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

II. The Impact of Residual Chloride

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The impact of residual chloride on the properties and performance of a series of Ru/Al_2O_3 catalysts has been studied. This work departs from previous studies in that it examines the poisoning and promoting effects of this electronegative element in CO hydrogenation as a function of the dispersion of the catalyst. The dispersion and structure of the particles are regulated by the choice of the precursor used during preparation and by the impregnation conditions. We find that, in general, chloride residues poison catalysts with a high dispersion but provide a promotional effect for catalysts with a poor dispersion. © 1989 Academic Press, Inc.

INTRODUCTION

Much of the current research carried out on supported ruthenium catalysts has focused on the precise characterization of the surface carbon formed subsequent to CO dissociation and on the effects of residual chloride on metal surface-area measurements. In the former case, we have proposed that the higher the activity of the catalyst the higher the propensity to incorporate carbon onto the catalyst surface during steady-state CO hydrogenation (*1*). The activity was shown to be a strong function of the dispersion, those catalysts with the lowest dispersion being the most active. The dispersion of these alumina-supported ruthenium catalysts could be conveniently adjusted by proper choice of the catalytic precursor.

The effect of chlorine on the chemisorptive and reactive properties of Ru/Al_2O_3 catalysts has been studied in a significant number of papers appearing within the last year (*2–6*). In their study of the effects of residual chloride on a 10.8%-Ru/Al_2O_3 catalyst, Gonzalez *et al.* (*3*) found that during reduction, the Cl^- ions migrated along the surface of the catalyst and that roughly half of the total chloride was then incorporated into the alumina. This is in direct contrast to the case for ruthenium supported on SiO_2, where it was found that all of the Cl^- could be removed from the metal by simply increasing the reduction temperature (*2*). Nonetheless, Gonzalez and co-workers proposed that chloride associated with Ru blocked the chemisorption of CO, thus rendering potential sites for CO hydrogenation inaccessible. A study by Blanchard and Charcosset (*7*) showed that the presence of Cl^- is an indication of incomplete reduction of Ru^{3+} to Ru^0, while White and co-workers (*8*) demonstrated that the presence of chloride ions affects the C–O bond strength and therefore the reactivity of the CO molecule. Although these studies look at the effects of chloride from different perspectives, it is clear that the propensity of alumina to scavenge chloride plays a role in the observed phenomena.

It is important to place these more recent studies of the effect of chloride on the catalytic properties of alumina-supported ruthe-

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nium catalysts into the proper perspective. The results have been obtained from catalysts having a limited range of dispersions. Since the performance of these catalysts is more strongly dependent on their dispersion, it is likely that the relative effect of chloride will vary depending on the particle size of the catalyst. The objective of this report is to demonstrate that, in fact, this is the case. Moreover, we find that in some instances the presence of chloride has a promotional effect on the methanation activity.

The catalysts used in this study have been described in detail in Part I of this series (*1*). Wet impregnation and incipient wetness were the methods employed during preparation; ruthenium nitrosylnitrate and ruthenium trichloride were the reagents. The former case provides a standard against which those catalysts prepared from chloride-containing precursors can be compared. In the latter case, either Ru(III)/Ru(IV) chloro species or mixtures of Ru(II) hydrazine complexes were the catalytic precursors. These reagents were used to form catalysts with weight loadings that ranged from 0.7 to 5% by weight and which had dispersions between 1 and 50%.

EXPERIMENTAL

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.

The reagents and impregnation procedures have been described in detail elsewhere (*1*).

AMMONIA-EXCHANGED $RuCl_3$ AND Ru(II) CATALYSTS

A 250-mg sample of both $RuCl_3/Al_2O_3$ and $Ru(II)/Al_2O_3$ catalysts was reduced in H_2 using the procedures to be described shortly; the flow rate of H_2 was adjusted to 75 cm^3/min to account for this large amount of sample. At the end of the temperature program, the sample was cooled to room temperature in a 75 cm^3/min flow of helium. The catalyst was then placed in a Teflon beaker and contacted with an appropriate amount of 0.1 *M* NH_4OH. For the low and intermediate weight-loading samples of each group, the samples were in contact with 25 ml of ammonia, while 50 ml was used for the high weight-loading catalysts. Each beaker was tightly sealed with Parafilm and constantly agitated for 12 h. At the end of this cycle, the sample was carefully filtered and allowed to dry at room temperature with constant shaking. Once dry, the catalysts were stored in a desiccator until characterization.

A 1 ml aliquot of each wash solution was removed and diluted by air-saturated distilled water to facilitate chloride analysis. The low weight-loading samples were diluted in a 25 ml flask, whereas the samples of intermediate and high weight-loading were diluted in 100 ml flasks. These diluted samples, along with their mother wash solutions were stored in plastic vials until further analysis.

In a recent publication (*3*), Gonzalez *et al.* claim that it is possible to strip chloride from the surface of alumina-supported ruthenium catalysts by washing the reduced samples in a dilute ammonia solution. Gonzalez and co-workers used a chloride ion-specific electrode to analyze their wash solutions for Cl content. These electrodes are commonly used to detect chloride levels of 0.2 ppm and higher (*9*). To obtain better accuracy, a Dionex Model 2020i Chloride Ion Chromatograph, sensitive to 1 ppb (*10*), was used to determine the amount of chloride present in the wash solutions. The range of chloride standards used was 0.1 to 2.0 ppm, and the diluted wash solutions were run sequentially in the chromatograph.

As a check, the wash solutions were analyzed for any dissolved ruthenium that may have been leached from the samples. An atomic absorption spectrophotometer was used to determine the Ru concentration; the procedures have been described before (*1*). No ruthenium was detected in any of the wash solutions. This was expected, as the purpose of reducing the catalyst prior to washing was to strongly bind the metal to the support.

CATALYST CHARACTERIZATION

Techniques and Apparatus

Each of the catalysts was subjected to the following characterization techniques: (1) temperature-programmed reaction (TPR) of CO (*11*), (2) steady-state CO hydrogenation kinetics (*12, 13*), and (3) temperature-programmed surface reaction (TPSR) (*14*). 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.

The apparatus used in these studies is described in a number of publications (*1, 15–18*).

Procedures

To satisfy differential conditions and ensure no mass-transfer limitations, 100 mg of each catalyst was used for all the studies (*19*). The samples were reduced according to the procedures given by King (*20*). The flow rate of hydrogen was 30 cm^3/min and the temperature program involved a heating rate of 5 K/min from room temperature to 373 K, holding that temperature at 373 K for 1 h, then heating at 5 K/min to 523 K, holding at 523 K for 1 h, heating at 5 K/min to 723 K, followed by a 1 h soak at 723 K. The catalyst was then flushed with helium at 723 K for 5 min and cooled to room temperature.

Procedures to conduct CO-TPR, steady-state, and TPSR experiments have been described before (*1*). It is important to note here that additional evidence for the state of the catalyst surface can be obtained by close examination of the results of the TPSR experiments. The appearance of a peak in the CH_4 evolved under these conditions, at a temperature that corresponds to the maximum in the CO-TPR spectrum, is a fingerprint for the carbon–oxygen content of the total carbon inventory on the catalyst after steady-state reaction. We would expect that if the presence of chloride decreased the CO chemisorption on a catalyst, the CO uptake would increase after washing. Such effects would manifest themselves in an increase in this contribution to the TPSR spectra. Although difficult to quantify because of the possibility of CO removal during cooling prior to TPSR, variations in the spectra are a qualitative indication of the influence of residual chloride.

RESULTS

The method for removing residual chloride from Ru/Al_2O_3 catalysts was selected so that the results from this work could be compared to those of previous investigators (*2, 3*). Through the use of an extremely accurate instrument to detect chloride levels in the wash solutions, it is apparent that the ammonia exchange technique is not as effective as originally reported. This conclusion is illustrated in Fig. 1, which shows that for a constant ammonia contact time, the amount of chloride removal is a function of the Ru weight loading. In Fig. 1, the percentage of chloride removed is based on the total amount of chloride in the impregnating solution. For catalysts of low weight loading, it was possible to recover all of the chloride initially deposited on the catalyst's surface during impregnation. This suggests that the chloride is fixed to the catalyst and is not burned off during reduction. However, at high weight loadings, complete Cl^- removal was not achieved. By displaying the data in terms of the initial amount of

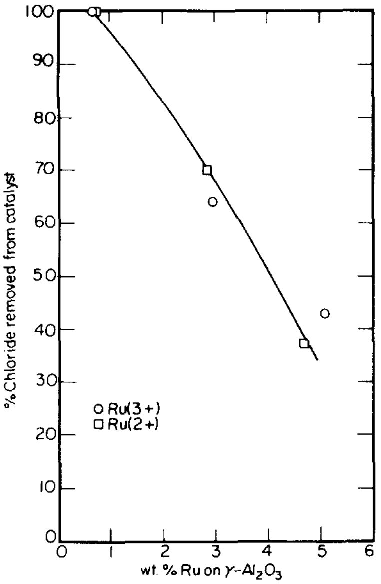

FIG. 1. Percentage chloride removed (based on the amount of chloride present in the impregnating solution) as a function of Ru weight loading.

chloride in the impregnating solution, we show in Fig. 1 the maximum concentration of chloride remaining on the catalyst surface. It is likely that the remaining chloride is still fixed to the catalyst, but the possibility of chloride "burn-off" during reduction cannot be eliminated. Nonetheless, the data in Fig. 1 represent conservative estimates of the actual chloride concentration to ensure that we do not overstate the effectiveness of the ammonia wash procedure.

The effects of residual chloride on Ru/Al_2O_3 catalyst performance are given in Table 1. The amount of Cl^- initially associated with the impregnation solution is always in great excess of the amount of surface ruthenium atoms associated with the catalyst; a substantial amount of chloride must be associated with the support, in addition to that affiliated with the metal for each (unwashed) catalyst.

One of the initial objectives of this research program was to study the effects of catalyst preparation on catalytic activity for the Ru/Al_2O_3 system and to assess the impact of residual chloride on catalysts derived from $RuCl_3$. To initiate the studies, ruthenium nitrosylnitrate was chosen as the Ru precursor containing no chloride. It was expected that the results from the characterization and performance tests could then

TABLE 1

Summary of Chloride Effects on Ru/Al_2O_3 Catalysts

Ru (wt %)	Amt. Cl^- initially (μmol/g cat.)	Amt. of Cl^- after wash[a] (μmol/g cat.)	Dispersion	TOF at 523 K (10^{-3} s^{-1})	E_a (kJ/mol)	Total C dep (μmol/g cat.)
			(a) $RuCl_3/Al_2O_3$ catalysts			
0.76	227		14.1	6.3	114.4	33.2
0.76	227	0	14.0	13.0	95.3	42.3
3.0	889		14.8	4.6	114.8	31.4
3.0	889	321	14.0	145.0	105.2	35.9
5.1	1481		8.7	102.0	132.7	21.0
5.1	1481	851	9.8	193.0	141.4	24.3
			(b) $Ru(II)/Al_2O_3$ catalysts			
0.78	219		12.6	20.0	127.7	19.3
0.78	219	0	24.6	37.0	122.7	33.7
2.9	819		1.9	484.0	123.0	32.8
2.9	819	271	4.2	285.0	114.8	47.7
4.7	1482		1.6	472.0	109.8	34.2
4.7	1482	929	2.9	195.0	104.4	50.8

[a] Denotes the amount of chloride remaining on the catalyst after washing in ammonia.

be compared to $RuCl_3$ catalysts supported on alumina in order to determine the effects of residual chloride. However, different Ru precursors result in a wide range of dispersions. In Part I of this series (*1*) it was shown that differences in particle size have a dramatic effect on catalyst performance. Thus, the effects due to changes in dispersion confuse direct interpretation of the effects due to residual chloride.

Figure 2a shows the effect of the ammonia-exchange technique on the dispersion (as determined by CO adsorption) of $RuCl_3/Al_2O_3$ catalysts for various weight loadings. Recall that no metal was leached from the catalyst as has been reported for high weight loadings of Ru on Al_2O_3 (*7*). Note that there are no significant variations in metal dispersion as a result of the washing procedure. However, it is clear that the washing procedure does have an effect when one considers the trends shown in Fig. 2b. In each case, the ammonia-washed samples have a larger total carbon deposition, the effect being greatest for the low weight-loading sample. The washed catalysts contain a slightly larger number of carbon-containing residues per metal site than their unwashed counterparts. This occurs because more carbon is deposited on the washed samples, and is not due to a decrease in the number of Ru sites.

The trends exhibited by the $Ru(II)/Al_2O_3$ catalysts are markedly different from those listed above. Figure 3a shows that the ammonia washing procedure leads, in each

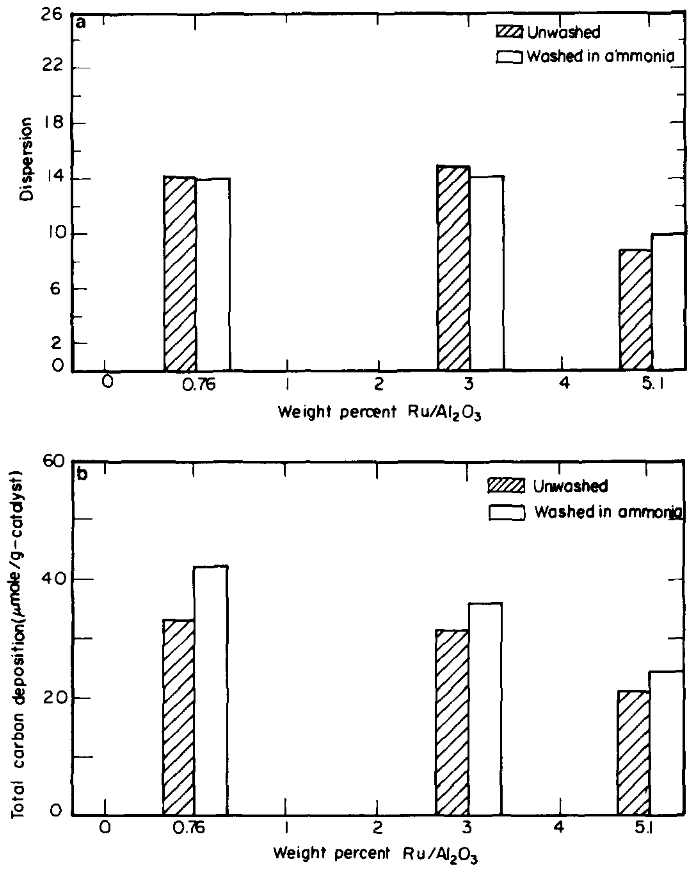

FIG. 2. Effects of ammonia-washing on (a) dispersion, (b) total carbon deposition for the $RuCl_3/Al_2O_3$ catalysts.

case, to a twofold (approximately) increase in dispersion of the metal. Figure 3b shows that the total carbon reservoir is increased as a result of washing, and this is in agreement with the trend shown in Fig. 2b for the $RuCl_3$ samples. A consistent picture of the combined effects of particle size variations and the impact of washing can be obtained by considerations provided in the next section.

DISCUSSION

To study the effects of residual Cl^- on Ru/Al_2O_3 catalysts, it is useful to develop a classification scheme. The catalysts will be divided into groups based on the size of the Ru particles formed on their surfaces. Type I particles include all of the $RuCl_3/Al_2O_3$ catalysts. The 2.9% and 4.7% $Ru(II)/Al_2O_3$ catalysts comprise the Type II species as they have the largest particles observed in this study. The low weight-loading $Ru(II)/Al_2O_3$ samples exhibit behavior intermediate between Types I and II, and as such, are designated as Type I(a) species. $RuNO(NO_3)_3$-based catalysts are devoid of chloride; they will be designated as Type 0 species in this scheme.

In order to provide an interpretation that is consistent with the trends observed in Figs. 2 and 3, we will use the above classification scheme. Based on the observations of Gonzalez and co-workers (*3*), it is assumed that a significant fraction of the chloride initially associated with the metal migrates to the support during reduction. In general, the samples of low weight loading are composed of relatively small particles. The amount of chloride associated with each catalyst is low. As a result, it is possible to remove from the low weight-loading catalysts all of the chloride from the metal in addition to any chloride from the support. For catalysts of higher weight loading, more chloride is present in the impregnant and therefore associated with the samples. Consequently, more chloride is expected to remain on the catalyst after a fixed contact time with the wash solution, even though some weakly bound chloride species may be removed during reduction.

The Type I particles were formed under severe conditions, as the initial solution pH was below 1.6 for each $RuCl_3/Al_2O_3$ catalyst. Consequently, there was a substantial amount of alumina dissolution throughout the drying period due to the strong buffering capacity of the dissolved Ru species (*21*). For these samples, the turnover frequency and total carbon deposition were observed to increase with ammonia washing. The enhanced TOF values are the result of Cl^- removal from the metal, which is indicated by their TPSR spectra. For each weight loading, the contribution of CO to the total carbon inventory increases with ammonia washing, indicating that Cl^- is stripped from the metal. Furthermore, the removal of chloride from the alumina allows for the support to accommodate more carbon, which results in larger total carbon deposits. Finally, it was observed that methanation activity increased with weight loading for the $RuCl_3/Al_2O_3$ catalysts, suggesting a particle size effect. Although the size of the particles increases from approximately 28 to 40 Å as weight loading increases (*1*), this effect is slight. Clearly, the effects of residual chloride on the properties of Type I catalysts dominate.

The morphology of the particles formed on low weight-loading $Ru(II)/Al_2O_3$ catalysts is similar to the Type II species in that there was an insignificant amount of alumina dissolution during impregnation. However, the behavior of these Type I(a) particles is similar to that of the Type I particles previously discussed in that the washed sample exhibits larger turnover frequencies and more total carbon deposition than their unwashed counterparts. The increase in the amount of carbon deposited is consistent with the premise that chloride removal provides more space for carbon deposition on the catalyst surface. On the other hand, an examination of the unwashed and washed samples' TPSR spectra indicates that the contribution of CO to the

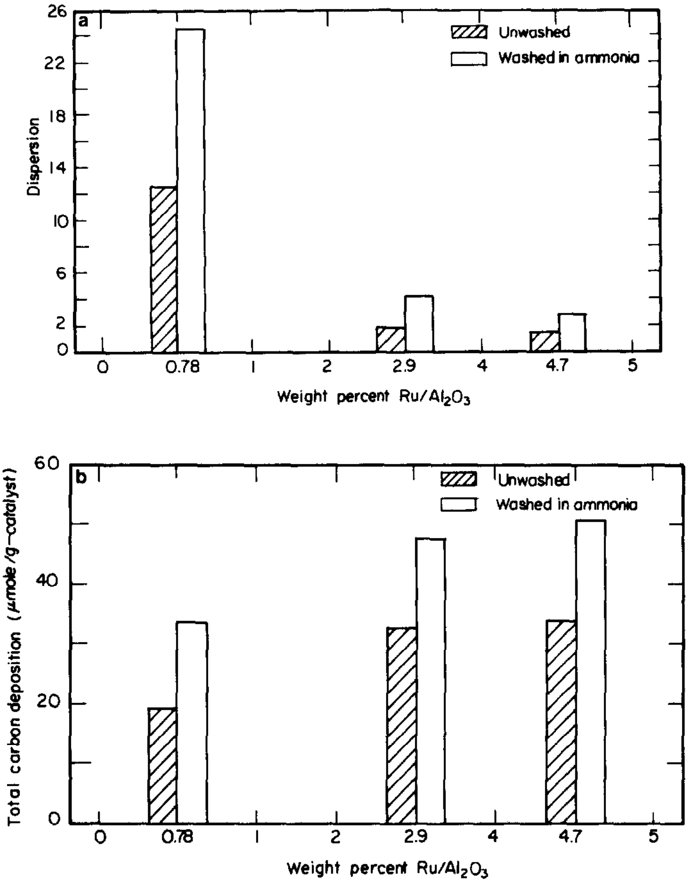

FIG. 3. Effects of ammonia-washing on (a) dispersion, (b) total carbon deposition for the Ru(II)/ Al_2O_3 catalysts.

total carbon inventory is negligible. We propose that higher turnover frequencies are the result of chloride being removed from Ru planar sites. Since these sites are more active (*1*), their exposure enhances CO dissociation, lowering the apparent activation energy and increasing the number of carbon-containing reaction intermediates. It must be noted that these Type I(a) species only represent a subgroup of a larger population, and cannot stand alone as there are too few samples to substantiate arguments for a separate grouping.

Before considering the anomalous behavior exhibited by the high weight-loading Ru(II)/Al_2O_3 catalysts, the properties of the Type 0, nonchloride-containing RuNO $(NO_3)_3/Al_2O_3$ samples will be presented. As with the Type I particles, the Type 0 species were formed under strongly acidic conditions. The resulting catalytic particles, by virtue of their higher dispersion, expose more defect sites which can lead to $Ru(CO)_2$ and $Ru(CO)_3$ formation. Indeed, this was apparent from their corresponding TPSR spectra. In general, increases in turnover frequency are associated with increases in Ru weight loading, but with no corresponding particle size effects. Moreover, the activation energies are highest for the Type 0 species, which is consistent with their small size and correspondingly larger fraction of exposed defect sites.

The reactivity patterns for the high weight-loading (2.9%, 4.7%) Ru(II)/Al_2O_3 samples are anomalous when compared to the trends found for the other alumina-supported Ru catalysts. As a group, these Type II species have the lowest apparent activation energy for methanation. This observation is consistent with the existence of large particles comprised of mostly planar surfaces on which the enhanced contribution due to backbonding weakens the C–O bond and facilitates its dissociation. However, the effects of chloride removal due to ammonia washing are more difficult to understand. Unwashed Type II samples show a higher TOF than the washed samples. On the other hand, these latter catalysts exhibit a greater amount of carbon residue due to steady-state reaction. As before, this effect can be interpreted as the result of providing more "room" for the carbon reservoir on both the metal and the support phase. Furthermore, the unwashed samples show essentially no change in TOF with increasing Ru weight loading, whereas the washed samples exhibit a decrease in TOF with increasing weight loading even though the particle size increases by approximately 50%.

In the first part of this series, we have demonstrated that the dominant factor controlling the performance of Ru/Al_2O_3 catalysts is their dispersion, and that the dispersion can be conveniently manipulated by choice of ruthenium precursor. In this study, the Type II particles are by far the largest, and as a result, their behavior must be investigated from a different perspective. In order to understand the apparent promoter effects of Cl^- on these catalysts, it is necessary to turn to the surface science literature, which provides evidence for the effects of electronegative adducts on the reaction properties of H_2 and CO.

The effect of electronegative elements on CO adsorption on supported ruthenium catalysts has been reported by White and co-workers (*8*). For either oxygen or chlorine, they found that although there was a decrease in the back-bonding contribution of Ru to the adsorbed CO, there was an *increase* in the forward bonding between the carbon 5*s* electrons and those of the metal. This effect leads to an increase in the Ru–CO bond strength, thereby enhancing CO dissociation, which is observed as a greater rate of methane production.

Enhanced methanation activity due to the presence of an electronegative element has been reported before. Palmer and Vroom (*22*) found higher turnover frequencies than expected for Ni and Co polycrystalline foils that were cycled in O_2 prior to reduction. Similarly, Sexton and Somorjai (*23*) reported a fivefold increase in the activity of Rh foils due to oxygen treatment. Palmer and Vroom conclude that the presence of oxygen appears to be a favorable factor in promoting the catalytic activity of certain transition metals. If one extends these conclusions to include electronegative elements in general, then the enhanced methanation activity over the unwashed Type II catalysts can be rationalized.

To conclude, it was observed that the effects of ammonia washing on dispersion were negligible for the Type I particles, but significant for Types I(a) and II. Our data support the fact that strong chloride–metal interactions result for catalysts in the Type I grouping. Since these samples were prepared under highly acidic conditions and the Type (Ia) and II catalysts were formed in a strongly basic environment, it is reasonable to suggest that alumina dissolution plays a role in determining the strength of the metal–chloride interactions by affecting the deposition of the Ru precursor. Studies are in progress to assess the "architecture" of the chlorinated and unchlorinated Ru/Al_2O_3 samples in order to gain a better understanding of the effect of preparation conditions on the structure and performance of these catalysts.

SUMMARY

The impact of residual chloride on Ru/Al_2O_3 has been investigated. It is convenient to discuss the effects of Cl^- on the performance of Ru/Al_2O_3 catalysts by classifying the samples according to particle

size. Type 0 particles are small and contain no residual chloride. Type I species are slightly larger and like the Type 0 samples, were formed under strongly acidic conditions. For catalysts within the Type I grouping, the effects of residual chloride on methanation dominate particle size effects. Type I(a) particles exhibit behavior similar to that of the Type I catalysts. Finally, particles in the Type II classification are by far the largest in this study, and consequently exhibit anomalous behavior compared to the other groups. An interpretation of the promotional effects of Cl^- on the methanation activity of Type II catalysts was founded on evidence provided in the surface science literature.

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