

The Effect of Metal Loading on the Adsorption Parameters of Carbon Dioxide on Coprecipitated Nickel-Alumina Catalysts

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A coprecipitation method has been developed and modified for the preparation of nickel-alumina catalysts having metal loadings in the 0-25 wt% Ni range. The effect of metal loading on CO_2 adsorption was investigated under isothermal chromatographic conditions using an elution technique in the temperature range 483-533 K. Average enthalpies of adsorption were determined using the isosteres obtained from the experimental adsorption isotherms. The isotherms were also fitted to the Langmuir equation for the evaluation of adsorption equilibrium coefficients, Gibbs free energies, average adsorption enthalpies and entropies.

Keywords: nickel-alumina, coprecipitated nickel-alumina, CO_2 adsorption

Introduction

Nickel is recognized to be the most suitable transition metal for the catalytic hydrogenation of carbon oxides¹⁻⁵. The activity and selectivity of Ni/Al_2O_3 catalysts in CO hydrogenation have received considerable attention due to renewed interest in the production of synthetic fuels^{2,6}. Studies of CO_2 hydrogenation, which is also important in the cyclic use of carbon sources, have been far less extensive than those of CO hydrogenation^{6,7}. A large majority of these studies have been conducted on impregnated catalysts².

A second major method used in the preparation of commercial catalysts is coprecipitation^{1,8}. Research devoted to establishing the structure of coprecipitated nickel-alumina catalysts indicates that large changes in the alumina content of these catalysts lead to quantitative changes in their solid structure⁹. Preparation conditions play an important role in this respect. Adsorption characteristics are known to vary with the nature of the support, the metal loading, the method of preparation and the structure of the catalyst, which in most cases directly determine the metal-support interaction.

In this study, a series of coprecipitated Ni/Al_2O_3 catalysts were prepared by modifying and developing the procedures reported in the literature^{8,9} to obtain metal loadings of 0-25 wt% Ni. Since the determination of adsorption parameters within the range of reaction temperatures is useful in the interpretation of reaction data, the effect of nickel content on the adsorption parameters of CO_2 was investigated in the 483-533 K

range, where methanation is known to occur. Adsorption isotherms of CO_2 on alumina and nickel-alumina catalysts with four different nickel loadings were determined under isothermal chromatographic conditions using the elution technique^{10,11}, and the isotherms were used to obtain isosteric adsorption enthalpies. The adsorption data were then fitted to the Langmuir equation for the evaluation of adsorption equilibrium coefficients, Gibbs free energies, average enthalpies and entropies of adsorption.

Experimental

Catalyst Preparation

Coprecipitated Ni/Al_2O_3 catalysts containing 5-25 wt% Ni were prepared in a semibatch system by coprecipitation from nickel nitrate and aluminum nitrate solutions with sodium hydroxide. The system used for catalyst preparation was equipped with a cold bath kept at 279 K and controlled to ± 0.1 K. The $NaOH$ solution was gradually added to the aluminum nitrate solution using a Masterflex computerized-drive peristaltic pump while the latter solution was mixed vigorously. The nickel nitrate solution prepared was then added to the aluminum hydroxide solution formed to complete the reaction resulting in the coprecipitation of aluminum hydroxide and nickel hydroxide. The concentration and the rate of addition of the nickel nitrate solution were varied to obtain different metal loadings between 5-25 wt%. A catalyst containing 0 wt% Ni (only Al_2O_3) was also prepared by modifying the same procedure and was used as a reference in all the experiments. The precipitate was filtered and washed several times to get rid of the sodium salt and other possible impurities, vacuum dried at 378 K for 24 hrs, and then sieved to 200-250 microns. The metal loadings of the four coprecipitated catalyst samples were determined using a Varian 250 Plus atomic absorption spectrometer after they were reduced in a stream of hydrogen.

Pretreatment

In the adsorption experiments, the fresh catalyst samples were reduced in situ in a stream of 100 mL/min pure hydrogen at a heating rate of 1.8 K/min with a 16-hour hold at 623 K. This was followed by 3 hours of flushing with 100 mL/min He at 623 K. In adsorption experiments on the same catalyst sample, a short reduction scheme consisting of 2.5 hours of reduction with 100 mL/min H_2 at 623 K followed by 45 minutes of flushing with 100 mL/min He at 623 K was used before changing the adsorption temperature.

The samples to be used for the measurement of physical properties were reduced in a flow system having a 3.5 mm ID stainless steel microreactor tube placed in a 2.4 cm ID tubular furnace that was controlled to ± 0.1 K by a Shimaden FP-21 programmable temperature controller. The same reduction procedure described above was used. The reduced samples were passivated with 1% air in N_2 when necessary. Gas flowrates were controlled by calibrated Omega mass flow controllers, and research grade gases from pressurized cylinders were passed through molecular sieve and silica gel traps before entering the flow system.

Physical Property Measurements

The total surface area and the total pore volume measurements were made on a Micromeritics Flowsorb II-2300 system. Total surface areas of the reduced catalyst samples were determined by N_2 adsorption from N_2 -He mixtures, using a multipoint technique together with the BET equation. Total pore volumes were measured by the N_2 adsorption-desorption method.

Adsorption Experiments

A Shimadzu GC-14A gas chromatograph having a thermal conductivity detector was fitted with 50 cm long, 3 mm ID stainless steel columns that were filled with alumina or nickel-alumina particles sieved to 200-250 microns. The fresh catalyst sample packed into the column was reduced in situ as described above. During the adsorption experiments, helium was used as carrier at a 25 mL/min flowrate, and N_2 was selected for measuring dead time values. A 1-mL calibrated sample loop was used for sending successive reproducible pulses of adsorbate (CO_2) into the column packed with catalyst until constant peak size was reached.

Results and Discussion

Catalyst Properties

The metal contents of the four coprecipitated Ni/Al_2O_3 samples were determined by atomic absorption measurements to be 5, 11, 16.5 and 25 wt% Ni. The corresponding target metal loadings, according to which the coprecipitation procedure was modified, were 5, 12.5, 17.5 and 25wt % Ni, respectively. Since coprecipitation procedures are affected by various parameters that need to be carefully controlled (such as precipitation pH, temperature, amount of precipitation agent, batch size, etc.), the deviations from the target metal loadings were considered to be acceptable.

The total surface areas (S_g) and total pore volumes (V_g) of the five catalyst samples (including 0 wt% Ni) were measured in order to study the relation between their metal content and physical properties (Table 1). The S_g and V_g values in Table 1 indicate that the total surface area initially increases with

Table 1. Physical properties of 0-25 wt% Ni/Al_2O_3 samples

Metal Loading (wt%)	0	5	11	16.5	25
$S_g(m^2/g) \pm 2\%$	207	312	382	392	313
$V_g(cm^3/g) \pm 2\%$	0.037	0.137	0.274	0.237	0.229

nickel content but then gets to a maximum at around 16.5 wt% Ni, while the total pore volume reaches its maximum at 11wt% Ni. These results emphasize the difference between coprecipitated and impregnated catalysts. In the case of impregnated catalysts, the metal and the support are two separate phases and their interaction does not lead to any major change in the support structure. As a result, S_g and V_g decrease with increasing metal loading, since the added metal covers pore walls and eventually fills up the pores. In coprecipitated Ni/Al_2O_3 catalysts, on the other hand, metal-support interaction is virtually complete in the oxide form since the catalysts are made via a mixed solution and, upon reduction, the metal-support interaction becomes extensive and intracrystallite, which allows the nickel to have a direct influence on the support structure⁹.

Adsorption Parameters

Adsorption isotherms (gas phase partial pressures of CO_2 in mm Hg or atm. versus surface concentration of CO_2 in gmole per gram of catalyst) were determined from the diffuse rear boundaries of elution peaks^{10,11}. These were obtained at several temperatures in the 483-533 K range for all the alumina and nickel alumina samples. Representative adsorption isotherms of CO_2 on alumina and on 25 wt% Ni/Al_2O_3 are given in Figures 1 and 2. The isosteres ($\ln p$ versus $1/T$ at constant surface concentration) were obtained from these

adsorption isotherms, and the isosteric adsorption enthalpies, ΔH_{st} , were calculated by linear regression from the slopes of the isosteres using the Clausius-Clapeyron equation:

$$\{d(\ln p)/d(1/T)\}_\theta = \Delta H_{st}/R, \quad (1)$$

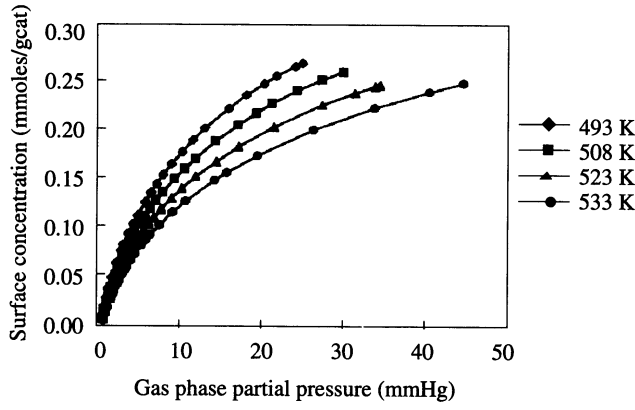


Figure 1. Adsorption isotherms of CO_2 on alumina

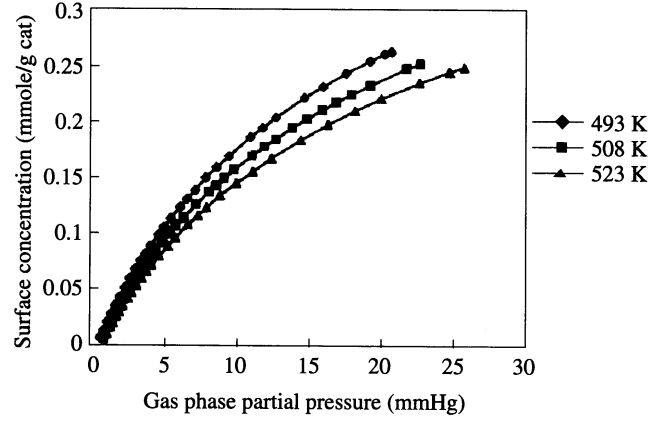


Figure 2. Adsorption isotherms of CO_2 on 25 wt% Ni/Al_2O_3

where θ denotes fractional surface coverage by the adsorbate. The isosteric enthalpies calculated for CO_2 adsorption on the five catalyst samples are presented in Table 2. It is clearly seen in Table 2 that the $(-\Delta H_{st})$ values initially decrease rapidly as the metal loading is increased from 0 to 11 wt% Ni, dropping to a minimum in the 11-16.5 wt% Ni range and then show an appreciable increase as 25 wt% Ni loading is reached. The variation of adsorption enthalpies with metal content reflects the structural change in the catalyst samples and parallels the change in the physical properties of the catalysts. The S_g and ΔH_{st} values are plotted versus metal loading in Figure 3 to point out this relationship.

Table 2. Isosteric Adsorption Enthalpies of CO_2

Catalyst	Metal Loading (wt%)	Temperature Range (K)	$-\Delta H_{st}$ (kJ/mol)
Al_2O_3	0	493-533	38 ± 1
Ni/Al_2O_3	5	483-523	21 ± 1
Ni/Al_2O_3	11	493-523	12 ± 1
Ni/Al_2O_3	16.5	493-533	12 ± 1
Ni/Al_2O_3	25	493-523	22 ± 1

Langmuir Model

Considering the experimental temperature range used and its correspondence to methanation temperatures, activated adsorption may be assumed to occur. The simplest model describing adsorption equilibrium between gases and solid surfaces is the Langmuir model:

$$\theta = (C_{is}/C_{st}) = K_i p_i / (1 + K_i p_i), \quad (2)$$

where C_{is} is the surface concentration of the adsorbate (mol/g), C_{ts} is a temperature-independent constant giving the total number of surface sites (mol/g), and K_i is the adsorption equilibrium coefficient of the adsorbate (atm^{-1}). The temperature dependence of K_i is given by the van't Hoff functionality:

$$K_i = K_o \exp(-B/RT). \quad (3)$$

It can be shown that the average enthalpy of adsorption is equal to B, and the entropy of adsorption is given by $R \ln K_o$. Combining Equations (2) and (3), the following equation is obtained:

$$C_{is} = \frac{C_{ts}(K_o e^{-B/RT})p_i}{1 + (K_o e^{-B/RT})p_i}. \quad (4)$$

The experimental adsorption isotherms determined by the elution technique were fitted to Equation (4). The constants K_o and B were estimated by nonlinear regression from the p_i versus C_{is} data obtained at various temperatures by a hybrid method using the Gauss-Newton and the Levenberg-Marquardt algorithms. The CO_2 adsorption data on alumina and the four nickel-alumina catalysts were found to give a good fit to the Langmuir equation in the range of adsorbate partial pressures and surface concentrations involved. Figure 4 compares experimental adsorption data with isotherms calculated from Equation (4) using the K_o and B values estimated for the 16.5 wt% Ni/Al_2O_3 catalyst.

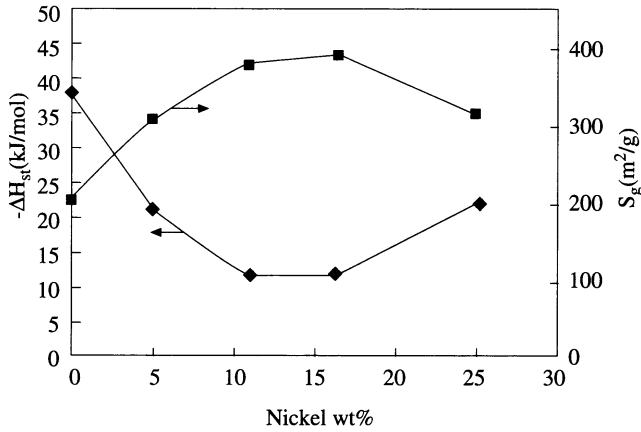


Figure 3. The effect of metal loading on total surface area and isosteric enthalpy of adsorption

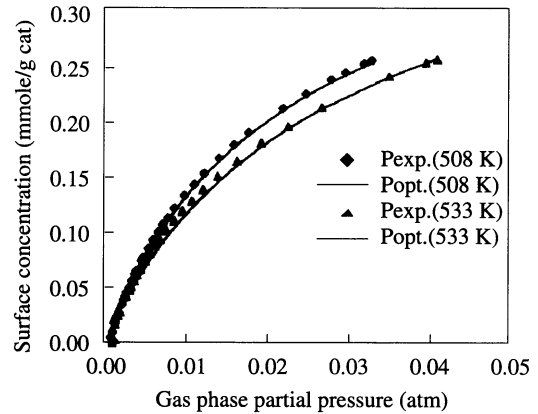


Figure 4. Comparison of experimental adsorption data with isotherms obtained from the Langmuir model for the 16.5 wt% Ni/Al_2O_3

The calculated average enthalpies and entropies of adsorption, ΔH_{ads} and ΔS_{ads} , are presented in Table 3. The agreement between the ΔH_{ads} values calculated from the model and the ΔH_{st} values obtained from experimental measurements for 0, 5 and 25 wt% Ni/Al_2O_3 catalysts is excellent. For the 11 and 16.5 wt% Ni/Al_2O_3 catalysts, the general variation in adsorption enthalpies with metal loading is predicted correctly, although the calculated values deviate from the experimental ΔH_{st} values.

The adsorption equilibrium coefficients of CO_2 on the five catalyst samples tested were calculated from Equation (3) and are presented in Table 4 together with the corresponding Gibbs free energies of adsorption obtained by using the relation:

$$-\Delta G_{ads} = RT \ln K_i. \quad (5)$$

The calculated adsorption equilibrium coefficients decrease with increasing temperature, and the negative Gibbs free energies increase with increasing temperature, as would be expected. At a given temperature, K values seem to decrease with increasing metal content; the increase in the enthalpy of adsorption at 25 wt% Ni is not reflected in the K values calculated.

Table 3. Average enthalpies and entropies of adsorption for CO_2 calculated from the Langmuir model (475-550 K)

Catalyst	Metal Loading (wt%)	$-\Delta H_{ads}$ (kJ/mol)	$-\Delta S_{ads}$ (J/mol K)
Al_2O_3	0	37.2	39.4
Ni/Al_2O_3	5	19.4	6.2
Ni/Al_2O_3	11	16.4	0.7
Ni/Al_2O_3	16.5	16.7	1.6
Ni/Al_2O_3	25	21.3	13.5

Table 4. Adsorption equilibrium coefficients and free energies of adsorption for CO_2 on Ni/Al_2O_3 catalysts

Catalyst	Metal Loading (wt %)	Temperature (K)	K (atm^{-1})	$-\Delta G_{ads}$ (kJ/mol)
Al_2O_3	0	475	107.7	18.48
		500	67.3	17.49
		525	43.9	16.51
		550	29.8	15.55
Ni/Al_2O_3	5	475	65.0	16.48
		500	50.8	16.33
		525	40.7	16.18
		550	33.3	16.02
Ni/Al_2O_3	11	475	59.0	16.10
		500	47.9	16.08
		525	39.7	16.07
		550	33.4	16.05
Ni/Al_2O_3	16.5	475	57.5	16.00
		500	46.5	15.96
		525	38.4	15.92
		550	32.3	15.88
Ni/Al_2O_3	25	475	43.9	14.93
		500	33.5	14.60
		525	26.2	14.26
		550	21.0	13.92

Conclusions

A series of five coprecipitated Ni/Al_2O_3 catalysts with metal loadings between 0-25 wt% Ni were prepared by modifying and further developing available procedures. The effect of metal loading on such catalyst physical properties as total surface area and total pore volume indicates that in coprecipitated catalysts, the metal-support interaction is intracrystallite and that the metal content can alter the support structure. Isothermic enthalpies of adsorption obtained from the experimental adsorption isotherms reflect the structural change in the catalyst samples with increasing metal content. Within the range of adsorbate partial pressures used and the corresponding surface concentrations, the statistical fit of the adsorption data to the Langmuir model is excellent. The parameters calculated from the regression constants confirm this close correlation and may be used in the interpretation of reaction data.

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