

Support and Crystallite Size Effects in CO Hydrogenation on Nickel

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Adsorption and CO hydrogenation activity/selectivity properties of well-defined Ni/SiO₂, Ni/Al₂O₃, and Ni/TiO₂ catalysts representing wide ranges of dispersion and nickel concentration were investigated. CO and H₂ adsorption uptakes were determined for all of the catalysts. The extent of reduction to the metal was also determined for all catalysts by oxygen titration or nickel carbonyl extraction. Specific activities for CO/H₂ synthesis were measured for each of the catalysts at 500–550 K and 140 kPa. Effects of strong metal–support interactions are evident in Ni/TiO₂, in well-dispersed Ni/Al₂O₃, and to a lesser extent in very well-dispersed Ni/SiO₂ from (i) changes in the nature and stoichiometry of CO and H₂ adsorption and (ii) significant changes in activity and selectivity properties for CO/H₂ synthesis with changes in metal dispersion, support, preparation technique, and catalyst pretreatment. Both CO/H adsorption ratio and selectivity to C₂₊ hydrocarbons increase with increasing metal dispersion in Ni/SiO₂ and Ni/Al₂O₃ systems, suggesting that metal–support interactions affect selectivity by changing the relative abundance of adsorbed CO and H₂ during reaction.

INTRODUCTION

Modifications in the adsorption and activity/selectivity properties of nickel as a result of changes in support and metal crystallite size were reported nearly two decades ago (1, 2). However, only recently has the significance of such effects found widespread appreciation. Indeed several recent studies (3–7) provide evidence that CO and H₂ adsorption and CO hydrogenation activity/selectivity properties of nickel are significantly influenced by such effects.

Vannice reported the kinetic behavior of nickel catalysts on a variety of supports and as a function of metal crystallite size (3). There was evidence from his results that the specific activity of nickel is sensitive to the support material and varies with metal crystallite size within an order of magnitude. Bhatia *et al.* (4) reported that methanation activities for a series of Ni/Al₂O₃ catalysts were influenced significantly by particle size and nickel concentration. Vannice and Garten (5) found evidence that strong metal–support interactions markedly influence H₂ and CO adsorption and

activity/selectivity properties in H₂/CO synthesis on Ni/TiO₂.

Although these previous studies (3–5) suggested ways in which support and crystallite size influence adsorption and activity/selectivity properties of nickel, they did not establish consistent, unambiguous trends for either support or crystallite size effects nor a relationship between the two kinds of effects. Moreover, comparisons of adsorption and activity/selectivity properties of different catalysts were made without due regard to effects of preparation, metal loading, metal dispersion, and extent of reduction to the metal, all of which could have influenced the outcome of these comparisons.

In recent companion studies (6, 7) we investigated the influence of support and metal dispersion on CO and H₂ adsorption stoichiometries on Ni/Al₂O₃, Ni/SiO₂, and Ni/TiO₂ catalysts. Metal crystallite size was determined by X-ray diffraction and transmission electron microscopy, extent of reduction by oxygen titration (8). Room temperature hydrogen adsorption on alumina- and silica-supported nickel was

found to occur with a stoichiometry of one hydrogen atom per surface nickel atom over a wide range of nickel loading and dispersion. However, on Ni/Al₂O₃ catalysts containing less than 3 wt% Ni and on Ni/TiO₂ catalysts less than monolayer adsorption of H₂ occurred at 298 K, presumably as a result of strong metal-support interactions. CO adsorption was considerably more complex, the stoichiometry of which was observed to vary with equilibration pressure, temperature, nickel loading, and dispersion. In the Ni/Al₂O₃ system, the CO/H adsorption ratio was found to increase with decreasing nickel concentration and extent of reduction to the metal. The modification of H₂ and CO adsorption properties of nickel by the support, it was felt, should have significant effects on the reaction between these two molecules in CO/H₂ synthesis.

The present study was undertaken to investigate systematically the influence of support, nickel loading, and nickel dispersion on CO hydrogenation activity and selectivity for the same well-characterized Ni/Al₂O₃, Ni/SiO₂, and Ni/TiO₂ catalysts used in the adsorption studies. The effects of catalyst preparation, pretreatment, and extent of reduction to the metal were simultaneously considered.

EXPERIMENTAL

Materials

Hydrogen and nitrogen gases (99.99%, Whitmore) were simultaneously purified using a Pd Deoxo catalyst (Engelhard) followed by a Molecular Sieve 5A (Linde) trap. CO (99.99%, Matheson) was also passed through a molecular sieve trap to remove iron carbonyl.

Alumina-supported catalyst (with the exception of 2.9% Ni/Al₂O₃) were prepared by impregnation with a Ni(NO₃)₂ solution to incipient wetness of Kaiser SAS 5 × 8 mesh alumina (301 m²/g) previously calcined 2 hr at 873 K; after impregnation the catalysts were dried at 373 K in a

forced-air circulation oven for at least 24 hr. Several impregnations were used in order to distribute the active catalytic material more uniformly through the internals of the support. Two Ni/SiO₂ catalysts and one 2.8% Ni/TiO₂ catalyst were prepared by similar impregnations of Cab-O-Sil SiO₂ (200 m²/g, Cabot Corporation) and P-25 TiO₂ (Degussa Corp.). The TiO₂ material (anatase form) was prepared commercially by flame hydrolysis of TiCl₄ and had a BET surface area of about 50 m²/g. Two other silica-supported catalysts, a 2.9% Ni/Al₂O₃ and a 2.8% Ni/TiO₂, were prepared by means of a controlled pH precipitation technique described by van Dillen *et al.* (9) using the same alumina silica, and titania. All of these samples were also dried 24 hr at 373 K.

Large samples (50–100 g) of each catalyst were reduced in a large reduction apparatus using flowing hydrogen at a space velocity of 1500–2000 hr⁻¹ according to a temperature schedule previously reported (8, 10) followed by a 15-hour hold at 725 K. After cooling to 298 K, the samples were passivated using a 1% air in N₂ stream at 2000–5000 hr⁻¹. Percentage nickel loadings were determined for most of the catalysts by Rocky Mountain Geochemical Corporation using atomic absorption spectroscopy.

Apparatus and Procedure

Chemisorption measurements. Gas adsorption measurements were carried out in a conventional Pyrex glass volumetric adsorption apparatus previously described (10, 11). Measurement of total H₂ uptake at 298 K and irreversible CO uptake at 190 and 273 K were also described previously (10, 11). The accuracy of the adsorption measurements was generally ±10%. Calculations of nickel surface area, dispersion, and average metal crystallite size for supported nickel were discussed previously (7, 10). The site density of 6.77 × 10⁻² (nm)²/atom used in these calculations was based on an equal distribution of the three lowest index planes of nickel (fcc). In cal-

culating metal dispersion (or the fraction of metal atoms exposed) the metal loading was multiplied by the fraction of nickel reduced to the metallic state, based on the assumption that unreduced nickel is present in a separate dispersed phase in intimate contact with the support (7). Thus the equation used to calculate dispersion was:

$$\%D = \frac{1.17X}{Wf} \quad (1)$$

where X = H_2 uptake in μ moles/g of catalyst, W = the weight percent of nickel, and f = the fraction of nickel reduced to the metal. Average crystallite diameters were calculated from $\%D$ assuming spherical metal crystallites, all having the same size d . Thus

$$d = 971/(\%D). \quad (2)$$

Extent of reduction to the metal was determined for Ni/Al₂O₃ and Ni/SiO₂ catalysts by O₂ titration at 723 K and for Ni/TiO₂ catalysts by Ni(CO)₄ extraction (8).

Rate measurements. Measurements of CO/H₂ synthesis activity were performed in a differential, fixed bed Pyrex reactor (10) mounted in a laboratory reactor system previously described (10). Samples of 0.2–0.5 g were pretreated in flowing H₂ at 725 K for 2 hr and reactor tested at 500, 525, and 550 K (140 kPa). Space velocities were varied from 30,000 to 100,000 hr⁻¹ to maintain differential conditions and yet unsure measurable conversions (2–10%) to CH₄. The reactant feed was a 1% CO, 4% H₂, and 95% N₂ mixture. The N₂ diluent served to maintain isothermal operation at low conversions and thus the absence of heat and mass transport influences. Reactant and product gas samples were automatically analyzed by a programmable gas chromatograph (Hewlett–Packard) equipped with thermal conductivity and flame ionization detectors and activated carbon, molecular sieve, and Chromosorb-102 columns. The analysis for product gases was repeated five to six times for each catalyst

sample and temperature. For the majority of catalysts, activity measurements were repeated for two to four aliquot samples of the same catalyst preparation; repeatability was generally $\pm 25\%$ or better.

RESULTS

Adsorption and CO hydrogenation activity data for Ni/Al₂O₃, Ni/SiO₂, and Ni/TiO₂ catalysts are summarized in Tables 1–3, respectively. Some of the adsorption data for Ni/Al₂O₃ and Ni/SiO₂ were reported elsewhere (6) but are nevertheless included to enable complete and comprehensive comparisons. Table 1 reveals several interesting trends for Ni/Al₂O₃ catalysts. H₂ adsorption uptake, percentage reduction to the metal, and methane yield (fraction of converted CO which appears as methane) increase, while CO/H ratio and percentage dispersion (% Ni exposed) decrease with increasing nickel content.

Specific activities in the form of turnover numbers (the molecules of CO converted or CH₄ produced per catalytic site per second) for Ni/Al₂O₃ are also listed in Table 1 and plotted against dispersion in Figs. 1 and 2. If CO adsorption is used as the basis for 0.5 and 1% Ni/Al₂O₃ and either CO or H₂ adsorption as the basis for other catalysts, the N_{CO} values (for catalysts prepared by impregnation) lie in the range of 1.4 to 5.5×10^{-3} sec⁻¹ with no evident trend as a function of metal loading or dispersion (see Table 1 and Fig. 1). Methane turnover number clearly decreases with increasing dispersion (see Fig. 2).

Data for Ni/SiO₂ in Table 2 reveal trends in percentage reduction and CO/H values with loading and dispersion similar to those for Ni/Al₂O₃. However, the extent of reduction to the metal and methane yield are larger for larger nickel contents and smaller dispersions. Values of methane turnover numbers at 525 K apparently also decrease with increasing nickel dispersion (see Fig. 2), although the variations over the range are smaller. A striking similarity is evident in the curves of C₂₊ yield/CH₄ yield versus

TABLE 1
Adsorption and CO Hydrogenation Activity Data for Ni/Al₂O₃ Catalysts

| Sample (wt% Ni) | H ₂ Uptake ^a (μmoles/g) | CO/H ^b | Percentage reduction ^c | Percentage dispersion ^d | Average crystallite diameter (nm) | Turnover number ^e × 10 ³ at 500 K (sec ⁻¹) | | Percentage yield ^f at 500 K | | | E _{act} ^g (kJ/mol) |
|------------------------|--|-------------------|--------------------------------------|---------------------------------------|--|--|-----------------------------|--|-----------------|-----------------|--|
| | | | | | | N _{CO} | N _{CH₄} | CH ₄ | CO ₂ | C ₂₊ | |
| | | | | | | | | | | | |
| 0.5 | 0.8 | 28 | 29 | 59 | 1.6 | 17(2.2) ^j | 3.0(0.4) ^j | 18 | 0 | 82 | 117 |
| 1.0 | 4.6 | 9.9 | 42 | 42 | 2.3 | 17(5.5) ^j | 5.2(1.6) ^j | 30 | 0 | 70 | 88 |
| 2.9 ^h fresh | 37 | 3.6 | 68 | 22 | 4.4 | 14 | 2.1 ± 0.8 | 15 | 0 | 85 | 96 |
| calcined ⁱ | 5 | 20 | 19 | 11 | 8.8 | 14 | 4.3 | 30 | 0 | 70 | 71 |
| 3 | 36 | 1.9 | 64 | 22 | 4.4 | 1.9 | 1.3 ± 0.3 | 68 | 0 | 32 | 111 |
| | 26 | — | — | 16 | 6.1 | 1.4 | 1.0 | — | — | — | 111 |
| 9 | 108 | 1.1 | 75 | 19 | 5.1 | 2.2 | 1.8 | 82 | 3 | 15 | 90 |
| 14 | 188 | 0.95 | 84 | 17 | 5.7 | 2.0 | 1.7 | 85 | 7 | 8 | 107 |
| 23 | 283 | 0.8 | 97 | 15 | 6.5 | 4.0 | 3.4 | 84 | 2 | 14 | 87 |
| | 208 | — | 94 | 11 | 8.8 | 4.2 | 3.5 | — | — | — | 110 |

^a Total H₂ uptake at 298 K corrected for 0.5 μmoles/g adsorption on support.

^b Molecules of CO adsorbed per atom of hydrogen adsorbed.

^c Based on O₂ uptake at 725 K assuming formation of NiO.

^d Based on H₂ uptake at 298 K, corrected for the amount reduced to the metal. Values for 0.5 and 1.0% Ni/Al₂O₃ are based upon CO adsorption, assuming CO/Ni_s = 3.

^e Molecules CO converted or CH₄ produced per catalytic site per second; site density measured by H₂ adsorption at 298 K.

^f Yield is the fraction of converted CO appearing as a given product.

^g Activation energy calculated from turnover numbers at 500 and 525 K.

^h Prepared by precipitation; all other catalysts were prepared by impregnation.

ⁱ Calcined at 775 K.

^j Turnover numbers in parentheses are based on CO adsorption assuming CO/Ni_s = 3.

TABLE 2
Adsorption and CO Hydrogenation Activity Data for Ni/SiO₂ Catalysts

| Sample (wt% Ni) | H ₂ uptake ^a (μmoles/g) | CO/H ^b | Percentage reduction ^c | Percentage dispersion ^d | Average crystallite diameter ^e (nm) | Turnover number ^e × 10 ³ at 525 K (sec ⁻¹) | | Percentage yield ^f at 525 K | | | E _{act} ^g (kJ/mole) |
|-------------------------------|--|-------------------|--------------------------------------|---------------------------------------|---|--|-----------------------------|--|-----------------|-----------------|---|
| | | | | | | N _{CO} | N _{CH₄} | CH ₄ | CO ₂ | C ₂₊ | |
| | | | | | | | | | | | |
| 2.7 ^h fresh | 85 | 3.2 | 71 | 51 | 1.9 | 2.5 | 1.4 | 55 | 0 | 45 | 79 |
| calcined 575 K | 35 | 1.7 | 91 | 16 | 6.1 | 3.9 | 2.6 | 66 | 0 | 34 | 96 |
| calcined 775 K | 30 | 1.5 | 97 | 13 | 7.5 | 5.5 | 4.9 | 89 | 0 | 11 | 83 |
| 3.6 ⁱ fresh | 81 | 1.1 | 71 | 37 | 2.6 | 1.9 | 1.3 ± 0.3 | 68 | 0 | 32 | 104 |
| | 73 | — | — | 33 | 2.9 | 2.3 | 1.8 | 78 | 0 | 22 | 110 |
| | 58 | — | — | 26 | 3.3 | 1.7 | 1.4 | 81 | 0 | 19 | 112 |
| 13.5 ⁱ fresh | 442 | 1.1 | 93 | 41 | 2.4 | 3.0 | 2.4 ± 0.3 | 82 | 12 | 6 | 92 |
| | 362 | — | — | 34 | 2.9 | 2.8 | 2.1 | 74 | 2 | 24 | 92 |
| | 290 | — | — | 27 | 3.6 | 1.9 | 1.9 | 99 | 0 | 1 | 99 |
| 15 ^h fresh | 217 | 3.0 | 90 | 19 | 5.1 | 2.9 | 2.3 | 80 | 0 | 20 | 100 |
| reduced with H ₂ O | 115 | 1.0 | 73 | 12 | 8.1 | 4.7 | 4.6 | 97 | 0 | 3 | 89 |
| calcined 575 K | 68 | 1.3 | 90 | 5.9 | 16 | 4.1 | 4.1 | 100 | 0 | 0 | 88 |
| calcined 775 K | 61 | 0.65 | 82 | 5.8 | 17 | 4.8 | 4.1 | 85 | 0 | 15 | 88 |

^a Total H₂ uptake at 298 K corrected for 0.4 μmoles/g adsorption on support.

^b Molecules of CO adsorbed per atom of hydrogen adsorbed.

^c Based on O₂ uptake at 725 K assuming formation of NiO.

^d Based on H₂ adsorption at 298 K, corrected for the amount reduced to the metal.

^e Molecules CO converted or CH₄ produced per catalytic site per second; site density measured by H₂ adsorption at 298 K.

^f Yield is the fraction of converted CO appearing as a given product.

^g Activation energy calculated from turnover numbers at 500 and 525 K.

^h Prepared by impregnation.

ⁱ Prepared by precipitation.

TABLE 3
Adsorption and CO Hydrogenation Activity Data for Ni/TiO₂ Catalysts

| Sample (wt% Ni) | H ₂ uptake ^a (μmoles/g) | CO/H ^b | Percentage reduction ^c | Percentage dispersion ^d | Average crystallite diameter ^d (nm) | Turnover number ^e × 10 ³ at 500 K (sec ⁻¹) | | Percentage yield ^f at 500 K | | | E _{act} ^g (kJ/mole) |
|--------------------|--|-------------------|--------------------------------------|---------------------------------------|---|--|-----------------------------|--|-----------------|-----------------|---|
| | | | | | | N _{CO} | N _{CH₄} | CH ₄ | CO ₂ | C ₂₊ | |
| 2.8 ^h | 21 | 1.6 | 75 | 12 | 8.1 | 16 | 5.5 ± 1.4 | 35 | 0 | 65 | 88 |
| 2.8 ⁱ | 20 | 2.2 | 74 | 11(18) | 8.8(5.5) | 22 | 13 ± 2.1 | 60 | 0 | 40 | 84 |
| 15 ^j | 49 | — | 90 | 4.3(9.7) | 23(10) | — | — | — | — | — | — |
| 15 ^j | 1 | — | — | 0.1(2.7) | 1000(35) | — | — | — | — | — | — |

^a Total H₂ uptake at 298 K.

^b Molecules of CO adsorbed per atom of hydrogen adsorbed.

^c Determined by extraction of the metal as Ni(CO)₄ at 80°C according to Ref. (16).

^d Based on H₂ adsorption at 298 K, corrected for the amount reduced to the metal. Percentage dispersion and average crystallite diameter in parentheses were determined by transmission electron microscopy.

^e Molecules CO converted or CH₄ produced per catalytic site per second; site density measured by H₂ adsorption at 298 K.

^f Yield is the fraction of converted CO appearing as a given product.

^g Activation energy calculated from turnover numbers at 500 and 525 K.

^h Prepared by precipitation.

ⁱ Prepared by impregnation.

^j Sintered 3 hr at 1023 K in H₂.

nickel dispersion for Ni/SiO₂ and Ni/Al₂O₃ in Fig. 3. Indeed, the two plots are nearly superimposed, when the ordinate scale for Ni/Al₂O₃ is reduced by a factor of 5.

Data for three Ni/TiO₂ catalysts in Table 3 reveal at least two interesting facts: (i) average crystallite diameters determined by hydrogen adsorption are a factor of 2 larger than those determined from transmission

electron microscopy and (ii) methane yield is significantly lower for the 2.8% catalyst prepared by precipitation.

The effects of support and catalyst preparation on the activity and selectivity properties of nickel are illustrated in Table 4 and Figs. 4 and 5. Table 4 lists turnover numbers for CO conversion and methane production on unsupported nickel and nickel

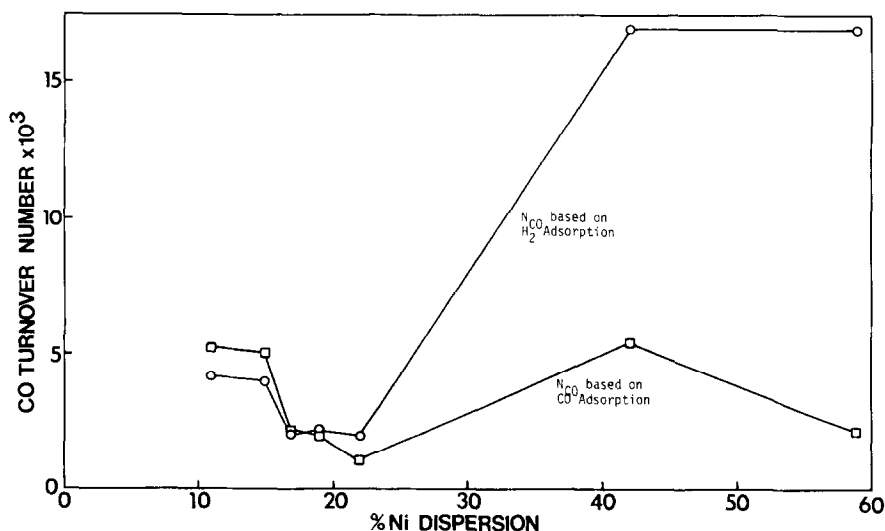


FIG. 1. CO turnover number at 500 K versus nickel dispersion for impregnated Ni/Al₂O₃ catalysts: ○ based on H₂ adsorption; □ based on CO adsorption.

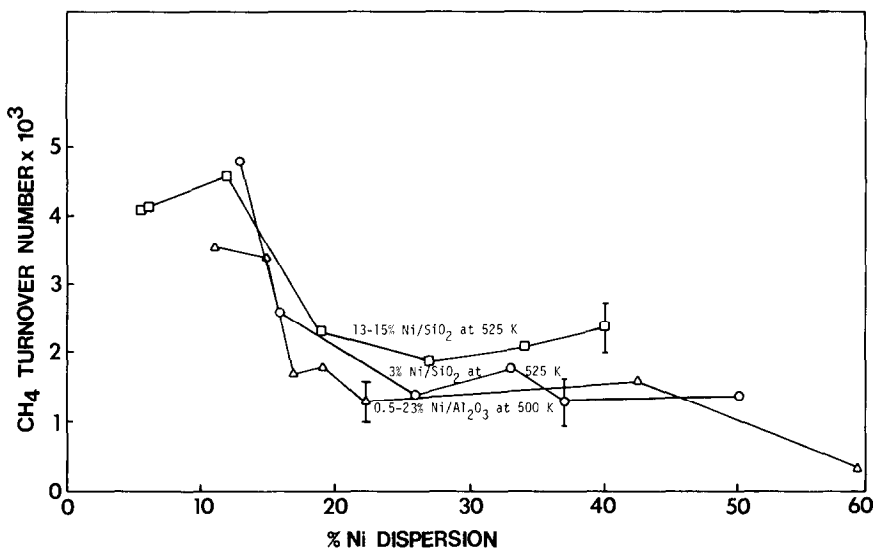


FIG. 2. CH₄ turnover number versus percentage Ni dispersion for Ni/SiO₂ and Ni/Al₂O₃ catalysts: ○ 3% Ni/SiO₂ at 525 K; □ 13-15% Ni/SiO₂ at 525 K; △ 0.5-23% Ni/Al₂O₃ at 500 K.

supported on alumina, silica, and titania, each prepared by two different techniques, impregnation and precipitation. An effort was made to prepare and compare supported catalysts having approximately the same metal dispersion and nickel content. The data in Table 4 and Fig. 4 reveal that both Ni/SiO₂ catalysts of moderately low dispersion display activities and selectivities comparable to those of unsupported nickel. Ni/Al₂O₃ and Ni/TiO₂ catalysts have significantly higher turnover numbers; indeed, the order of decreasing activity is Ni/TiO₂ > Ni/Al₂O₃ > Ni/SiO₂ = Ni.

Figure 5 compares methane yields for the freshly reduced 3% nickel catalysts at three different temperatures, 500, 525, and 550 K. Selectivity to methane obviously increases with increasing temperature. At any given temperature, methane yields for precipitated Ni/Al₂O₃ and Ni/TiO₂ are significantly less than for the impregnated catalysts.

DISCUSSION

The results of this and companion studies (6, 7) conducted over wide ranges of nickel loading and dispersion on three different

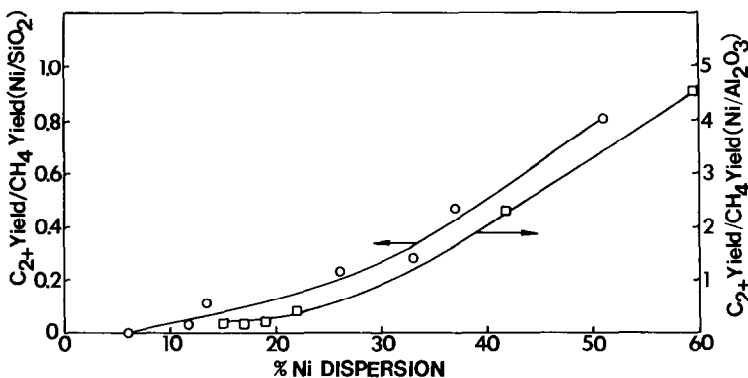


FIG. 3. Ratio of C₂₊ hydrocarbon and methane yields versus percentage Ni dispersion: ○ Ni/SiO₂ at 525 K; □ Ni/Al₂O₃ at 500 K.

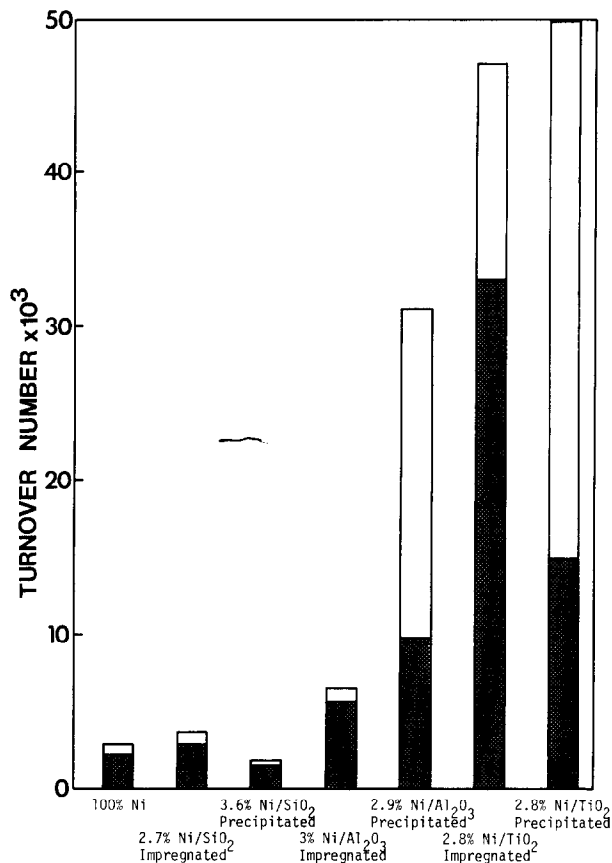


FIG. 4. Effects of support and preparation on methane turnover number at 525 K for Ni: ■ CH₄ turnover No.; □ C₂₊ hydrocarbon turnover No.; total bar length is CO turnover No.

supports provide considerable insight into how nickel-support interactions and nickel metal dispersion influence the nature of H₂

and CO adsorption on nickel and its catalytic activity/selectivity properties in CO/H₂ synthesis.

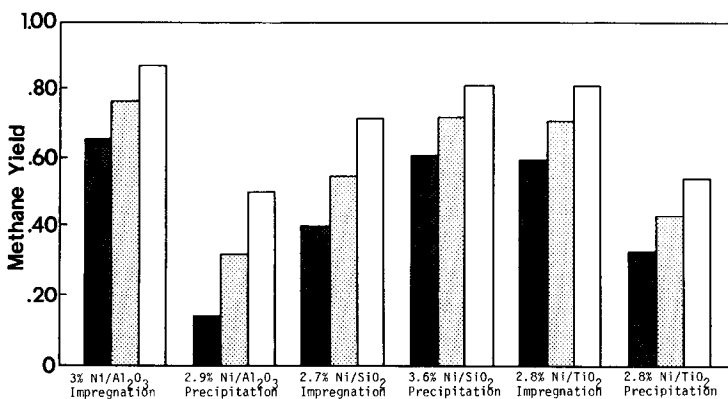


FIG. 5. Effects of support and preparation on methane yield of nickel: ■ 500 K; ▨ 525 K; □ 550 K.

TABLE 4
Effect of Support and Preparation on CO
Hydrogenation Activity/Selectivity Properties

| Catalyst | Percentage dispersion ^a | Turnover number ^b × 10 ³ (sec ⁻¹) at 525 K | | CH ₄ yield |
|--|------------------------------------|---|-----------------------------|-----------------------|
| | | N _{CO} | N _{CH₄} | |
| 100% Ni (INCO) | 0.05 | 2.8 | 2.2 | 0.79 |
| 2.7% Ni/SiO ₂ (impregnated) | 16 | 3.9 | 2.6 | 0.66 |
| 3.6% Ni/SiO ₂ (precipitated) | 26 | 1.7 | 1.4 | 0.82 |
| 3% Ni/Al ₂ O ₃ (impregnated) | 22 | 6.4 | 5.7 | 0.89 |
| 2.9% Ni/Al ₂ O ₃ (precipitated) | 22 | 31 | 9.8 | 0.32 |
| 2.8% Ni/TiO ₂ (impregnated) | 11(18) ^d | 47(29) ^d | 33(20) ^d | 0.70 |
| 2.8% Ni/TiO ₂ (precipitated) | 12 | 50 | 15 | 0.30 |

^a Percentage Ni exposed based on H₂ adsorption.

^b Molecules CO converted or CH₄ produced per nickel site per second based on H₂ adsorption.

^c Fraction of converted CO appearing as methane.

^d Percentage dispersion or turnover number based on transmission electron microscopy.

Effects of Dispersion and Support on CO and H₂ Adsorption Properties

Effects of dispersion. The data for Ni/Al₂O₃ catalysts in Table 1 suggest that (i) CO/Ni_s increases with increasing dispersion and (ii) that H/Ni_s < 1 in the case of 0.5 and 1.0% Ni/Al₂O₃ since abnormally large CO/H values of 28 and 9.9 are observed for these two catalysts. The first hypothesis is consistent with recent infrared studies (12, 13) which indicate that strongly adsorbed, bridged species are predominant on poorly dispersed nickel, moderately strongly adsorbed, linear species on moderately dispersed nickel, and weakly adsorbed, subcarbonyl species (Ni(CO)_x, x = 2,3) on very well-dispersed nickel. The second postulate is the most reasonable explanation for such large values of CO/H. Both the decrease in H₂ adsorption and increase in CO adsorption on small nickel crystallites can be attributed to a strong nickel-alumina interaction, i.e., an increasingly more intimate electronic interaction of the metal crystallite with the support

with decreasing metal crystallite size which weakens the chemisorption bond. This explanation is consistent with data trends in Table 1, particularly the decreasing fraction of reduced nickel metal in the catalyst with decreasing nickel concentration and metal crystallite size. These trends suggest that at low nickel concentrations and high dispersions, a large fraction of the nickel interacts strongly with the support and thus cannot be easily reduced to the metallic state.

The observation of suppression of H₂ adsorption and multiple CO adsorption on highly dispersed Ni/Al₂O₃ is new, although suppression of H₂ adsorption was observed in TiO₂-supported nickel (5, 7) and noble metals (14, 15) and subcarbonyl species were reported in CO adsorption on well-dispersed Rh/Al₂O₃ (16, 17). Differences in the nature of CO adsorption on Ni/Al₂O₃ and Ni/SiO₂ catalysts of different dispersions and metal loadings were previously interpreted in terms of geometrical effects (18, 19) and differences in extent of reduction to the metal (12); however, we believe they are more directly a manifestation of a metal-support interaction.

Effects of support. The results of this study provide strong evidence of modifications in the adsorption behavior of CO on nickel due to interaction with each of the supports Al₂O₃, SiO₂, and TiO₂ and the suppression of H₂ adsorption in both Ni/Al₂O₃ and Ni/TiO₂. Indeed, the extent of interaction clearly increases in the order Ni/SiO₂, Ni/Al₂O₃, Ni/TiO₂ for catalysts of the same loading (compare CO/H ratios in Tables 1-3 for precipitated 3 wt% catalysts); moreover, suppression of H₂ adsorption is observed in Ni/TiO₂ at significantly higher loadings and lower dispersions than in Ni/Al₂O₃. For example, comparison of dispersion and crystallite size data from H₂ adsorption with those from transmission electron microscopy (TEM) for Ni/TiO₂ in Table 3 reveals significant inhibition of H₂ adsorption at nickel loadings of 3-15% (nickel dispersions of 10-20%) while such behavior was evident in Ni/Al₂O₃ catalysts

at loadings of 0.5 and 1% (dispersions of 59 and 42%) only. Comparison of H₂ adsorption, XRD, and TEM data (7) for some of the Ni/SiO₂ and Ni/Al₂O₃ catalysts described in this study reveals no suppression of H₂ adsorption (i.e., H/Ni_s = 1) at nickel loadings of 3–15% for Ni/SiO₂ and 15–23% for Ni/Al₂O₃. Significant modifications in CO adsorption (CO/H > 1) occur only at very high dispersions (51%) for 2.7% Ni/SiO₂ and at moderate dispersions (11–22%) for 3% Ni/Al₂O₃ and Ni/TiO₂ catalysts. These observed modifications in the adsorption properties of CO and H₂ on nickel due to support effects are qualitatively consistent with those reported in earlier studies (1, 5). Direct evidence that nickel interacts most strongly with TiO₂ is provided by electron micrographs (7) showing the presence of two-dimensional raft-like crystallites in Ni/TiO₂, while three-dimensional crystallites are observed in Ni/SiO₂ and Ni/Al₂O₃.

Effects of preparation and pretreatment. The method of catalyst preparation clearly affects H₂ and CO adsorption properties of Ni, as evidenced by data in Tables 1 and 2 showing larger CO/H ratios for the precipitated 2.9% Ni/Al₂O₃ and the impregnated 2.7% Ni/SiO₂. The special controlled-pH precipitation technique (9) used to prepare catalysts for this study results in Ni/SiO₂ (and presumably Ni/Al₂O₃ and Ni/TiO₂) catalysts with significantly sharper metal crystallite size distributions (7, 20). The significantly broader crystallite size distribution and thus the presence of extremely small crystallites in the impregnated Ni/SiO₂ catalysts may account for their significantly larger CO/H adsorption ratios. In the case of 2.9% Ni/Al₂O₃, the precipitation technique presumably resulted in a more uniform distribution of the metal on the support and possibly a more intimate interaction of the metal with the support leading to the larger CO/H adsorption ratio compared to that for impregnated 3% Ni/Al₂O₃.

In addition to preparation, it is evident

from data in Tables 1 and 2 that catalyst pretreatments such as calcination and reduction in the presence of water significantly influence the adsorption properties, generally lowering CO/H ratios in Ni/SiO₂ but increasing the CO/H ratio for 2.9% Ni/Al₂O₃. The changes in the adsorption of CO on Ni/SiO₂ were mainly due to changes in dispersion, while the calcination of Ni/Al₂O₃ significantly increases the interaction of the nickel with the support as evidenced by the substantially lower extent of reduction to the metal.

Effects of Dispersion and Support on Specific Activity

Effects of dispersion. From the data in Table 2 and Fig. 2, it is apparent that changes in specific activity in the form of CO and CH₄ turnover numbers for Ni/SiO₂ catalysts are modest, i.e., not more than a factor of 3–4 over a wide range of dispersion. However for Ni/Al₂O₃ (Table 1 and Figs. 1 and 2) the corresponding changes in N_{CO} and N_{CH₄} are at least double those for Ni/SiO₂, even when the suppression of H₂ adsorption on 0.5 and 1% Ni/Al₂O₃ catalysts is taken into account by basing turnover numbers on CO adsorption. The trend of decreasing methane turnover number with increasing dispersion is the same for both Ni/Al₂O₃ and Ni/SiO₂ catalysts (see Fig. 2) and in agreement with the data of Vannice and Fontaine (3, 21) for Ni/SiO₂ and of Bhatia *et al.* (4) for Ni/Al₂O₃, both data sets being over smaller ranges of dispersion than the one of this study.

We believe that the dispersions reported by Bhatia *et al.* (4) based on CO adsorption are erroneously large by a factor of 2, since these authors assumed bridged adsorption while the linear CO species would most likely predominate for their catalysts (1, 6, 18). Thus, the range of dispersion of their Ni/Al₂O₃ catalysts was more likely 3.5 to 24% rather than the reported range of 7 to 48%. Moreover, their calculations of dispersion are suspect for two other rea-

sons: (i) no corrections were made for physical and chemical adsorption of CO on the support and (ii) their calculations of dispersion involved corrections using unspecified values of percentage reduction to the metal determined by acidic evolution of H₂, a technique which was reported earlier to give erroneous results (8). In addition, their reported trend of increasing methane turnover number with decreasing nickel concentration is based on one very questionable point; i.e., their lowest loading catalyst, a 5% Ni/Al₂O₃, is reported to have the lowest dispersion. The remainder of their data (four other catalysts) show the expected trend (in agreement with our data) of increasing metal dispersion and decreasing methane turnover number with decreasing nickel concentration. Our adsorption data for impregnated Ni/Al₂O₃ catalysts were reproduced within 25% for two to three separately prepared batches each; thus, we are confident in our reported trend of increasing dispersion with decreasing nickel concentration for Ni/Al₂O₃.

Bhatia and co-workers (4) assumed that changes in activity with dispersion were evidence of structure sensitivity, although they did not rule out the contribution of metal-support interactions. The results of this study, however, coupled with recent evidence (22, 23) support the conclusion that these changes are mainly due to the interaction of metal and support. Probably the most important evidence comes from Kelley and co-workers (22), who found that the methane turnover number is the same within experimental error on two different single crystal faces of nickel. Somorjai (23) attributed this structure insensitivity to the leveling effect of an active carbon layer which covers the surface during reaction. Finally, data from this study (Tables 2 and 4), showing that either moderately or poorly dispersed Ni/SiO₂ of high nickel content (in which the metal-support interaction is expected to be fairly weak) displays activity/selectivity properties almost

identical to those for very poorly dispersed, bulk nickel, provide further evidence that crystallite size or surface structure itself is not important in determining specific activity.

Effect of support. The data in Table 4 and Fig. 4 showing 3% Ni/Al₂O₃ and Ni/TiO₂ catalysts to have 3–30 times greater specific activity for conversion of CO than unsupported nickel or Ni/SiO₂ catalysts provide strong, unambiguous evidence that strong metal-support interactions (SMSI) increase the activity of nickel for CO hydrogenation. Since catalysts of approximately the same dispersion and preparation are compared, the results cannot be attributed to variations in these variables. Indeed, the order of decreasing activity for CO hydrogenation Ni/TiO₂ > Ni/Al₂O₃ > Ni/SiO₂ is valid for catalysts prepared by either precipitation or impregnation. Even if the turnover numbers for Ni/TiO₂ are based on the number of nickel sites estimated from TEM, this order is still valid and N_{CO} is still a factor of 10 greater than for unsupported nickel or Ni/SiO₂. These results find good qualitative agreement with those obtained by Vannice and Garten (5) for Ni/TiO₂ catalysts.

The results of this study provide the first unambiguous evidence that nickel supported on γ -Al₂O₃ is more active than nickel supported on silica gel. Previous comparisons (3, 5) involved catalysts of widely differing dispersions, metal concentrations, preparations, and pretreatments. The data from this study establish that these properties can significantly influence activity and selectivity in CO/H₂ synthesis. Some of the previous comparisons (3, 5) also involved commercial catalysts with different kinds of supports (probably aluminas and silica-aluminas) some of which were undoubtedly precalcined at high temperatures so that the nickel was supported on mixed oxides or spinels such as NiO · Al₂O₃ or NiAl₂O₄, supports with significantly different properties than pure γ -Al₂O₃. This explains, for example, why

the data obtained by Bhatia *et al* (4) for commercial nickel catalysts did not fit the correlations involving their own catalysts.

One of the most surprising results of this study is the large specific activity observed for the precipitated 2.9% Ni/Al₂O₃. Indeed, this catalyst exhibits activity/selectivity properties very similar to the precipitated 2.8% Ni/TiO₂ (see Table 4 and Fig. 4). To our knowledge the data in this study are the first reported for Ni/Al₂O₃ and Ni/TiO₂ catalysts prepared by this special precipitation technique and provide the first indication of SMSIs in the Ni/Al₂O₃ system of the same magnitude observed for the Ni/TiO₂ system.

Effects of Dispersion and Support on Product Selectivity

Effects of dispersion. Previous studies have not established definitive correlations and/or explanations for differences in selectivity in CO/H₂ synthesis on nickel catalysts of varying dispersion and support. The unmistakable correlation of increasing hydrocarbon yield with increasing percentage dispersion (decreasing metal crystallite size) for both Ni/Al₂O₃ and NiSiO₂ catalysts as illustrated in Fig. 3 is most interesting. Since the change in the yield ratio for Ni/Al₂O₃ is a factor of 5 greater than for Ni/SiO₂, this phenomenon is clearly an effect of metal-support interactions rather than an indication of structure sensitivity. Most importantly, when considered carefully against other trends from Tables 1 and 2, this correlation suggests an important general principle regarding selectivity in CO/H₂ synthesis. Since the CO/H adsorption ratio also increases with increasing dispersion in the Ni/Al₂O₃ and Ni/SiO₂ systems, *the yield of C₂₊ hydrocarbons apparently depends upon the CO/H ratio. Thus the larger the CO/H adsorption ratio for a given catalyst, the higher its selectivity to C₂₊ hydrocarbons.* In other words, we hypothesize that small nickel crystallites which interact strongly with the support produce hydrogen-poor hydrocarbons com-

pared to methane simply because the adsorbed species on the crystallite surface during reaction are deficient in hydrogen.

Effects of support and preparation. From the data in Tables 1–4 and Fig. 5 it is evident that the mode of preparation can influence selectivity to the same or even greater degree than does the support. As might be expected, the effects of preparation are most dramatic for nickel in combination with Al₂O₃ or TiO₂ supports. Indeed, the precipitated forms of Ni/Al₂O₃ and Ni/TiO₂ (see Table 4 and Fig. 5) produce unusually high yields of C₂₊ hydrocarbons (60–80% at 500–550 K) and low yields of methane (20–40% at 500–550 K) compared to impregnated catalysts with selectivity behavior more characteristic of unsupported nickel.

Finally it should be emphasized that the relationship between CO/H adsorption ratio and selectivity proposed earlier in connection with effects of dispersion also explains the effects of support and preparation. That is, those supports and preparations which appear to modify selectivity in the direction of higher molecular weight hydrocarbons are also associated with the catalysts having the highest CO/H ratios. For example, the CO/H ratio for precipitated 2.9% Ni/Al₂O₃ is 3.6 compared to 1.9 for impregnated 3% Ni/Al₂O₃ and in accordance with the proposed correlation, the C₂₊ hydrocarbon yield at 500 K for the precipitated catalyst is 85% compared to 32% for the impregnated catalyst (see Table 1 and Fig. 5).

CONCLUSIONS

(1) Interactions between support and metal in Ni/Al₂O₃, Ni/SiO₂, and Ni/TiO₂ systems result in dramatic modifications in the nature and stoichiometry of CO and H₂ adsorption on nickel. CO/H adsorption ratios generally increase with increasing metal dispersion in Ni/SiO₂ and Ni/Al₂O₃ catalysts. H₂ adsorption is apparently suppressed on all Ni/TiO₂ catalysts and on well-dispersed Ni/Al₂O₃ catalysts of low

nickel content. These modifications in the nature and stoichiometry of CO and H₂ adsorption occur presumably because SMSIs weaken the nickel adsorbate bond.

(2) SMSIs apparently increase the activity of available nickel sites for CO hydrogenation in Ni/Al₂O₃ and Ni/TiO₂ catalysts. The order of decreasing activity for CO hydrogenation is Ni/TiO₂ > Ni/Al₂O₃ > Ni/SiO₂ = Bulk Ni. In the Ni/Al₂O₃ system activity is greatly influenced by the mode of preparation; indeed, 2.9% Ni/Al₂O₃ prepared by precipitation is significantly more active than 3% Ni/Al₂O₃ prepared by impregnation. Effects of support on activity and selectivity are evident for Ni/SiO₂ only at high dispersions, for Ni/Al₂O₃ at moderate and high dispersions, and for Ni/TiO₂ at all dispersions (moderate and low) investigated thus far.

(3) Selectivity in CO/H₂ synthesis over nickel is influenced by metal dispersion, preparation, and support. Selectivity to high-molecular-weight hydrocarbons increases with increasing dispersion in both Ni/SiO₂ and Ni/Al₂O₃ systems, although the magnitude of the increase is significantly greater in Ni/Al₂O₃. The order of decreasing methane yield in CO/H₂ synthesis is Ni (unsupported) ≅ (Ni/SiO₂)_{mod. disp.} ≅ Ni(Al₂O₃)_{impreg.} > (Ni/SiO₂)_{high disp.} ≅ (Ni/TiO₂)_{impreg.} > (Ni/TiO₂)_{ppt.} ≅ (Ni/Al₂O₃)_{ppt.} A general pattern of selectivity in CO hydrogenation is evident, namely, increasing C₂₊ hydrocarbon yield with increasing CO/H adsorption ratio, suggesting that the relative availability of adsorbed H₂ and CO determines product distribution during reaction.

(4) On the basis of this and previous studies we hypothesize that the observed changes in adsorption, activity, and selectivity with dispersion and support are the result of intimate electronic interactions between the support and metal crystallite rather than geometrical effects. We speculate that electrons are withdrawn from the nickel crystallites by the support leading to

a metallic behavior more characteristic of cobalt, which is known to have a high specific activity and high selectivity for high-molecular-weight hydrocarbons in CO/H₂ synthesis (24).

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