

## Alkali Promoters on Supported Nickel: Effect of Support, Preparation, and Alkali Concentration

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The effect of potassium promoter for CO hydrogenation on supported nickel catalysts was studied in a differential reactor. The influences of the support ( $\text{SiO}_2$ ,  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ), the promoter concentration (0.05–4% K), the alkali salt (KCl,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{C}_2\text{O}_4$ , KOH,  $\text{KNO}_3$ ), and the method of preparation (pre- and coimpregnation, and calcination) were studied. The activity and selectivity of promoted catalysts are shown to depend on the support; modifications in catalytic properties are not just due to a K–Ni interaction. On  $\text{Ni/SiO}_2$  an exponential decrease in total activity with increased promoter concentration is seen; this decrease is not due to a decrease in percentage nickel exposed (dispersion). A large increase in olefin/paraffin ratios is seen on  $\text{Ni/SiO}_2$  as the promoter decreases hydrogenation rates. In contrast, on  $\text{Ni/SiO}_2 \cdot \text{Al}_2\text{O}_3$ , the rate of paraffin formation, including methane, increases and exhibits a maximum with increased promoter concentration. Olefin selectivities decrease and higher paraffin selectivities increase. Much of the potassium salt may react with the silica–alumina support to modify the catalytic properties. The method of preparation has a lesser influence on the catalyst than the potassium concentration. The use of different potassium salts resulted in similar catalytic properties, indicating that for a given support the same potassium compound formed during preparation. A good correlation was found between  $\text{C}_2$  and  $\text{C}_3$  olefin/paraffin ratios and inverse total activity, showing that olefin selectivities increase as hydrogenation rates decrease. © 1985 Academic Press, Inc.

### INTRODUCTION

Alkali promoters significantly modify the catalytic activity and selectivity of Group VIII metals for CO hydrogenation. However, there is disagreement in the literature on what effect they have. For example, Kruissink *et al.* (1) found that 0.5% Na decreased the methanation activity of coprecipitated  $\text{Ni/Al}_2\text{O}_3$  by a factor of about 3, and 1.0% Na decreased the methanation activity by a factor of about 10. Campbell and Goodman (2) reported that dosing 0.1 monolayer of potassium on a Ni(100) surface decreased the rate of CO methanation by at least a factor of 2, while the percentage of  $\text{C}_2^+$  hydrocarbons increased. Similarly, Gonzalez and Miura (3) demonstrated that turnover numbers for both methane and higher hydrocarbons decreased, while the fractional yields of higher hydrocarbons and olefins increased with potassium content on  $\text{Ru/SiO}_2$  catalysts. Huang and

Richardson (4) found, however, that sodium increased the turnover numbers for methanation on an 8%  $\text{Ni/SiO}_2 \cdot \text{Al}_2\text{O}_3$  catalyst. A maximum in turnover number was observed for 0.3% Na; the rate was six times the unpromoted value.

Recently we have seen that at the same promoter concentration and for the same preparation method, the support has a large influence on the rate of methanation and higher hydrocarbon yield. This was observed both with temperature-programmed reaction (5) and with steady-state differential reactor studies (6). On  $\text{Ni/SiO}_2$  and  $\text{Ni/TiO}_2$  catalysts, sodium and potassium significantly decreased the specific rate of hydrogenation to methane and ethane, whereas sodium and potassium slightly increased the rate of hydrogenation on  $\text{Ni/SiO}_2 \cdot \text{Al}_2\text{O}_3$  (5, 6). These previous studies were done using only one promoter concentration and one preparation method. In this paper we used a differential reactor to

study CO hydrogenation on 12 Ni/SiO<sub>2</sub> and 8 Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts for a range of potassium concentrations and for several methods of promoter addition. Significant differences in activities and selectivities of promoted catalysts are observed for the two supports, and a strong dependence on promoter concentration is seen.

#### EXPERIMENTAL

A series of supported nickel catalysts was prepared with nickel concentrations near 10%, and potassium promoters were either added before or during nickel addition. Potassium concentrations from 0.05 to 4% were used, and K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, KCl, KNO<sub>3</sub>, and KOH were used as sources of potassium. Some catalysts were also calcined after nickel addition. The nickel and potassium contents were measured by atomic absorption.

The activity and selectivity for CO hydrogenation were measured in a continuous-flow, differential reactor with a 3:1 mixture of H<sub>2</sub>:CO at 1.2 atm. The 6-mm-o.d. Pyrex reactor had a 60-cm-long preheater coil and contained 100 mg of catalyst supported on a glass frit. A fluidized sand-bath heater was used for heating the reactor, and the catalyst temperature was measured with a Chromel–Alumel thermocouple. Product distributions were measured with an HP 5790A gas chromatograph with thermal conductivity and flame ionization detection. Olefins and paraffins up to C<sub>4</sub> were separated on a 1.8-cm Porapak Q column that was programmed between 311 and 423 K. An HP 3390A reporting integrator analyzed the data.

Kinetic data were obtained at four to eight temperatures for each catalyst. The reduced and passivated catalysts were preheated for 2 hr at 773 K in flowing H<sub>2</sub>, and in between exposures to the H<sub>2</sub>/CO mixture, a pure H<sub>2</sub> stream was used to clean the catalysts. All conversions were below 5% and flow rate and particle size changes indicated no diffusion limitations. Moreover, activation energies and turnover numbers

for the unpromoted catalysts were close to those reported by others. In repeat experiments on two different samples of each of the unpromoted catalysts, the activities at 553 K differed by 3.7% for Ni/SiO<sub>2</sub> and by 0.8% for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>.

The CO/H<sub>2</sub> premixed gas was purified with activated carbon and molecular sieve to remove carbonyls. The hydrogen (UHP grade, 99.999%) was purified through a Deoxo catalyst followed by a 5A molecular sieve in liquid nitrogen. The flow rates were controlled by a Tylan mass flow controller and typical rates were 150 cm<sup>3</sup>/min. The gas chromatograph was calibrated with a mixture of He and hydrocarbons purchased from Scientific Gas Products.

The nickel surface areas were measured by static chemisorption of H<sub>2</sub> in a diffusion-pumped vacuum system equipped with a Texas Instruments pressure gauge. The accuracy of the chemisorption system was checked with an ASTM standard Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### *Catalyst Preparation*

Davison grade 970 silica–alumina and Davison grade 57 silica were used for supports. This silica–alumina was 86.5% SiO<sub>2</sub> and 13.0% Al<sub>2</sub>O<sub>3</sub>, and it had a BET surface area of 100 m<sup>2</sup>/g. Its average pore diameter was 11.2 nm. The silica was 99.5% SiO<sub>2</sub> and had a BET surface area of 300 m<sup>2</sup>/g. The average pore diameter was 13.3 nm. These supports (60–80 mesh) were heated to 773 K in air for 24 hr before use. The unpromoted catalysts were prepared from nickel nitrate solution by incipient wetness (7). The catalysts were dried under vacuum at 400 K and then reduced in flowing hydrogen at 503 K for 1 hr. They were then heated to 773 K at 1 K/min and reduced for 10 hr at 773 K. They were finally passivated with a low concentration of O<sub>2</sub> in He.

The promoted catalysts were prepared as follows:

*Method A: Preimpregnation.* A potassium salt solution (K<sub>2</sub>CO<sub>3</sub> or KCl) was added dropwise to the oxide support, which

was then dried for 24 hr at 423 K. The support was then calcined at 743 K in flowing air for 3 hr. The resulting oxide was impregnated with  $\text{Ni}(\text{NO}_3)_2$  and reduced using the same procedure described for the unpromoted catalysts.

**Method B: Coimpregnation.** Three preparations were used, but they were all considered coimpregnation since no calcination or reduction steps were carried out between the impregnation steps. In method B1, the support was impregnated with  $\text{K}_2\text{C}_2\text{O}_4$ , dried, and then impregnated with  $\text{Ni}(\text{NO}_3)_2$ . In method B2, the support was impregnated with a solution of  $\text{Ni}(\text{NO}_3)_2$  and either  $\text{K}_2\text{C}_2\text{O}_4$ , KCl, or  $\text{KNO}_3$ . In method B3, the support was impregnated with  $\text{Ni}(\text{NO}_3)_2$ , dried and then impregnated with  $\text{K}_2\text{C}_2\text{O}_4$ . After impregnation, the catalysts were reduced using the same procedures described for the unpromoted catalysts.

**Method C: Calcination and postimpregnation.** Nickel nitrate solution was added to the support as described above. The dried sample was then calcined at 743 K in flowing air for 3 hr. A salt solution of  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{C}_2\text{O}_4$ , or KOH was then impregnated onto the sample. After drying, the sample was calcined again for 3 hr at 743 or 873 K in air; the catalyst was then reduced at 723 K in flowing  $\text{H}_2$  for 5 hr and passivated.

## RESULTS

A series of 12 Ni/SiO<sub>2</sub> catalysts was prepared with a range of potassium concentrations and with different promoter salts ( $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{KNO}_3$ , KCl, KOH) and different methods of preparation (A, B, C). The measured nickel and potassium weight loadings, the preparation methods, and the potassium salts are listed in Table 1. The percentage exposed is also listed for most of the catalysts. Note that the K : Ni atomic ratio for the promoted catalysts varied from 0.008 to 0.67. The atomic ratio is 1.5 times the weight ratio.

Similarly, 8 Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts

TABLE 1  
Ni/SiO<sub>2</sub> Catalyst Properties

No.	% Ni	% K	Preparation method	Promoter salt	Percentage exposed
1	9.2	0.0	Impregnation	Unpromoted	12.9
2	9.0	0.05	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	15.4
3	11.0	0.25	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	15.4
4	9.2	0.68	Coimpregnation (B1)	$\text{K}_2\text{C}_2\text{O}_4$	—
5	9.2	0.70	Coimpregnation (B2)	$\text{K}_2\text{C}_2\text{O}_4$	10.8
6	8.9	0.74	Coimpregnation (B3)	$\text{K}_2\text{C}_2\text{O}_4$	—
7	9.2	0.80	Calcination (C)	$\text{K}_2\text{C}_2\text{O}_4$	—
8	11.0	0.81	Preimpregnation (A)	KCl	4.5
9	9.8	0.82	Coimpregnation (B2)	KCl	3.0
10	10.5	0.83	Coimpregnation (B2)	$\text{KNO}_3$	7.5
11	9.8	0.89	Calcination (C)	KOH	—
12	9.2	4.1	Calcination (C)	KOH	6.7

were prepared (methods A, C) with a range of potassium concentrations using either  $\text{K}_2\text{CO}_3$  or KCl salts. The measured weight loadings are listed in Table 2, as are the preparation methods and promoter salts used. The K : Ni atomic ratio varied from 0.03 to 0.50. Table 2 lists the percentage exposed for five catalysts.

### Promoter Concentration and Support

**Ni/SiO<sub>2</sub>.** Activities for formation of methane and higher paraffins on Ni/SiO<sub>2</sub> catalysts decreased rapidly with potassium concentration while activities for olefin formation either increased or remained constant (Table 3). As a result, total activity decreased rapidly (Fig. 1) while the selectivities to olefins increased, as shown in Fig. 2. For example, addition of 0.74% K decreased the  $\text{CH}_4$  formation rate a factor of 22 but increased the rate of ethylene for-

TABLE 2  
Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> Catalyst Properties

No.	% Ni	% K	Preparation method	Promoter salt	Percentage exposed
13	9.5	0.0	Impregnation	Unpromoted	9.6
14	11.5	0.25	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	13.9
15	12.0	0.43	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	12.6
16	9.7	0.81	Preimpregnation (A)	KCl	11.3
17	11.0	0.93	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	—
18	11.0	0.97	Calcination (C)	$\text{K}_2\text{CO}_3$	—
19	11.5	3.9	Preimpregnation (A)	$\text{K}_2\text{CO}_3$	5.4
20	11.0	4.1	Calcination (C)	$\text{K}_2\text{CO}_3$	—

TABLE 3  
Kinetic Data at 553 K for Ni/SiO<sub>2</sub> Catalysts

Catalyst No.	% K	CH <sub>4</sub> Activity (μmol/g Ni · s)	E <sub>CH<sub>4</sub></sub> (kJ/mol)	Total activity (μmol/g Ni · s)	TON <sup>a</sup> × 10 <sup>2</sup> (s <sup>-1</sup> )	C <sub>2</sub> H <sub>4</sub> Activity (μmol/g Ni · s)
1	0.0	145	122 ± 3	182	8.3	0.06
2	0.05	89	109 ± 6	116	4.0	0.09
3	0.25	47	94 ± 9	67	2.6	0.13
4	0.68	5.1	131 ± 2	10.3	—	0.74
5	0.70	3.6	138 ± 2	7.3	0.35	0.58
6	0.74	4.0	128 ± 7	8.5	—	0.68
7	0.80	2.5	136 ± 2	5.9	—	0.67
8	0.81	2.2	126 ± 11	4.1	0.54	0.43
9	0.82	1.8	134 ± 3	3.6	0.61	0.30
10	0.83	4.5	121 ± 4	7.9	0.55	0.43
11	0.89	1.5	141 ± 3	3.5	—	0.46
12	4.1	~0.3	113	~0.3	~0.03	—

<sup>a</sup> Turnover number for CO conversion.

mation a factor of 10. Thus, the ethylene selectivity increased a factor of 220. The C<sub>3</sub> olefin formation rate did not increase as dramatically as C<sub>2</sub>, or it decreased. Table 4 presents product distributions for all the Ni/SiO<sub>2</sub> catalysts studied. Note that at 553 K a

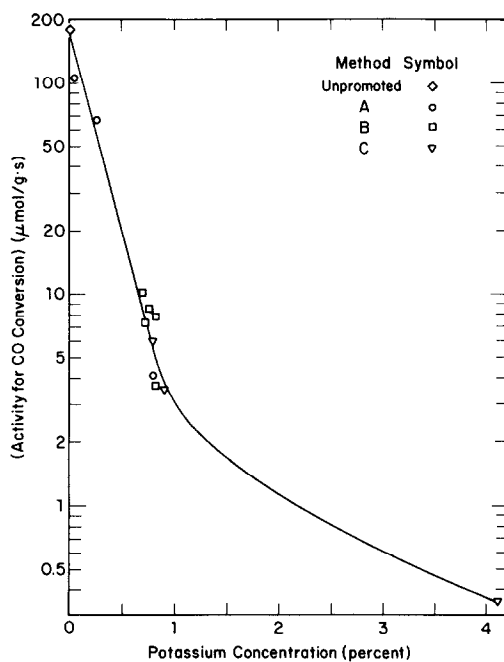


FIG. 1. Logarithm of total activity (μmol/g Ni · s) at 553 K versus potassium concentration for Ni/SiO<sub>2</sub> catalysts.

large fraction of the products are ethylene or propylene, and only a small fraction is propane at higher promoter concentrations.

Figure 1 and Table 3 present activity data on a per gram nickel basis to show the effectiveness of the nickel after promoter addition. The percentage nickel exposed increased slightly at low K loading and decreased at higher K loadings (Table 1). The turnover numbers (Table 3) thus followed similar trends to those shown in Fig. 1; the large decreases in rates with addition of alkali promoter are not due to the decreased surface areas.

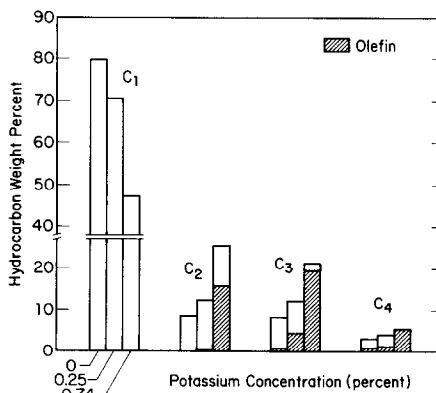


FIG. 2. Product distributions for Ni/SiO<sub>2</sub> catalysts at 553 K as a function of potassium concentration.

TABLE 4  
Ni/SiO<sub>2</sub> Catalysts: Selectivities at 553 K

No.	% K	C <sub>1</sub>	C <sub>2</sub> <sup>-</sup>	C <sub>2</sub>	C <sub>3</sub> <sup>-</sup>	C <sub>3</sub>	C <sub>4</sub> <sup>-</sup>	C <sub>4</sub>
1	0.0	79.7	0.1	8.6	0.8	7.6	0.9	2.3
2	0.05	76.2	0.2	9.7	1.6	7.8	1.2	3.3
3	0.25	70.8	0.4	12.3	4.6	7.6	1.3	3.0
4	0.68	49.2	14.3	10.5	19.7	1.6	4.7	~0
5	0.70	50.0	16.0	10.0	18.3	1.0	4.7	~0
6	0.74	47.3	15.9	9.7	19.5	1.8	5.8	~0
7	0.80	43.2	22.6	5.3	21.6	0.7	6.6	~0
8	0.81	54.5	21.3	3.5	19.3	1.3	—	0.15
9	0.82	50.6	16.5	5.7	16.1	1.0	10.1	~0
10	0.83	56.4	10.8	10.8	16.1	1.6	4.3	~0
11	0.89	42.4	26.1	4.2	19.5	~0	7.8	~0
12	4.1	~100	—	—	—	—	—	—

For most of the Ni/SiO<sub>2</sub> catalysts, the change in CH<sub>4</sub> apparent activation energy with addition of promoter (Table 3) was not large; values ranged from 94 to 141 kJ/mol, and most values were between 121 and 141 kJ/mol. No trend in activation energies with promoter concentration was evident.

Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>. Potassium had a significantly different effect on both activity and selectivity for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts. The methane and total conversion activities increased at low promoter concentrations and a decrease was only seen above 0.93% K. Thus, the paraffin activities went through a maximum at low potassium concentrations, as shown in Fig. 3. The selectivity to methane, however, decreased monotonically with promoter concentration

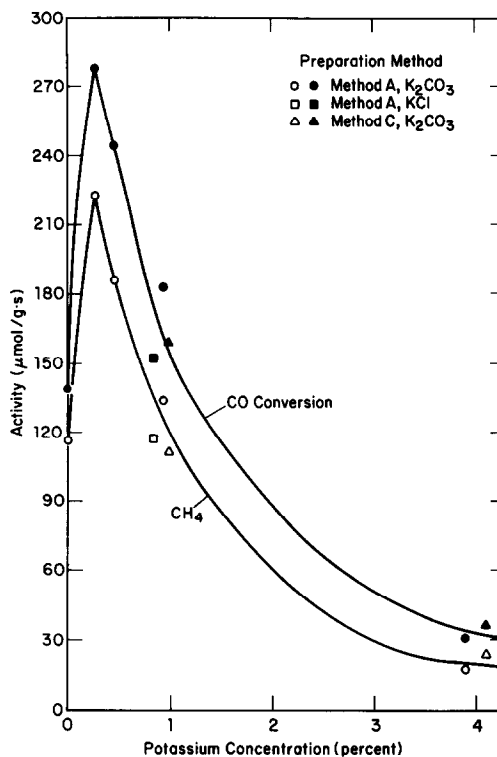


FIG. 3. Activity at 553 K for CH<sub>4</sub> formation and for CO conversion on Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts, versus potassium concentration.

because of increased activities for formation of higher paraffins.

Percentage exposed increased at the lower promoter concentrations, but turnover numbers (Table 5) also exhibited the

TABLE 5  
Kinetic Data at 553 K for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> Catalysts

Catalyst No.	% K	CH <sub>4</sub> Activity (μmol/g Ni · s)	E <sub>CH<sub>4</sub></sub> (kJ/mol)	Total activity (μmol/g Ni · s)	TON <sup>a</sup> × 10 <sup>2</sup> (s <sup>-1</sup> )	C <sub>2</sub> H <sub>4</sub> Activity (μmol/g Ni · s)
13	0.0	116	110 ± 7	140	8.6	0.08
14	0.25	222	107 ± 4	278	11.7	0.06
15	0.43	187	115 ± 5	244	11.4	0.07
16	0.81	117	125 ± 9	151	7.8	0.11
17	0.93	134	119 ± 4	183	—	0.09
18	0.97	112	113 ± 7	160	—	0.20
19	3.9	18	116 ± 2	31	3.4	0.39
20	4.1	23	109 ± 6	37	—	0.61

<sup>a</sup> Turnover number for CO conversion.

same trend as in Fig. 3; the decrease in turnover number was slower at higher promoter concentration because the percentage exposed decreased at higher promoter concentrations. For a promoter loading of 3.9%, the turnover number was 40% of that for the unpromoted Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>.

Olefin selectivities decreased on Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>, in contrast to Ni/SiO<sub>2</sub>. As shown in Fig. 4 and Table 5, only above 0.93% K did olefin activities and selectivities increase significantly. Even for a catalyst with 3.9% K, the C<sub>2</sub> olefin/paraffin ratio was only 0.18, a value well below that seen on promoted Ni/SiO<sub>2</sub> catalysts.

Though the activities and selectivities changed for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts, the activation energies were essentially constant; the average value was 114 ± 6 kJ/mol (Table 5).

Physical mixtures of catalyst with excess support had the same activities and selectivities for Ni/SiO<sub>2</sub> and for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> as the pure catalysts, indicating that secondary reactions on the supports were probably not important under these reaction conditions.

#### Effect of Potassium Salt

Two coimpregnation Ni/SiO<sub>2</sub> catalysts with the same K loadings were prepared using KCl (No. 9) and KNO<sub>3</sub> (No. 10).

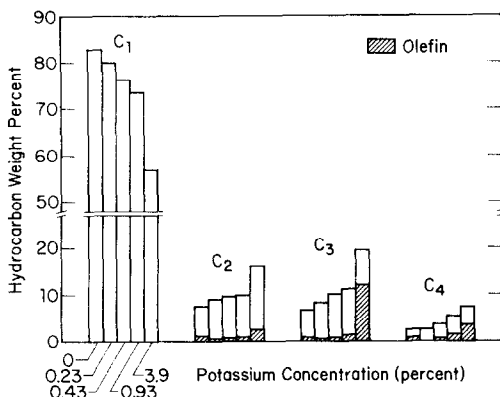


FIG. 4. Product distributions for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts at 553 K as a function of potassium concentration. Promoted catalysts were prepared by preimpregnation of K<sub>2</sub>CO<sub>3</sub>.

They had different percentages exposed but the same turnover numbers. Likewise, catalysts 7 and 11 had similar K loadings but used K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and KOH, respectively, in preparation; the slight differences in activities are apparently due to differences in K loading, not the K salt used.

The smooth fit of the activity versus concentration curves (Figs. 1 and 3), which are for catalysts prepared with five different potassium salts, show that for a given support the K loading is the major cause of activity differences; the changes in catalytic properties for different potassium salts are similar.

#### Preparation Method

Three catalysts (4–6) prepared by coimpregnation with K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to the same K loading (0.7%) on Ni/SiO<sub>2</sub> had similar activities (within 30% of each other), similar product distributions, and their activation energies were within 10 kJ/mol of each other. Since three methods of coimpregnation (B1, B2, B3) were used to prepare these catalysts, the order of promoter addition does not appear to be important.

Since the use of different promoter salts had similar influences on changes in activities and selectivities, the smooth curves in Figs. 1 and 3 also indicate that the preparation methods (A, B, C) made little difference in the changes observed due to promoter addition. For example, catalysts 19 and 20 had similar K loading and similar activities though catalyst 19 was made by preimpregnation and catalyst 20 was made by calcination. Similarly, catalysts 8 and 9 were prepared by two different methods with the same K loading and the same K salt; their turnover numbers were almost identical and their percentage exposed were similar. Catalysts 7 and 8 were prepared with different promoter salts (K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and KCl) and by different methods (C, A), but their methanation activities were within 15% of each other, again demonstrating the small effects due to different preparation methods.

### Olefin/Paraffin Ratios

In Fig. 5 the olefin/paraffin ratio is plotted, on a log-log scale, for  $C_2$  and  $C_3$  hydrocarbon products as a function of inverse total activity for all the catalysts studied. An excellent correlation is obtained between olefin/paraffin ratio and inverse total activity. These plots show that for all preparations and promoter salts, except perhaps at very low total activity, the olefin/paraffin ratio increased as the total activity decreased. Figure 5 also shows that for all catalysts studied, the olefin/paraffin ratio is an order of magnitude larger for  $C_3$  than for  $C_2$  hydrocarbons over the entire range of activities.

### DISCUSSION

The catalyst support and the promoter concentration are the major factors influencing the activity and selectivity of alkali-promoted nickel catalysts for CO hydrogenation. The method of preparation, for the methods used, and the potassium salt make little difference for the same promoter loading. Some decomposition of the salts apparently occurs to form the same potassium compound. Percentage nickel exposed increased slightly at low promoter concentrations and decreased a factor of 2 or 3 at higher promoter concentrations.

The differences in activities and selectivities of promoted  $Ni/SiO_2$  and  $Ni/SiO_2 \cdot Al_2O_3$  are not just a matter of degree. Alkali promoters decrease hydrogenation rates exponentially with concentration and increase olefin selectivities on  $Ni/SiO_2$ ; on  $Ni/SiO_2 \cdot Al_2O_3$ , hydrogenation rates increase and olefin selectivities decrease, except at high K loadings. The strong dependence on support indicates that more than just a K-Ni interaction is responsible for the changes in kinetics that occur due to addition of alkali promoters. Since a large fraction of the total surface area of the catalyst is the support, much of the promoter, at least during initial catalyst preparation,

may be on the support. This promoter may react with acid sites on  $Ni/SiO_2 \cdot Al_2O_3$  catalysts.

### $Ni/SiO_2$ Catalysts

Turnover numbers decreased exponentially on  $Ni/SiO_2$  catalysts and olefin selectivities increased significantly with increased promoter concentration. The olefin selectivity is higher due to decreased conversion, but comparisons at the same conversions also showed higher olefin selectivities for promoted catalysts. This is seen even though this comparison requires a higher temperature for the promoted catalyst, and higher temperatures favor paraffins. Other studies have also reported that alkali promoters decrease methanation ac-

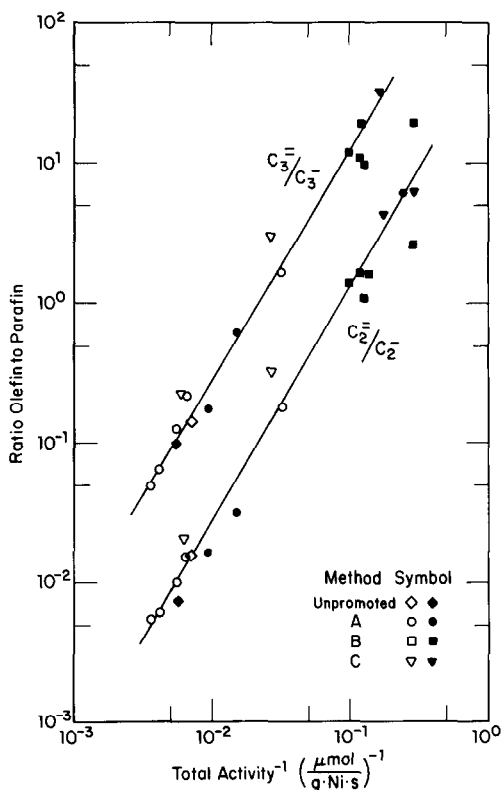


Fig. 5. Logarithm of olefin/paraffin ratio for  $C_2$  and  $C_3$  hydrocarbons versus logarithm of the inverse of total activity for CO conversion at 553 K. Solid symbols are  $Ni/SiO_2$  catalysts and open symbols are  $Ni/SiO_2 \cdot Al_2O_3$  catalysts.

tivity (1–3, 8) and increase olefin selectivity (2, 3) on transition metal catalysts. The turnover number for methane formation at 548 K on unpromoted Ni/SiO<sub>2</sub> ( $5.2 \times 10^{-2} \text{ s}^{-1}$ ) is in excellent agreement with Vanice's value of  $4.5 \times 10^{-2} \text{ s}^{-1}$  (9).

#### *Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> Catalysts*

The Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalysts behaved quite differently from Ni/SiO<sub>2</sub> when potassium promoter was added. Instead of decreasing hydrogenation rates, alkali promoters increase the activities for methane and higher paraffin formation. The turnover numbers for CO conversion exhibit a maximum at low concentrations, and even at high concentrations the decrease in rate is small. The turnover number for unpromoted Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> is close to that measured for Ni/SiO<sub>2</sub>. The turnover number for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> with 3.9% K, however, is 130 times that of Ni/SiO<sub>2</sub> with the same promoter concentration. Note in Figs. 1 and 3 that the activity for Ni/SiO<sub>2</sub> is on a log scale, while that for Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> is on a linear scale. Also note that the turnover number for unpromoted Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> is approximately nine times the value measured by Huang and Richardson (4) on unpromoted Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>.

Though methanation activity increases with promoter addition, CH<sub>4</sub> selectivity decreases as higher paraffin selectivity increases. Also, for K concentrations below 0.97%, olefin selectivity decreases, in sharp contrast to the promoted Ni/SiO<sub>2</sub> catalysts. As the activity for paraffin formation drops at higher promoter concentrations, the activity for olefin formation increases. Thus, the percentage of higher hydrocarbons (saturated and unsaturated) increases monotonically with promoter concentration.

Huang and Richardson (4) observed a similar maximum in CH<sub>4</sub> yield with sodium promoter concentration; they did not measure the yield of higher hydrocarbons. They used preimpregnation of NaCl so the results are directly comparable to our catalysts prepared by K<sub>2</sub>CO<sub>3</sub> and KCl preimpregnation.

Their silica–alumina had 25% Al<sub>2</sub>O<sub>3</sub> and they used sodium promoters so the location and magnitude of the maximum rate would be expected to be different from our results. Their maximum was at a ratio of 0.062 promoter atoms per nickel while ours was at 0.033 promoter atoms per nickel. Huang and Richardson also observed a systematic change in activation energy with promoters, and we did not.

#### CONCLUSIONS

On supported nickel the modifications in catalytic properties by alkali promoters are not just due to a K–Ni interaction. The activity and selectivity for CO hydrogenation on promoted catalysts are shown to depend on the oxide support as strongly as the promoter concentration. Similar turnover numbers are observed for unpromoted Ni/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>; on promoted Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>, the hydrogenation turnover number is 130 times larger than that for promoted Ni/SiO<sub>2</sub>. Total hydrogenation activity decreases exponentially with promoter concentration for Ni/SiO<sub>2</sub> while activities for olefin formation increase; potassium on Ni/SiO<sub>2</sub> decreases hydrogenation rates. On Ni/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> hydrogenation rates to form paraffins increase and olefin selectivities decrease with promoter addition, except at high potassium concentrations. Maximums in methane and total CO conversion turnover numbers are seen.

For the preparation methods used, changing the preparation method or the potassium salt did not significantly change the activity or selectivity. At low concentrations, potassium increased the percentage exposed, at higher concentrations it decreased percentage exposed. A good correlation was seen between the olefin/paraffin ratio and the inverse overall activity. The olefin/paraffin ratio was 10 times larger for C<sub>3</sub> than for C<sub>2</sub> hydrocarbons.

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