24. Anderson, J. R., and Avery, N. R., *J. Catal.* **8**, 48 (1967).

25. Anderson, J. R., and Kemball, C., *Proc. Roy. Soc. Ser. A* **223**, 361 (1954).

26. Clay, R. D., and Peterson, E. E., *J. Catal.* **16**, 383 (1970).

27. Sridhar, T. S., and Ruthven, D. M., *J. Catal.* **24**, 153 (1972).

28. Schlatter, J. C., and Boudart, M., *J. Catal.* **25**, 93 (1972).

29. Compagnon, P. A., Hoang-Van, C., and Teichner, S. J., *in* "Sixth International Congress on Catalysis, London, July 1976," Paper A4.

30. Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).

31. Rostrup-Nielsen, J. R., *J. Catal.* **21**, 171 (1971).

32. Pines, H., Shamaiengar, M., and Postl, W. S., *J. Amer. Chem. Soc.* **77**, 5099 (1955).

33. Pines, H., and Postl, W. S., *J. Amer. Chem. Soc.* **79**, 1769 (1957).

34. Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catal.* **3**, 512 (1964).

35. Larson, J. G., Gerberich, H. R., and Hall, W. K., *J. Amer. Chem. Soc.* **87**, 1880 (1965).

36. Wallace, H. F., and Hayes, K. E., *J. Catal.* **29**, 83 (1973).