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The Effect of Catalyst Preparation on the Performance of Alumina-Supported Ruthenium Catalysts

I. The Impact of Catalytic Precursor on Particle Size and Catalytic Activity

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The effect of preparation method and the choice of metallic precursor on the performance of a series of Ru/Al_2O_3 catalysts were studied. Wet impregnation and incipient wetness were the methods employed; ruthenium nitrosylnitrate and ruthenium trichloride were the reagents. In the latter case, either Ru(III)/Ru(IV) chlorospecies or mixtures of Ru(II) hydrazine complexes were the catalytic precursors. The series of Ru/Al_2O_3 catalysts, with metal loadings from 0.7–5% by weight, were subjected to a battery of performance tests: CO temperature-programmed reaction, steady-state CO hydrogenation, and temperature-programmed surface reaction. The methanation activity and carbon deposited during steady-state reaction varied systematically with the dispersion of Ru on the alumina. High rates of methane production were found on catalysts containing a large reservoir of carbon-containing reaction intermediates. The performance of these catalysts depended on the precursor used in their preparation. The effects of weight loading, method of preparation, and variations in the impregnant pH were small within a group prepared from a common precursor.

INTRODUCTION

In his studies of methanation and higher hydrocarbon synthesis over a series of Group VIII metals supported on alumina, Vannice (*1*) compared the specific activities of the metals by normalizing the methane production to the available metal surface area. Of the Group VIII metals supported on alumina that were studied, ruthenium had the highest specific methanation activity. Although ruthenium catalysts have not found widespread application in industry due to their expense, these catalysts have been used quite extensively in research aimed at deciphering the mechanism of Fischer–Tropsch synthesis (*2*). The reasons for implementing ruthenium in catalytic studies are clear: high specific activity, ability to form long-chain hydrocarbons at low pressures, ease of reduction of the metal even at low loadings (*3*), and simplified analysis because the products have virtually no oxygen content. In addition, bulk carbides do not form under reaction conditions and therefore reactions proceeding on the Ru surface can be studied in the absence of accompanying bulk processes (*4*).

Two schools of thought have developed concerning the mechanism of Fischer–Tropsch synthesis. The first, which was popular in the mid-1970s, favored the direct hydrogenation of CO to form oxygenated intermediates (*5–7*). However, this mechanism fails to explain certain facts, such as why alcohols can initiate synthesis but cannot contribute to chain growth by dehydrocondensation (*8*). As a result, a second school has formed from work in the early 1980s that claims hydrocarbon synthesis is initiated by the dissociation of adsorbed CO to form carbon, which is subsequently hydrogenated (*4, 9–15*). The carbon formed is extremely reactive and can produce long

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chain hydrocarbons in addition to methane. Ekerdt and Bell (*13*) observed large amounts of carbon on a Ru/SiO_2 catalyst and noted that these deposits were hydrogenated at a rate in notable excess of steady-state synthesis rates. A number of different forms of carbon have been identified (*15, 16*), each exhibiting quite different properties. The atomic carbon formed by the dissociation of CO not only leads to the synthesis of hydrocarbons, but also acts as a precursor for carburization of the catalyst (*15*). Observation of decreases in BET surface areas (*17*) and hydrogen adsorption (*18*) have been attributed to carbon deactivation of supported ruthenium catalysts.

A characteristic of Group VIII metal catalysts is their structure sensitivity for hydrocarbon synthesis from CO and H_2. Boudart and McDonald (*19*) report that turnover frequencies of structure-sensitive reactions should vary appreciably with varying catalyst structure. For Ni/Al_2O_3 catalysts, particle size effects have been shown to increase with the magnitude of metal–support interactions (*20*). However, particle size effects are more apparent for Ru than Ni. King (*3*) observed a fourfold increase in the site-time yield for methanation and CO conversion for a 2.5% Ru/Al_2O_3 catalyst with a dispersion value of 23% compared to a 0.5% Ru/Al_2O_3 catalyst with 60% dispersion. Kellner and Bell (*21*) found that Fischer–Tropsch activity increases with increasing particle size for Ru/Al_2O_3 catalysts with dispersions less than 70% due to an increasing number of planar sites on Ru crystallites. This work provided a comprehensive analysis for the mechanism of CO hydrogenation over Ru/Al_2O_3, yet only three catalysts were used in the study. Differences in dispersion were related to sintering of the particles and the time the catalysts were on stream. In related work, King (*3*) studied the effects of metal particle size and nature of the support on the specific activity for methane production. His work spanned a wide range of metal dispersions, yet the ruthenium crystallites formed were often small and thus the turnover frequencies for methane production were quite low. Other studies disputing the claims of Ru particle size effects (*22, 23*) have been rejected due to the insensitivity of the measuring systems employed.

In this, the first of two papers from our laboratory dealing with alumina-supported ruthenium catalysts, a number of catalysts with a wide range of dispersions were studied. These catalysts were prepared using different precursors; impregnation conditions were also systematically varied. The objective of this paper is to demonstrate that the particle size distribution and, hence, performance of this catalyst system can be conveniently manipulated by proper choice of catalytic precursor. In accomplishing this objective it was found that although many of the Ru/Al_2O_3 catalysts studied had dispersions that fell within the range of King's data, there is a group of poorly dispersed catalysts whose turnover frequencies are much larger than those measured by King. This is due to the fact that the ruthenium particles formed on the surface are large, which is a direct consequence of the preparation conditions. The overall objective of this research is based on determining the effects of the formulation procedures during catalyst preparation on the properties of Ru/Al_2O_3 catalysts.

EXPERIMENTAL

Wet impregnation and incipient wetness were the methods employed in preparing the catalysts used in this study. Ruthenium nitrosylnitrate (lot no. 03911701) and ruthenium trichloride (lot. no. 03706201) supplied by Johnson Matthey were the reagents. Both compounds were designated analytical grade; no assay was available from the supplier. In the latter case, either Ru(III)/Ru(IV) chloro-species or mixtures of Ru(II) hydrazine complexes were the catalytic precursors. The presence of residual chloride is a possible concern when trying to relate the effect of preparation to the performance of the finished catalyst. It was found that these effects do exist but the performance of the catalyst is more strongly dependent on the choice of precursor. The effects of chloride on the properties and performance of Ru/Al_2O_3 catalysts will be discussed in Part II of this series (*24*). The data reported herein were obtained from catalysts in which no attempt was made to remove the chloride residues.

CATALYST PREPARATION

The support material used throughout this work is a $\frac{1}{16}$-in. extrudate γ-alumina (American Cyanamid, lot 85-NA-1402) ground to 40–80 mesh. Before use, it was calcined in a 5 cm^3/min flow of air at 773 K for 3 h.

$RuNO(NO_3)_3/Al_2O_3$

A number of precautions are necessary when preparing solutions of ruthenium nitrosylnitrate. Freshly prepared solutions of $RuNO(NO_3)_3$ undergo a sequence of reactions at room temperature (*25*) that involve (i) the formation of cationic species, (ii) changes in color and spectrophotometric absorption of the solution, and (iii) the release of H^+ and NO_3^-. In addition, air and light must be excluded (*26*) to avoid slow oxidation to Ru(IV) polymer. Therefore, all solutions of $RuNO(NO_3)_3$ were prepared in Teflon beakers at room temperature, in the dark, under a nitrogen atmosphere, and allowed to age for 24 h with the same conditions prevailing (*26*) to ensure equilibrium.

Wet impregnation. A number of impregnation solutions containing ruthenium nitrosylnitrate dissolved in air-saturated distilled water (pH = 6.06) were prepared. The concentration of ruthenium in these solutions was such that the loadings of metal on the catalysts were 0.73%, 1.7%, 3.3%, and 4.2% by weight of ruthenium on the alumina. The pH values of the aged solutions prior to alumina addition were 1.85, 1.39, 0.67, and 0.58, respectively. Measurements were made using a Fisher Accumet temperature-compensated pH meter (Model 805MP) calibrated by standard buffers (Fisher SO-B-140 and SO-B-108) at pH values 1 and 7. To study pH effects within a particular group, an extra three solutions of the low-weight-loading sample were prepared at the same time as the 0.73% catalyst. The pH of these solutions was adjusted using base [NH_4OH (2.5M)] and the values were 2.16, 2.83, and 3.55.

The ruthenium concentration in solution before and after contact with the support was determined by a Perkin–Elmer Model 2380 atomic absorption spectrophotometer, utilizing an air/acetylene flame. The AA was calibrated with a ruthenium reference solution (Johnson–Matthey, lot no. 6-052 G) diluted to 20 ppm that contained 10% by volume HCl and 1000 mg/liter La (Lanthanum oxide from Morton Thiokol, lot no. F01G). One milliliter of each impregnating solution was removed using a fresh Corning pyrex disposable serological pipet (1 +/− 0.005 ml), and diluted within the calibration limits of the AA in 10% HCl and 1000 mg/liter La. The remaining 24 ml of each impregnating solution was added to 2 g of alumina and the beaker covered tightly with Parafilm. The samples were then removed from the nitrogen atmosphere (still in the dark) and placed on a wrist-action shaker for 1 h. After contact, the solutions were carefully filtered and the catalysts were dried at room temperature. One milliliter of the solution contacted with alumina was diluted in 10% HCl and 1000 mg/liter La as described above, while the pH of the remaining solution was recorded. The diluted Ru species before and after alumina addition were run sequentially in the AA, with the average of five readings taken as the ruthenium concentration dissolved. The instrument was recalibrated with the standard between sample readings.

The weight loadings as determined by the above procedure compared well with the intended weight loadings based on the pore-filling volume for the 1.7%, 3.0%, and 5.0% samples. However, there was some uncertainty in the results for the low-weight-loading samples, and a technique similar to that developed by Ko *et al.* (*27*) was used to determine the Ru weight loadings. Equal amounts of catalyst were added separately to known amounts of a HCl/H_2SO_4 mixture and heated until the sample completely dissolved. The Ru content was determined using the AA; measurements were automatically background-corrected (*28*) due to the high acid concentration.

Incipient wetness. Three groups of ruthenium catalysts were prepared with weight loadings of 0.76%, 3.1%, and 5.0% by contacting 2 g of Al_2O_3 with 5 ml of aged $RuNO(NO_3)_3$ solution in a Teflon beaker. To study pH effects, a series of five catalysts of intermediate weight loading (1.1%) were prepared from the same mother solution. NH_4OH was added to four of the samples in order to have approximately the same initial pH values as studied for the wet impregnation case. A sample containing no added base was also included in this group. The initial pH values for the 1.1% samples were 1.56, 1.85, 2.38, 2.92, and 3.50.

After the initial addition of support to the electrolyte, the sample was stirred under the nitrogen atmosphere for approximately 30 min. The sample was then removed and constantly shaken (in the dark). The drying time at room temperature was no more than 24 h for each sample.

As a check, the dissolution method for determining weight loadings was applied to the low and high initial pH samples of the 1.1% batch. The weight loading obtained by this technique was 1.2% for each sample. This is in agreement with the intended loading.

$RuCl_3/Al_2O_3$

Three groups of catalysts derived from $RuCl_3$ were prepared with weight loadings of 0.76%, 3.0%, and 5.1% via the incipient wetness technique. The appropriate amounts of $RuCl_3$ were weighed under a nitrogen atmosphere in order to avoid wetting of the powder. Twice the amount of required metal was dissolved in 10 ml of air-saturated distilled water (pH = 5.59). The initial pH values were 1.55, 1.15, and 1.09 for the low, intermediate, and high weight-loading samples, respectively. Five ml of this $RuCl_3$ solution was removed and contacted with 2.5 g of alumina in a Teflon beaker. This suspension was kept under a constant flow of nitrogen for 10 h with occasional shaking. After this point, the sample was removed and allowed to dry at room temperature on a wrist-action shaker. Of the remaining $RuCl_3$ solution, 1 ml was removed, diluted properly, and analyzed for total ruthenium concentration using the AA. This was done in order to check that the intended weight loadings were in agreement with the calculated values.

$Ru(II)/Al_2O_3$

Three groups of catalysts in the (2+) oxidation state were prepared from the wet chemical reduction of $RuCl_3$ in hydrazine (*29*) via the incipient wetness technique. The weight loadings of the samples were 0.78%, 2.9%, and 4.7% with pH values of 9.96, 9.33, and 9.04 before the addition of support. As for the case of $RuCl_3/Al_2O_3$, twice the required amount of $RuCl_3$ was measured under a nitrogen atmosphere and dissolved in 10 ml of air-saturated distilled water. The beakers were then removed and placed in a fume hood prior to the addition of the reducing agent. A 2 ml aliquot of hydrazine hydrate was slowly added to each solution (*30*) with shaking. The initial reaction was vigorous as N_2, H_2, and NH_3 gases were evolved (*31*). After about 15 min, the bubbling subsided and 6 ml of the solution was added to 2.5 g of alumina in a Teflon beaker. The $[(RuCl_3/H_2NNH_2)/Al_2O_3]$ samples were constantly shaken and dried at room temperature. The drying time for each sample was no more than 24 h. A 1 ml aliquot of the remaining Ru(II) mother solution was removed, properly diluted, and analyzed for its total ruthenium concentration using the AA.

CATALYST CHARACTERIZATION

Techniques

Each of the catalysts was subjected to the following characterization techniques: (1) temperature-programmed reaction (TPR) of CO (*32*), (2) steady-state CO hydrogenation kinetics (*1, 22*), and (3) temperature-programmed surface reaction (TPSR) (*33*). The CO-TPR experiment provides structural information related to the accessibility of the surface ruthenium sites for CO adsorption. The steady-state CO hydrogenation reaction demonstrates the differences in performance for various catalysts while the TPSR experiment was conducted after the steady-state experiment to assess the amount of carbon-containing residues left on the catalyst surface.

Apparatus

The catalyst characterization experiments were carried out in a TPD apparatus. This apparatus consists of a gas-purification/flow-control section, a reactor unit, and a detector unit. The catalyst particles were contained in a stainless-steel tubular insert of the following dimensions: 20 mm long, 7.14 mm o.d., and 5.95 mm i.d. This insert had a 400-mesh stainless-steel wire cloth at the bottom to support the particles. The insert rested in a stainless-steel tube surrounded by a copper shell cooled by water circulation. The system was heated by a Micricon 823 microprocessor-controlled infrared oven, with the temperature measured at the center of the bed (*34*). The composition of the gas exiting from the bed was constantly monitored and recorded by an on-line UTI-100C quadrupole mass spectrometer with a computer data acquisition system.

Procedures

To satisfy differential conditions and ensure no mass transfer limitations, 100 mg of each catalyst was used for all the studies (*35*). The samples were reduced according to the procedures given by King (*3*). To saturate the catalyst surface, 40 pulses of carbon monoxide (0.25 cm^3/pulse) were injected into a helium flow whose flow rate was 10 cm^3/min. The formation of volatile ruthenium carbonyls under such low CO pressures is negligible (*36*). The system was flushed with helium for 10 min at 30 cm^3/min followed by a 10 min flush in 30 cm^3/min of hydrogen. A TPR experiment was then performed at a 20 K/min heating rate to 773 K in a 30 cm^3/min flow of hydrogen. The peaks corresponding to $m/e = 2$, 15, 28, and 44 were monitored throughout the course of the experiment. After a 1 h hold time, the system was flushed with helium at 773 K for 5 min and then cooled to room temperature. For a number of catalysts selected at random, a second TPR was performed. For every case, no methane or carbon monoxide was detected.

Steady-state carbon monoxide hydrogenation experiments were determined over the temperature range from 443 K to 573 K for all of the catalysts, except for the 0.76% $RuNO(NO_3)_3/Al_2O_3$ catalyst prepared by wet impregnation. For this sample, it was necessary to increase the temperatures to lie between 513 K and 633 K in order to get a reliable methane signal from the mass spectrometer. A 3 : 1 H_2/CO mixture with a flow rate of 30 cm^3/min was used. The temperature was increased by 4 K/min in steps of 20 K without intermediate reduction of the catalyst, and held at each temperature for 20 min. The peaks at $m/e = 2$, 15, 28, 30, and 42 were recorded.

After the last measurement for the steady-state reaction was made, the catalyst was flushed with helium at the maximum temperature for 5 min and then cooled to room temperature. A TPSR experiment was then performed using a hydrogen flow rate of 30 cm^3/min and a heating rate of 20 K/min to 773 K in order to determine the amount of carbon-containing residues present on the surface of the catalyst subsequent to the steady-state experiment. The peaks corresponding to $m/e = 2$, 15, 28, 30, and 42 were continuously monitored during the TPSR experiments. The system was held at 773 K for 1 h to remove all of the carbon deposits. As with the CO-TPR experiments, a random number of catalysts were subjected to a second TPSR, and for every case, no methane signal was observed.

The surface of the catalysts after the steady-state experiments contained varying amounts of carbon. To ensure that we were not imparting any additional complexity to the catalyst surface by cooling in helium, four catalysts were selected at random and subjected to the same experiments as before. However, the only difference was that the catalyst was cooled to room temperature in the H_2/CO mixture after the steady-state experiment. It was found that cooling the catalyst under H_2/CO flow after the steady-state experiment led to the same spectrum and amount of carbon-containing residues as those derived from cooling in helium except for the appearance of a sharp peak attributed to CO methanation because the peak appeared at the same temperature as the peak from the CO-TPR experiment. In the discussions to follow, the results under the TPSR experiments reflect those obtained after the sample was cooled under a flow of helium after steady-state CO hydrogenation.

RESULTS

Catalyst Characterization

CO-TPR

Temperature-programmed reaction (TPR) of CO resulted in a single peak for all of the catalysts studied. A slight shoulder on the high-temperature side of the peak was observed in a few cases, primarily for the $RuCl_3$ and Ru(II) catalysts supported on alumina. Figures 1a–1c show the TPR spectra for a series of Ru(II)/Al_2O_3 catalysts prepared by incipient wetness.

Based on the fact that no CO or CO_2 desorption was observed, the total amount of methane produced is assumed to be the total CO uptake. The percentage of accessible ruthenium sites, which is designated as dispersion (*37*), can be calculated as the ratio of the surface ruthenium atoms accessible for CO adsorption to the total number of ruthenium atoms supported on Al_2O_3. CO chemisorption has been used quite frequently to determine the dispersion of supported ruthenium catalysts (*1, 38–41*); however, its implementation has been complicated by interference from CO adsorption on the support and by several CO molecules bonding to a single Ru atom. To avoid these complications, subatmospheric quantities of CO were pulsed onto the catalyst in a helium flow. A previous study (*35*) has demonstrated that CO adsorption on the support is negligible under these conditions. To check that residual chloride

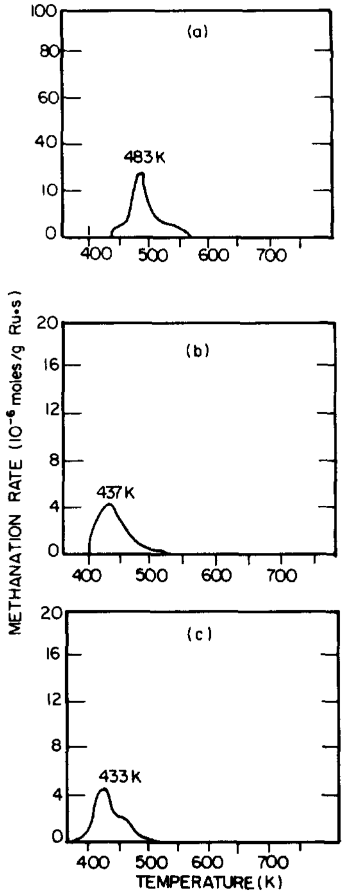

FIG. 1. CO-TPR spectra for Ru(II)/Al_2O_3 catalysts at (a) 0.78%; (b) 2.9%; and (c) 4.7%.

present on the catalysts derived from $RuCl_3$ was not enhancing CO adsorption on the alumina, a 0.17% Cl–Al_2O_3 sample was prepared by incipient wetness impregnation of the Al_2O_3 by HCl. The sample was dried at 473 K for 3 h and calcined at 773 K in an air flow for 3 h to fix the Cl^- onto the support. The Cl^- concentration was confirmed by XRF. The sample was reduced (in the same manner as the other samples in this study) and subjected to a CO-TPR. No methane peak was observed, thereby demonstrating that CO adsorption on pure and chlorinated alumina is negligible for the catalysts in this study.

Table 1 lists the dispersions for different catalysts from CO uptake data based on an adsorption stoichiometry of CO/Ru = 1 (*42, 43*). Note that for $RuNO(NO_3)_3/Al_2O_3$ catalysts prepared by incipient wetness and wet impregnation the effects of metal loading and pH on the dispersion are negligible. Similarly, the effects of metal loading on the dispersion were insignificant for the $RuCl_3/Al_2O_3$ catalysts. However, the dispersion was greatly affected by the ruthenium weight loading for the ruthenium catalysts in the (2+) oxidation state.

Hydrogen chemisorption is the technique used most often to determine metal disper-

TABLE 1

Summary of CO-TPR, Steady-State CO Hydrogenation, and TPSR Experiments

Ru wt%	pH	Dispersion	TOF at 523 K (10^{-3} s^{-1})	Act. energy (kJ/mol)	C/Ru	Total carbon (μmol/g catal.)
(a) $RuNO(NO_3)_3/Al_2O_3$ catalysts prepared by incipient wetness						
0.76		33.9	3.3	178.0	0.65	16.6
1.1	1.56	31.5	2.8	149.0	3.1	107.3
1.1	1.85	28.8	7.0	144.0	3.4	107.3
1.1	2.38	30.5	5.3	140.0	3.5	114.6
1.1	2.92	25.4	4.3	146.4	3.9	108.8
1.1	3.50	33.9	13.0	129.8	0.98	36.0
3.1		31.0	29.0	139.8	0.33	31.0
5.0	1.43	29.1	76.0	129.8	0.18	25.6
(b) $RuNO(NO_3)_3/Al_2O_3$ catalysts prepared by wet impregnation						
0.73	1.85	36.5	8.8	159.8	0.96	25.2
0.72	2.16	31.6	5.3	158.9	0.74	16.6
0.75	2.83	28.5	10.0	149.8	1.2	25.2
0.78	3.55	46.6	5.4	121.9	0.91	32.9
1.7	1.39	49.2	23.0	142.7	0.55	45.8
3.3	0.67	27.7	57.0	144.8	0.31	28.4
4.2	0.58	27.3	30.0	166.8	0.36	40.9
(c) $RuCl_3/Al_2O_3$ catalysts						
0.76	1.55	14.1	6.3	114.4	3.1	33.2
3.0	1.15	14.8	46.0	114.8	0.71	31.4
5.1	1.09	8.7	102.0	132.7	0.48	21.0
(d) Ru(II)/Al_2O_3 catalysts						
0.78	9.96	12.6	20.0	127.7	2.0	19.3
2.9	9.33	1.9	484.0	123.0	6.0	32.8
4.7	9.04	1.6	472.0	109.8	4.6	34.2

sions on supported ruthenium catalysts. To check that CO-TPR is an accurate method for determining metal dispersions in this system, the dispersion values of a test catalyst were determined using both H_2 chemisorption and CO-TPR. The test sample was a 3.55% Ru/Al_2O_3 catalyst prepared from ruthenium trichloride by the incipient wetness technique at the Exxon Research and Engineering Co. A dispersion of 14% was measured at Exxon for this sample using H_2 chemisorption (*44*). The catalyst was reduced in our laboratory under the same conditions employed for the other samples in this study, and a dispersion of 14.0% was measured via CO-TPR. From these results, it is evident that CO-TPR is a reliable method for determining metal dispersions on these supported catalysts.

Steady-State CO Hydrogenation

In this study, the majority of the product from the hydrogenation of CO was methane. Activities are given in terms of turnover frequency (TOF); CO uptake was used to calculate the total number of active sites by assuming an adsorption stoichiometry of CO/Ru = 1.

Except for the 0.76% $RuNO(NO_3)_3$ catalyst prepared by the incipient wetness technique, all of the catalysts were subjected to the same steady-state temperature cycle. In general, the more active catalysts had a lower range of temperatures over which a linear Arrhenius plot was found. Above this temperature range, a "bend over" (change in the slope of the Arrhenius plot) was observed due to heat and mass transfer effects in the bed. Table 1 also summarizes for each catalyst the activities for methane formation at 523 K and their apparent activation energies. The variation in the TOF for these catalysts appears to depend on the precursor used in its preparation. Other factors such as weight loading preparation method, and pH of impregnant contribute only relatively small variations. The activation energy was obtained for each catalyst in the linear range of the Arrhenius plot; reproducibility was better than ±6 kJ/mol.

TPSR

The carbon inventory is known to be extremely complex for Ru/Al_2O_3 catalysts (*18, 33*). As many as three forms of surface carbon have been observed (*33*) including a weakly adsorbed CO species, a relatively tightly sorbed amorphous carbon, and an unreactive graphitic carbon. The surface carbon species produced by the dissociation of CO serve not only as intermediates in methanation reactions (*4, 9–15*), but also as precursors to site-blocking poisons (*2, 17, 18*). In addition, the TPSR spectra provide an indication of the contribution of adsorbed CO to the total carbon inventory. These observations provide information about the structure of the catalyst, and can also be used to assess the impact of residual chloride on the catalysts derived from $RuCl_3$ (*24*). Figures 2a–2c show the TPSR spectra for $Ru(II)/Al_2O_3$ catalysts.

The fact that previous studies have indicated that the carbon-containing residues may serve as reaction intermediates in Fischer–Tropsch synthesis has led to the hypothesis that catalyst activity is directly related to the amount of residue present (*19*). The CO uptake was used to calculate the total number of carbon-containing residues per metal site (C/Ru). The results of this calculation are also given in Table 1. Note that for each ruthenium precursor, except the Ru(II) catalysts, the number of carbon-containing residues per metal site decreases with increasing activity. On the other hand, the number of carbon-containing residues per metal site increases with increasing activity for the $Ru(II)/Al_2O_3$ catalysts.

DISCUSSION

A number of previous publications have addressed the issue of dispersion effects on the performance of supported ruthenium catalysts. Dalla Betta *et al.* (*23*) observed that the methanation activity of alumina-

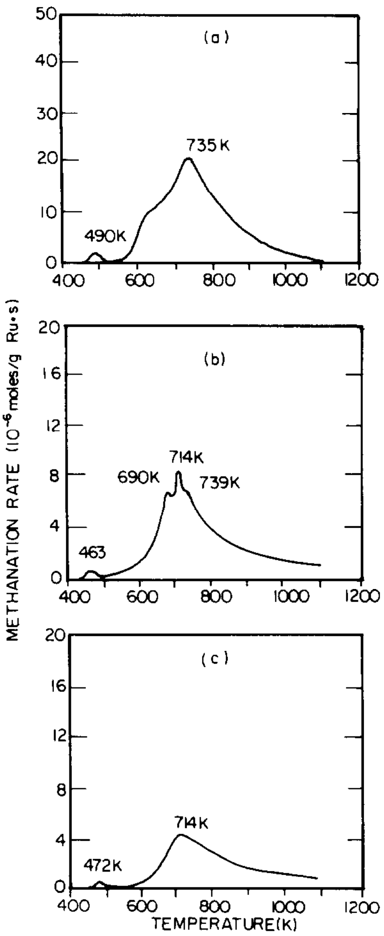

FIG. 2. TPSR spectra for $Ru(II)/Al_2O_3$ catalysts at (a) 0.78%; (b) 2.9%; and (c) 4.7%.

supported ruthenium catalysts decreases with increasing dispersion. Similarly, King (*3*) observed a monotonic decrease in methanation activity with increasing dispersion for ruthenium on a variety of oxide supports and zeolites. Changes in dispersion have also been observed as a result of catalyst sintering under reaction conditions (*1*, *21*). Kellner and Bell (*21*) have suggested that for Ru dispersions below 75%, the decrease in the specific activity for the synthesis of methane with increasing dispersion is due to a decrease in the fraction of sites present on planar surfaces. While these and related studies are significant in that they disclose the various means by which one can achieve changes in dispersion of Ru on alumina-supported catalysts, they cannot be considered exhaustive as they do not address the issue of ruthenium precursor variations on the dispersion of fresh Ru/Al_2O_3 catalysts. A study by Bossi *et al.* (*45*) demonstrated the effects of ruthenium precursor on the dispersion for six different ruthenium salts of equal weight loading supported on alumina. However, they did not subject their catalysts to any performance tests and thus the effects of ruthenium precursor on the dispersion *and* activity of alumina-supported catalysts have yet to be established.

Figure 3 shows the methanation activity at 523 K as a function of Ru dispersion. Included in this plot are data from King (*3*), Dalla Betta *et al.* (*23*), and Vannice (*1*). King's work is the most comprehensive in terms of spanning a wide range of Ru dis-

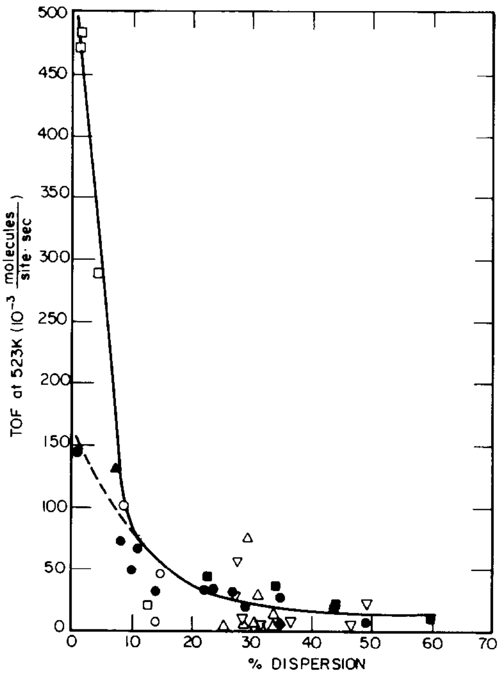

FIG. 3. TOF at 523 K as a function of Ru dispersion. ●, ■, Ref. (*3*); ▲, Ref. (*7*); ◆, Refs. (*22*) and (*23*). △, This study, $RuNO(NO_3)_3/Al_2O_3$ by incipient wetness; ▽, this study, $RuNO(NO_3)_3/Al_2O_3$ by wet impregnation; ○, this study, $RuCl_3/Al_2O_3$; □, this study, $Ru(II)/Al_2O_3$.

persions, yet none of his supported catalysts has a turnover frequency greater than 75×10^{-3} s^{-1}. The experimental data are in agreement with the results of previous investigators, as a monotonic decrease in activity with increasing dispersion is observed. The turnover frequencies reported here approach 500×10^{-3} s^{-1} and thus expand the range of methanation activities studied previously.

In Fig. 3 none of the supported Ru catalysts prepared by King had a dispersion below 8.5%. To obtain information at lower dispersions, he used Vannice's Ru/Al_2O_3 results in conjunction with the data from an unsupported Ru catalyst. By incorporating these final two samples, King's work spanned a range of dispersions from 0.3 to 60%, and the dashed line in Fig. 3 represents a summary of his conclusions. However, King's interpretation is misleading in that the anomalous behavior exhibited by unsupported Ru catalysts (*3*) excludes them from comparison with supported materials.

We conclude from Fig. 3 that dramatic changes in the particle size distribution and hence, TOF, can be realized by altering the salt used during the preparation of Ru/Al_2O_3 catalysts. These changes in the size of Ru crystallites deposited on the alumina surface may be related to differences in the aqueous phase chemistry of the reagents studied. For example, the speciation of $RuCl_3$ impregnating solutions is very complex due to the multicomponent and heterogeneous nature of this reagent (*48, 53*). Polymeric ions form in $RuCl_3$ solutions due to the presence of Ru(IV) (*53*). Recall that the Ru(II) solutions were prepared via the aqueous reduction of $RuCl_3$ in hydrazine to $[Ru(NH_3)_5N_2]^{2+}$. Ru(II) complexes (formed during the initial contact of $RuCl_3$ with hydrazine) are larger than their parent $RuCl_3$ species (*31*). With respect to solutions of $RuNO(NO_3)_3$, carefully controlled preparation conditions (*26*) lead to a series of mononuclear complexes that are completely hydrolyzed at a pH greater than 2.

The above data provide a rational framework for the hypothesis that the variation in particle size distribution of supported-Ru catalysts is the result of differences in the states of aggregation of the aqueous Ru precursors. To illustrate this concept, consider the large variation in dispersion between the low (0.78%) and high (2.9% and 4.7%) weight-loading Ru(II)/Al_2O_3 catalysts. Since the amount of hydrazine used to prepare these samples was constant and always in excess of the stoichiometric amount, the number of $RuCl_3$ species retaining their composition at low weight-loadings was small. However, at the high weight-loadings, the concentration of $RuCl_3$ was increased, thereby forming roughly equal amounts of large Ru(II) complexes and somewhat smaller $RuCl_3$ species. The result of this situation would be a flocculation of ruthenium due to size and charge differences. The extremely large Ru particles subsequently formed and deposited on the alumina surface apparently lead to a poor dispersion of the catalyst upon activation.

This type of behavior was observed in Gay's studies of Ru(II)/SiO_2 (*30*), although no explanations for the phenomenon were offered. What Gay found was that by first adding $RuCl_3$ to the support and then reducing the suspension with hydrazine at a later point, much higher dispersions were realized than when the support was added *after* mixing the $RuCl_3$ species. The result was higher dispersions than when the large flocculated particles were allowed to form.

Although the exact relationship between the aggregation of the aqueous precursor in the impregnating solution and the particle-size distribution of the finished catalyst is still unclear, this work in conjunction with prior studies suggests that such a link exists. Research of the aqueous chemistry of ruthenium (*25, 26, 29, 31, 49–52*), Gay's work with Ru(II)/SiO_2 (*30*), and the Auger analyses of Bossi *et al.* (*45*) are consistent with the proposal that one can manipulate the dispersion of supported Ru catalysts by affecting the precursor size distribution during impregnation. This study adds to the prior work by showing that the homogeneous suspension formed from RuNO $(NO_3)_3$ led to the smallest particles deposited on the support, Ru polymerization in $RuCl_3$ solutions caused lower dispersions than observed with $RuNO(NO_3)_3$, and the complicated interactions of chlorinated Ru polymers with Ru(II) hydrazine complexes gave rise to the largest catalytic particles and hence, the lowest dispersions.

Consistency of this study with previous research is not limited to the effects of precursor chemistry on Ru dispersion. Figure 4 shows the turnover frequency at 523 K as a function of the peak methanation temperature from the CO-TPR studies. The shape of this curve is similar to that given in Fig. 3, and fits well with the observation that increases in methanation activity are accompanied by decreases in the CO-TPR peak temperatures (*46*, *47*). Although not incorporated in Fig. 4, turnover frequencies at various temperatures were plotted against the CO-TPR peak temperature. The shapes of the curves generated were similar to that given in Fig. 4, suggesting that this correlation between TOF and CO-TPR peak temperature is generally valid.

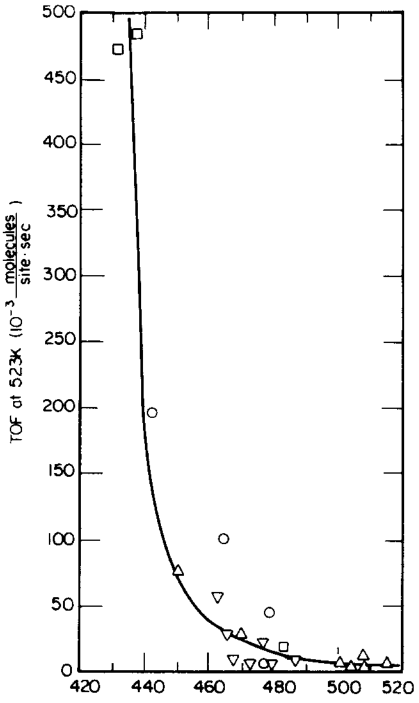

FIG. 4. TOF vs TPR peak temperature for methanation. △, $RuNO(NO_3)_3/Al_2O_3$ by incipient wetness; ▽, $RuNO(NO_3)_3/Al_2O_3$ by wet impregnation; ○, $RuCl_3/Al_2O_3$; □, $Ru(II)/Al_2O_3$.

Table 1 shows that variations in the particle-size distribution of Ru/Al_2O_3 catalysts affect the activity of these samples by modifying the number and amount of carbon-containing reaction intermediates on the surface. Note that the results of the TPSR experiments subsequent to steady-state CO hydrogenation are analyzed in terms of the number of surface Ru atoms available to participate in methanation. In this way, the contribution to the total carbon inventory of each Ru atom may be assessed. The total carbon deposition as a function of the number of surface atoms is shown in Fig. 5. This plot shows that for a catalyst containing a larger number of surface atoms (i.e., well-dispersed), the contribution of each atom to the total carbon inventory is low. Such is the case for small ruthenium particles, which have a large number of exposed metal atoms. On the other hand, the fraction of exposed Ru atoms is much smaller on large particles and therefore each surface atom contributes more carbon to the total inventory. We propose that high methanation activities are associated with large particles as these particles can accommodate more reactive carbon.

To test this hypothesis, the steady-state reaction time for two catalysts was adjusted so that each achieved the same turnover frequency. The samples were then subjected to a TPSR to determine the carbon inventory. The details of these experiments are given below. Note that catalysts derived from $RuNO(NO_3)_3$ were chosen for this set of experiments in order to avoid any obscuring effects due to residual chloride.

The 4.2% $RuNO(NO_3)_3/Al_2O_3$ catalyst prepared by wet impregnation was sub-

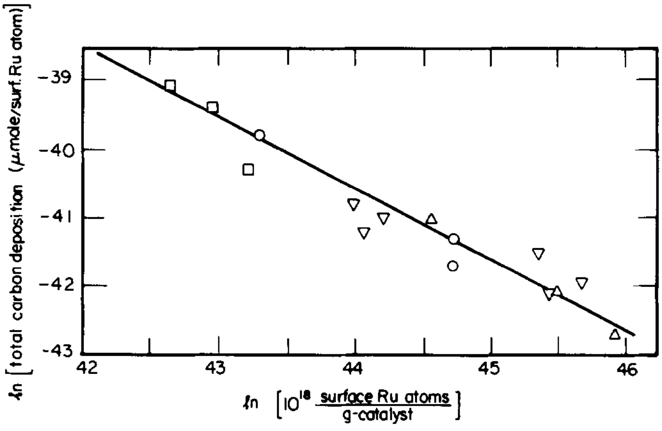

FIG. 5. Total carbon deposition vs total number of surface ruthenium atoms per gram of catalyst. △, $RuNO(NO_3)_3/Al_2O_3$ by incipient wetness; ▽, $RuNO(NO_3)_3/Al_2O_3$ by wet impregnation; ○, $RuCl_3/Al_2O_3$; □, $Ru(II)/Al_2O_3$.

jected to the routine battery of characterization tests: CO-TPR, followed by steady-state CO hydrogenation, and TPSR. The measured methanation activity for this catalyst was

$$\text{TOF at } 523 \text{ K} = 29.8 \times 10^{-3}\ \text{s}^{-1}.$$

After the TPSR experiment, the catalyst was cooled to room temperature under a flow of helium and the gas was switched to the 3 : 1 H_2/CO mixture used in the steady-state experiments. The temperature was then increased at a rate of 10 K/min to 523 K and held for 1 h. Based on the results from the first steady-state experiment the catalyst should then produce X molecules per site of methane,

$$X = 29.8 \times 10^{-3}\ \text{s}^{-1} \times 3600\ \text{s} = 107.3\ \text{molecules/site}$$

during this time frame. The catalyst was cooled under helium flow after this second methanation experiment, and a TPSR was performed to assess the carbon residues.

Next, the 1.7% $RuNO(NO_3)_3/Al_2O_3$ catalyst prepared by wet impregnation was subjected to the same battery of initial characterization tests. For this catalyst, the measured activity was slightly lower than for the 4.2% sample:

$$\text{TOF at } 523 \text{ K} = 23 \times 10^{-3}\ \text{s}^{-1}.$$

For the 1.7% catalyst to produce the same amount of methane as the 4.2% sample, the amount of time required to hold the catalyst under the 3 : 1 H_2/CO flow, t_m, was

$$t_m = (107.3\ \text{molec/site})/23 \times 10^{-3}\ \text{s}^{-1} = 4670\ \text{s}\ (77.8\ \text{min}).$$

A second methanation experiment was then performed in the same manner as with the 4.2% catalyst, but the soak time was 77.8 min. As before, the catalyst was cooled to room temperature in helium, and a TPSR was performed to assess the carbon-containing residues. The results of these experiments are given in Table 2 and demonstrate that more active catalysts have a larger carbon pool associated with their particles. For example, the 4.2% catalyst has a higher activity that the 1.7% sample based on the constant-time (initial) methanation experiment. After each catalyst produced the same amount of methane on a per site basis, the 4.2% sample had a total carbon deposition that was roughly 40% larger than for the 1.7% catalyst. The above data suggest that one of the reasons large particles are very active is that these aggregates can maintain larger amounts of carbon than small particles.

TABLE 2

Summary of Experiments for Constant-Time Methanation and Constant Methane Production for Ru/Al_2O_3 Catalysts Prepared by Wet Impregnation

Ru (wt%)	Initial TOF at 523 K (10^{-3} s^{-1})	Total C deposit after first s.s. (μmol/g catalyst)	Total C deposit[a] (μmol/g catalyst)
1.7	23.0	45.8	51.9
4.2	29.8	40.9	72.1

[a] Total carbon deposition after the catalyst has produced 107.3 molecules/site.

TABLE 3

Effects of Catalyst Sintering on the Methanation Activity of Ru/Al_2O_3

Sample	Initial CO-TPR		Second CO-TPR	
	Peak temp. (K)	D_{Ru}[a]	Peak temp. (K)	D_{Ru}[a]
1.7% $RuNO^{(3+)}$ wet impreg.	477	49.2	468	6.0
3.3% $RuNO^{(3+)}$ wet impreg.	463	27.7	458	11.2
5.1% $RuCl_3$	465	8.7	442	1.8
Test catalyst[b]	459	14.0	447	4.3

[a] Refers to the percentage of dispersion of Ru.

[b] 3.55% Ru/Al_2O_3 supplied by Exxon Research and Engineering Co.

To study the effects of catalyst sintering during characterization, a second CO-TPR experiment was performed for a number of catalysts after the catalysts were exposed to a different sequence of characterization tests. After the initial battery of experiments (i.e., CO-TPR, steady-state CO hydrogenation, and TPSR), the 1.7% and 3.3% $RuNO(NO_3)_3/Al_2O_3$ catalysts prepared by wet impregnation were subjected to the constant methanation experiments and a TPSR, followed by a second CO-TPR. The 5.1% $RuCl_3/Al_2O_3$ catalyst was simply exposed to a second CO-TPR after the initial round of tests, while the entire sequence was repeated for the Exxon test catalyst, with the only difference being that the gas flow was maintained as the 3 : 1 H_2/CO mixture during cooling subsequent to the second steady-state experiment. Table 3 presents the results of these experiments. Note that for every catalyst, the dispersion drops dramatically. Since the test catalyst was the only sample whose entire characterization sequence was repeated, it is the only sample whose methanation activities can be directly compared for fresh and used catalysts. The fresh catalyst had a dispersion of 14% and a TOF at 523 K of 299 · 10^{-3} s^{-1} with a dispersion of 4.3%. The ratio of the TOF at 523 K for the used catalyst to that at 523 K for the fresh sample is approximately 2. Using activity data based only on the initial dispersion of the catalyst, we find the ratio of the TOF at 523 K for a catalyst having a dispersion of 4.2% to that at 523 K for a catalyst having a dispersion of 14% is also roughly 2. Our procedures would appear to preclude that the decrease in dispersion after reaction is due to blockage of the metal by highly unreactive graphitic overlayers because a second temperature ramp in H_2 showed no release of CH_4. Thus, the results suggest that metal particles are indeed sintering and that other processes, such as a repartitioning of chloride to the support, are not occurring during characterization.

SUMMARY

Previous research has shown that changes in the size of supported Ru particles affect the performance of the finished catalyst. In addition, prior work has demonstrated that Ru particle size may be manipulated by increasing the metal loading on a given support of altering the support for a given Ru precursor. Our research extends this work by demonstrating that changes in dispersion can be easily accomplished by changing the precursor used in preparing a supported Ru catalyst. Indeed, much lower dispersions than previously measured for Ru/Al_2O_3 catalysts were achieved by preparing Ru(II) impregnating solutions. This led to methanation activities over three times larger than would be expected based on the work of King for catalysts of comparable dispersion. It is suggested that variations in the dispersion of the catalysts studied are related to differences in the aqueous chemistry of Ru precursors used. The formation of large species in solution leads to large catalytic particles on the support that can accommodate more reactive carbon intermediates, thereby enhancing the TOF.

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