

The Effects of Cs Promotion on Rh/Al₂O₃ Catalysts

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The adsorptive and reactive properties of a series of Rh/Al₂O₃ catalysts promoted with various levels of Cs were investigated by IR spectroscopy of CO adsorption, temperature-programmed desorption of H₂, and CO hydrogenation reactions. The results indicate that a significant fraction of the added Cs interacts directly with the support rather than with the Rh crystallites. The degree of interaction between the alkali species and both metal and support sites on the catalyst depends strongly on the method of preparation of the catalyst, which may affect the chemical state of the alkali species. Trends for CO hydrogenation reaction activity and product selectivity were consistent with those reported for promoted Rh on other supports except that the level of promotion required to achieve similar results is much higher for Rh supported on Al₂O₃. These investigations demonstrate how a combination of experimental techniques may provide significantly more information about the effects of alkali promotion than would any of the methods used alone. © 1986

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INTRODUCTION

Supported catalysts based on rhodium are of interest for CO hydrogenation reaction studies because of the variety of products that may be formed on Rh depending on the type of support and the reaction conditions employed (1, 2). Another parameter which may affect the catalyst activity and the product distribution is the addition of alkali promoters. The sensitivity of Rh-based catalysts to these preparation and reaction parameters suggests the possibility of ultimately preparing catalysts which are "tailor-made" for a certain desired product spectrum. The key to this, and also to the hope of generalizing this to other metal systems, lies in the fundamental understanding of the adsorptive and reactive properties of Rh catalyst systems and how these properties are altered with changes in preparation and concentration of promoter species.

The behavior of alkali promoters added to transition metals in reactions such as NH₃ synthesis and CO hydrogenation has

been studied for a number of years (3-7). Alkali species have been considered as electronic promoters and several different mechanisms for the promotion process have been discussed. Ertl and co-workers (7) have suggested from studies of alkali-promoted Fe single crystals that the promoter species acts to enhance the electron density of the metal. This in turn increases the extent of back-donation of electrons from Fe to anti-bonding orbitals of adsorbates such as N₂. Recent theoretical studies (8, 9) have suggested that the enhanced metal-adsorbate interaction observed when CO, H₂, or N₂ is adsorbed on alkali-promoted surfaces arises because of an electrostatic interaction between the adsorbate and the alkali metal. Lang *et al.* (8) have shown that this electrostatic interaction results in an increase in the population of the anti-bonding orbitals of adsorbates such as CO. Thus, while researchers may differ on the origin of the electronic effect of alkali promotion, they often agree on the net result.

Another effect that alkali species might have is a geometric one in that the adsorbed

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TABLE 1
Description of Catalysts

Catalyst ^a	Preparation method ^b	Rh:Cs ^c
I-1/0	Impregnation	1:0
CI-100/1	Coimpregnation	100:1
CI-10/1	Coimpregnation	10:1
CI-2/1	Coimpregnation	2:1
SI-1/2	Seq. impregnation	1:2
SI-1/5	Seq. impregnation	1:5

^a All catalysts are based on 3 wt% Rh/Al₂O₃.

^b See text for explanation of preparation methods.

^c Atomic ratio.

alkali may serve to dilute the metal surface. The result of this might be to suppress certain types of adsorption which require ensembles of adjacent metal atoms or to decrease coupling interactions (10–12) between adsorbed molecules. McClory and Gonzalez (13) cited geometric effects as the major influence of alkali promotion on Ru/SiO₂ from their studies of CO hydrogenation.

The investigation reported herein was undertaken to develop an understanding of the adsorptive and reactive properties of a series of Rh/Al₂O₃ catalysts promoted with different levels of cesium. It has been reported that CO hydrogenation reactions over Rh supported on Al₂O₃ are significantly less affected by alkali promoters than are those over Rh supported on SiO₂, TiO₂, or La₂O₃ (2). The suggested explanation is that the Al₂O₃ support scavenges the alkali species and hence the metal is left relatively unperturbed. Thus, it is important not only to study the interaction between alkali and metal but also to probe the location of the alkali species on the catalyst surface.

EXPERIMENTAL

The effects of increasing amounts of Cs on the adsorptive and reactive properties of Rh/Al₂O₃ catalysts were investigated by temperature-programmed desorption

(TPD) of H₂, by infrared (IR) spectroscopic study of CO adsorption, and by CO hydrogenation reactions.

Catalyst preparation. Catalysts were prepared by aqueous incipient wetness impregnation of γ -Al₂O₃ (Strem, 240 m²/g, 0.25 cm³/g pore volume) with RhCl₃ (Strem) to a nominal loading of 3 wt%. CsNO₃ (Alpha) was added to the catalysts in varying amounts and in two different ways. In the first (coimpregnation), the Rh and Cs salts were added to the support prior to any further treatment. The second method (sequential impregnation) involved decomposition and reduction of the RhCl₃-impregnated Al₂O₃ prior to a second impregnation with the CsNO₃. After preparation, all catalysts were dried in air at 363 K overnight. Catalysts were reduced at 673 K for 16 h in H₂ after a 1 K/min ramp to the reduction temperature. Table 1 describes the catalysts.

Procedures. IR spectra were taken using an Analect FX-6200 FTIR spectrometer. A standard T-shaped glass IR cell and a glass vacuum system capable of better than 10⁻⁶ Torr (1.3 × 10⁻⁷ kPa) were employed. 30 mg catalyst wafers of 1.8 cm diameter were pressed at 2.2 × 10⁴ kPa. Catalysts were rereduced under 400 Torr H₂ at 673 K for 1 h and then evacuated at 10⁻⁶ Torr and 673 K for 1 h. CO was added at ambient temperature to a final pressure of 50 Torr in the cell.

TPD spectra were obtained in an Altamira Instruments automated temperature-programmed system which is supported by an IBM personal computer for control of the experiment as well as for data collection and analysis. Catalyst samples were rereduced in the flow system in H₂ for 1 h at 673 K and cooled in H₂ to 353 K. The TPD experiments were performed at 40 K/min in Ar to 673 K. X-Ray diffraction line broadening measurements were performed in a General Electric XRD-5 spectrometer using Cu $k\alpha$ radiation. Particle sizes greater than about 4 nm may be determined from these measurements.

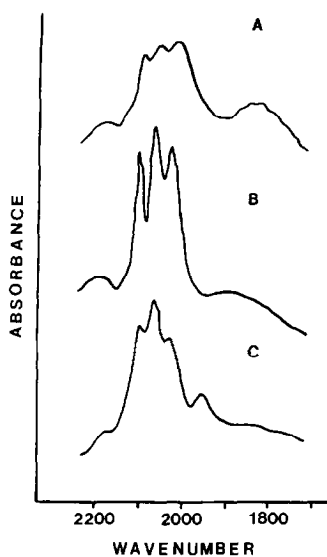


FIG. 1. IR spectra of CO adsorbed on coimpregnated Rh/Al₂O₃ catalysts. (A) Unpromoted Rh/Al₂O₃ (1-1/0), (B) Rh:Cs = 10:1 (CI-10/1), (C) Rh:Cs = 2:1 (CI-2/1).

CO hydrogenation studies were performed in a single-pass stainless-steel microreactor equipped with on-line gas chromatographic analysis. Details of the reaction system and analysis are described elsewhere (2). Catalyst samples (100–400 mg) were rereduced for 2 h in flowing hydrogen at 673 K after heating at 5 K/min. The reactor was cooled to about 40 K below the desired initial reaction temperature. CO hydrogenation was performed using a gaseous feed stream of an equimolar mixture of H₂/CO at the rate of 90 cm³/min (STP). Catalyst sample weights were chosen so as to maintain differential CO conversions. Reaction results were obtained at 526 K and 100 kPa after 16 h on stream.

All gases (Linde) used in pretreatment, adsorption, and reaction were ultrahigh purity grade and were further purified by molecular sieve traps. H₂ was also purified by a palladium thimble (Engelhard).

RESULTS

IR spectroscopy. Figure 1 shows IR spectra of CO adsorbed on Rh/Al₂O₃ and on Rh/Al₂O₃ coimpregnated with two different

levels of Cs. Figure 1A displays spectral features for Rh/Al₂O₃ which have been well documented in the literature (14–17). A pair of peaks at 2101 and 2032 cm⁻¹ have been assigned to a dicarbonyl species bound to partially oxidized Rh atoms isolated on the support. The peak at 2070 cm⁻¹ is indicative of a linear-CO species, and the broad peak near 1887 cm⁻¹ suggests the presence of some bridge-CO species. The relative amount of linear-CO compared to the dicarbonyl, and the presence of bridge-CO, suggest that this unpromoted Rh catalyst consisted of Rh crystallites varying in size from the partially oxidized atomic Rh isolated on the support to some significantly larger conglomerates of Rh on which the bridge-CO species was adsorbed.

Figures 1B and C show how the CO spectrum was altered upon Cs addition to the Rh catalyst. In Fig. 1B, for a 10:1 atomic Rh:Cs ratio, the bridge-CO species decreased and the amount of linear-CO relative to the amount of the dicarbonyl species increased slightly. In Fig. 1C it is seen that both of these trends continued as the level of promotion increased to Rh:Cs = 2:1. One important point to note is that the wavenumber of both the dicarbonyl and the linear-CO species remained unchanged with increasing Cs promotion.

Temperature-programmed desorption. The temperature-programmed desorption of H₂ from Rh/Al₂O₃ and from the Al₂O₃ support is shown in Fig. 2. Figure 2B shows that hydrogen may be adsorbed on Al₂O₃ even in the absence of the Rh metal. While some studies have not observed adsorbed hydrogen on Al₂O₃ in the absence of a metal, or of H₂O, or of some means to readily dissociate the molecular hydrogen (18–20), our studies indicate that hydrogen can adsorb fairly readily on Al₂O₃ if it contacts the support at an elevated temperature. This experiment has been repeated in two separate TPD systems under rigorous gas pretreatment procedures to confirm the absence of contamination with H₂O. The possibility of the presence of an impurity

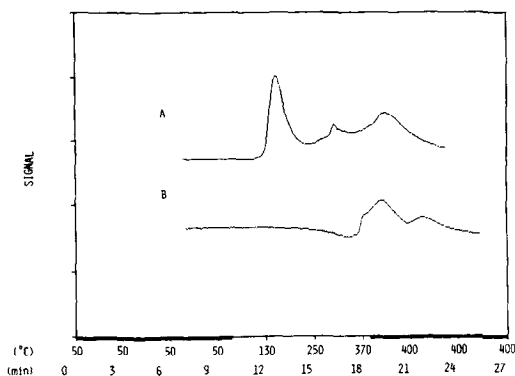


FIG. 2. Temperature-programmed desorption of H₂ from Rh/Al₂O₃ catalysts. (A) Rh/Al₂O₃ (I-1/0), (B) Al₂O₃.

such as Fe in the support material which could aid in the dissociation of H₂ has also been considered. However, a lack of activity of the blank Al₂O₃ in CO/H₂ reaction seems to indicate that a transition metal impurity was not present.

All of these TPD spectra were obtained from samples which had been cooled in H₂ from 673 to 323 K. The results of Fig. 2 suggest that the high-temperature portion of the TPD spectra for Al₂O₃-supported Rh may be attributed to adsorption on the support. With Rh present this adsorption may be aided by spillover of dissociated hydrogen atoms from the metal onto the support, a subject which has received much recent attention (21–23). These TPD spectra offer an elegant way to discriminate between sites on the metal and on the support for this catalyst system.

TPD spectra for H₂ desorption from several co-impregnated Cs-promoted Rh/Al₂O₃ catalysts are shown in Fig. 3. The spectrum for the unpromoted Rh/Al₂O₃ from Fig. 2A is reproduced here for comparison. The first and most striking feature to be noted is the significant change in the high-temperature part of the spectrum upon Cs addition to the catalysts. Even at the very low Cs loading of Rh:Cs = 100:1, this portion of the spectrum, attributed to adsorption on the support, was drastically reduced. The

low-temperature peak, assigned to adsorption of atomic H on Rh metal sites, also decreased as the promotion level increased, the Rh:Cs = 100:1 sample being an exception. The peak temperature increased from about 160°C (433 K) to 185°C (485 K) from the unpromoted to the Rh:Cs = 2:1.

Values for the apparent crystallite size of Rh based on a Rh:H_s stoichiometry of 1:1 have been calculated from the area of the low-temperature peak and are given in Table 2. The apparent dispersion decreased by a factor of 5 through the series of catalysts of Fig. 3. However, X-ray diffraction line broadening measurements revealed that none of the catalysts used in this series exhibited crystallite sizes greater than 4 nm.

When catalysts were prepared by sequential impregnation rather than coimpregnation, the TPD results differed as shown in Fig. 4. The TPD spectra of two sequential impregnation catalysts with different levels of Cs are shown along with the unpromoted Rh/Al₂O₃. An important point to note in Fig. 4B is that although the level of Cs was four times higher here than for the highest level of the coimpregnated catalysts, the effects are not as significant. There was still substantial adsorption on the support, as seen by the desorption in the high temperature region. The peak due to desorption from the metal decreased

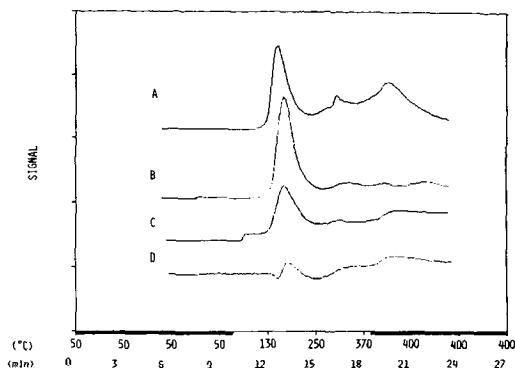


FIG. 3. Temperature-programmed desorption of H₂ from coimpregnated catalysts. (A) Unpromoted Rh/Al₂O₃ (I-1/0), (B) Rh:Cs = 100:1 (CI-100/1), (C) Rh:Cs = 10:1 (CI-10/1), (D) Rh:Cs = 2:1 (CI-2/1).

TABLE 2

H₂ Adsorption on Promoted Rh/Al₂O₃ Catalysts

Catalyst	$\mu\text{mol H}_2/\text{g cat}^a$	Apparent Rh crystallite size (nm) ^{b,c}
Al ₂ O ₃	169	—
I-1/0	339	1.4
CI-100/1	135	1.0
CI-10/1	62	2.2
CI-2/1	17	7.6
SI-1/2	39	3.4
SI-1/5	— ^d	— ^d

^a Based on the total area of the TPD spectrum.

^b Based on the area of the low-temperature peak in the TPD spectrum.

^c All catalysts exhibited crystallite sizes less than 4 nm as measured by XRD.

^d Signal too small to calculate.

only threefold, and its peak temperature increased only about 15 K, compared to the unpromoted catalyst.

Reaction results. CO hydrogenation reactions were carried out on some of the Rh/Al₂O₃ catalysts in this series. Since it has been shown (2) that these reactions are relatively unaffected for promoted Rh/Al₂O₃ catalysts up to Rh:Cs levels of 2:1, the promoted catalysts used here were the two sequential impregnation samples with high levels of Cs. Results for activity and selectivity were compared to those for the unpromoted Rh/Al₂O₃. Figure 5 shows a comparison of the rates of formation of various products as a function of Cs loading, relative to a normalized turnover number of unity for products formed on the unpromoted Rh/Al₂O₃. The figure shows that the rates of formation for all products were suppressed by the addition of alkali species. The rates of some products, however, were suppressed more than others. Product selectivities were compared as a function of Cs loading in Fig. 6. Hydrogenation to methane was suppressed more than was chain growth to higher hydrocarbons. The formation of oxygenated products was sup-

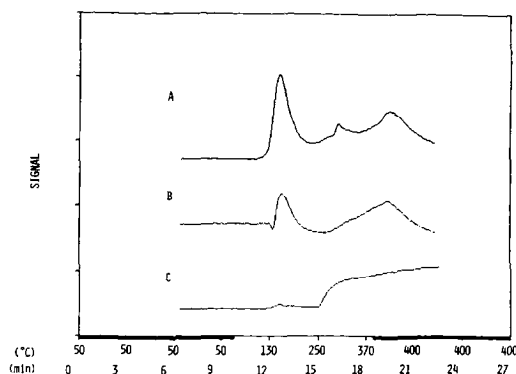


FIG. 4. Temperature-programmed desorption of H₂ from sequentially impregnated catalysts. (A) unpromoted Rh/Al₂O₃ (I-1/0), (B) Rh:Cs = 1:2 (SI-1/2), (C) Rh:Cs = 1:5 (SI-1/5).

pressed less than was the formation of hydrocarbons.

DISCUSSION

IR spectroscopy. The major effects of Cs promotion on the IR spectrum of CO adsorbed on Rh/Al₂O₃ were on the dicarbonyl species and on the bridge-CO species. A decrease in the amount of the dicarbonyl species with increasing promotion level seems to support the suggestion that the promoter initially partitions preferentially to the Al₂O₃ support, since the CO species most likely to be affected by a promoter located on the support would be the isolated Rh atoms on which the dicarbonyl species is formed.

A decrease in the amount of bridge-CO with Cs promotion implies that at least some of the Cs was found on the metal crystallites themselves. The spectra suggest a geometric effect in which Cs helped to disrupt the Rh ensembles required for the bridge-CO species. The fact that the wavenumber of the linear-CO species was unchanged suggests the absence of a strong electronic effect of the addition of Cs.

Recent studies (24, 25) have suggested that the use of CO adsorption as a probe of Rh surface structure and chemistry may be questioned because the adsorption may act to alter the surface structure of small Rh

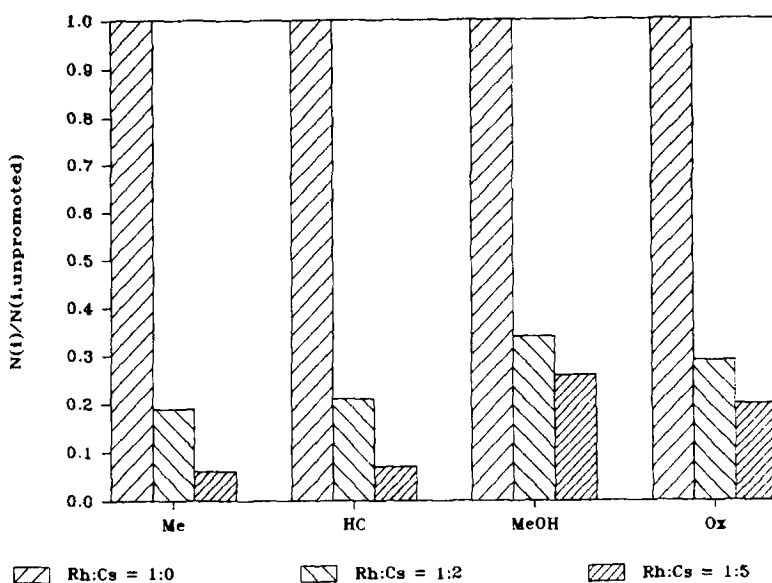


FIG. 5. Comparison of rates of formation of CO hydrogenation reaction products for promoted Rh catalysts compared to the unpromoted catalyst. Me = methane, HC = total hydrocarbon products, MeOH = methanol, Ox = total oxygenated products.

crystallites. It was found that CO adsorption may aid in breaking up Rh crystallites into isolated Rh(CO)₂ clusters on the surface of the support. This effect apparently

is important only for very small crystallites. Our IR spectra revealed that the Rh(CO)₂ species decreased in relative concentration as alkali promotion level increased. Per-

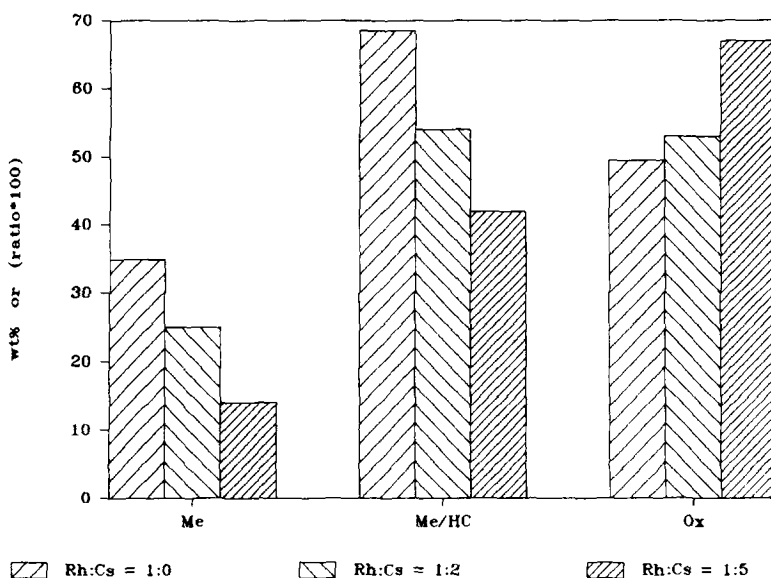


FIG. 6. Comparison of product selectivities in CO hydrogenation for promoted Rh catalysts compared to the unpromoted catalyst. Me = methane, Me/HC = ratio of methane to total hydrocarbon production, Ox = total oxygenated products.

haps the alkali species acts to block this redispersion of Rh crystallites caused by CO adsorption.

The IR spectroscopic results thus suggest that the primary effect of increasing Cs promotion on coimpregnated Rh/Al₂O₃ was either to perturb adsorption on the isolated Rh atoms interacting with the support or to prevent the redispersion of Rh crystallites as Rh(CO)₂ clusters upon CO adsorption. In addition, the alkali appeared to break up ensembles for bridge-CO adsorption on larger Rh crystallites.

Temperature-programmed desorption. X-Ray diffraction line broadening measurements revealed that none of the promoted or unpromoted catalysts exhibited crystallite sizes greater than 4 nm. This confirms that the observed decrease in area of the low-temperature peak assigned to adsorption of hydrogen on the metal with increasing Cs concentration was not due to an actual increase in the size of the Rh crystallites but to suppression of H₂ adsorption on Rh sites. This in turn indicates that at least a fraction of the Cs present was indeed interacting with the metal.

The upward shift in peak temperature which was observed for all promoted catalysts compared to the unpromoted Rh/Al₂O₃ might be explained in one of two ways. Since an upward temperature shift indicates a stronger metal-H interaction, it might be suggested that the addition of the Cs promoter causes an electronic interaction between the Cs and the Rh. It has been suggested (7-9) that this brings about an increase in the metal's electron density, causing it to interact more strongly with species adsorbed on the metal surface. This could explain the upward shift in the peak temperature for H₂ desorption. The results from the IR studies, however, showed no observable electronic effect of Cs on Rh. Hence, a second and simpler explanation might be invoked to interpret the peak temperature increase. Perhaps the increase in peak temperature with increasing Cs content is related to the decrease in the amount

of H₂ on the metal surface due to blocking of Rh sites by some of the Cs species. This decrease is tantamount to a decrease in surface coverage of hydrogen. As surface coverage decreased, interactions between neighboring adsorbed H atoms decreased, and the peak temperature for desorption increased. This has been observed in studies of single-crystal and unsupported Rh (26-29) and for H₂ desorption from Rh/SiO₂ (30).

The CI-100/1 sample exhibited an increased H₂ uptake compared to the unpromoted catalyst, contrary to the other catalysts with higher promotion levels in this series. Aika *et al.* (31) reported increased dispersions of coimpregnated alkali-promoted Ru/Al₂O₃ catalysts compared to the unpromoted catalyst. They suggested that the reduction of Ru salt was affected by the presence of an alkali salt, producing smaller Ru crystallites. Perhaps the small amount of alkali present in the CI-100/1 sample was sufficient to help increase the dispersion of Rh but not sufficient to cause the significant site-blocking for H₂ adsorption which was observed when the alkali was added in larger concentrations.

The TPD spectra of H₂ desorbed from sequentially impregnated catalysts differed from the spectra for coimpregnated catalysts just discussed. It is clear from these results that not only is the amount of Cs present an important parameter, but that the method in which the Cs is added is also critical to its ultimate effect on H₂ adsorption on the catalyst surface. Coimpregnated catalysts appeared to afford much more intimate metal-promoter and support-promoter interactions than did sequentially impregnated catalysts. This difference may stem from differences in the state of the Cs species in each case. It is unlikely that the Cs, added as an ionic salt, can be reduced to the metallic state under the conditions employed; what its ultimate chemical state is may differ with the preparation method.

The possible role of the Cs salt in helping to disperse the Rh crystallites for coim-

pregnated catalysts has already been suggested. Perhaps in addition the coimpregnation of the CsNO₃ with the RhCl₃ salt causes the Cs ions to interact strongly with the Cl ions, which upon decomposition and reduction of the salts are scavenged by the support and are not removed from the system. The suppression of hydrogen on the support as observed in the TPD spectra of Fig. 3 may in fact be due not only to the presence of Cs but also Cl species. A recent study (32) of Rh/TiO₂ catalysts prepared from the RhCl₃ salt found that a significant amount of Cl remained in the catalyst after decomposition and reduction treatments.

Another possibility to be considered is that different Cs species formed from the two preparation procedures may have differing tendencies to agglomerate into particles or to spread out and wet the catalyst surface. Thus a similar Cs loading could represent a very different degree of actual Cs-catalyst interaction for each preparation procedure.

The metal-alkali interaction may be highly dependent on the particular metal. Chai and Falconer (33) found no differences in CO hydrogenation activity or selectivity between Ni/SiO₂ catalysts prepared by two methods similar to the coimpregnation and sequential impregnation procedures outlined here. Praliaud *et al.* (34) found no evidence for site-blocking by K-promoted Ni catalysts. Hence conclusions drawn concerning the interaction between Rh and Cs should not be generalized to other catalyst systems without caution.

The TPD results show very clearly that it is possible to differentiate between hydrogen adsorbed on the metal and on the support for these Rh/Al₂O₃ catalysts. The spectra further show how each of these species were affected by the addition of Cs in increasing amounts. It is interesting to note, however, that while the IR results allowed distinction between different types of Rh sites, the TPD results did not allow this discrimination.

Reaction results. The trends observed were consistent with the results of other studies of alkali promotion of catalysts for CO hydrogenation reactions (32). One important difference, however, is that the levels of Cs promotion required to obtain these results were much greater than is normally observed with Rh on other supports. This again lends support to the suggestion that the support scavenged a significant fraction of the Cs species present on the catalyst.

CONCLUSIONS

The results of this study of Cs-promoted Rh/Al₂O₃ catalysts demonstrate that temperature-programmed desorption, infrared spectroscopy, and catalytic reaction studies may be used effectively as probes of the catalyst surface to investigate both the location of alkali species as well as the type and magnitude of its effects. The combination of these different techniques allowed an in-depth view of the adsorptive and reactive properties of promoted Rh/Al₂O₃ catalysts which could not have been achieved by using any one of the techniques alone.

CO adsorption (IR) and H₂ desorption (TPD) studies both led to the suggestion that a significant portion of the Cs species interacts directly with the Al₂O₃ support for these promoted Rh catalysts. Little evidence for a significant electronic effect of the Rh-Cs interaction was found, possibly because of the tendency of Cs to interact preferentially with the support and not the metal. The degree of interaction between the alkali species and the catalyst was found to depend on the method of preparation of the catalyst. Changes in preparation procedures may result in changes in the state of the alkali species. Trends for reaction activity and product selectivity for CO hydrogenation over these alkali-promoted catalysts were consistent with results from studies of alkali promotion for Rh on other supports, but significantly higher promotion levels were required to achieve the same result.

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