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Microcalorimetric Study of Silica- and Zeolite-Supported Platinum Catalysts

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Microcalorimetric measurements of the differential heats of hydrogen and carbon monoxide adsorption versus adsorbate coverage were made at 403 K for platinum supported on silica, magnesia/alumina, L-zeolite, Y-zeolite, and ZSM-5. The differential heats at zero coverage for hydrogen and carbon monoxide adsorption were 90 and 140 kJ/mol, respectively, for platinum supported on silica and nonacidic zeolites. The differential heats were larger by approximately 20 kJ/mol for hydrogen and carbon monoxide adsorption on platinum particles supported on basic supports such as potassium/silica, magnesia/alumina, and zeolites containing basic cations (K^+, Ba^{2+}) exchanged in excess of the zeolite framework aluminum content. The microcalorimetric results suggest that the high paraffin aromatization activity and selectivity observed for L-zeolite-supported platinum catalysts do not appear to be caused solely by changes in the adsorptive properties of the cluster-sized platinum particles located within the zeolite.

INTRODUCTION

The high activity and selectivity exhibited by base-exchanged, L-zeolite-supported platinum catalysts for the aromatization reaction of normal paraffins is documented in the literature (e.g., see Refs. (1–10)). Recent reports have suggested that platinum particles supported on basic supports, such as magnesia/alumina, may also show high aromatization activity and specificity (11).

The unique catalytic behavior of L-zeolite-supported platinum catalysts has been attributed to various factors. For example, it has been suggested that platinum particles located within the zeolite channels have a partial negative charge that leads to high catalytic activity for aromatization (3, 12). Alternatively, it has been suggested that the unidimensional channels of L-zeolite promote the formation of a preferred transition state that leads to aromatic products (13). More recently, it has also been proposed that L-zeolite-supported platinum catalysts are resistant to deactivation and maintain the intrinsically high aromatization activity of platinum during the life of the catalyst (14).

In the present study, we have employed microcalorimetry to study and compare the adsorptive properties of platinum catalysts supported on silica, Y-zeolite, ZSM-5, L-zeolite, and magnesia/alumina. The rationale for this work is to use microcalorimetry to investigate whether the adsorptive properties of platinum particles supported in zeolites and on magnesia/alumina are different from the properties of platinum particles supported on silica. Hydrogen and carbon monoxide are convenient probe molecules for this investigation since the adsorption stoichiometries of these molecules are known for platinum. Also, the molecular dimensions of hydrogen and carbon monoxide are small relative to the channel dimensions of the zeolites, and these probes are able to interact with the platinum particles without restrictions from the zeolite framework. Thus, microcalorimetrically measured heats of hydrogen and carbon monoxide adsorption provide information about the adsorbate-Pt bond strengths. In this respect, the differential heat of adsorption is a positive quantity defined as the negative of the enthalpy change of adsorption.

EXPERIMENTAL

The physical properties of the catalysts employed in this study are summarized in Table 1, along with their preparation methods. Chemical analyses were conducted by Galbraith Laboratories (Lexington, KY).

The 1 and 4% Pt/SiO_2 catalysts were prepared by the ion-exchange method of Benesi *et al.* (15) using $Pt(NH_3)_4(NO_3)_2$. The catalyst was subsequently dried at 423 K, calcined at 548 K in flowing oxygen (60 cm^3/min) for 1 h, and reduced at 673 K in flowing hydrogen (60 cm^3/min) for 2 h. The 7% Pt/SiO_2 catalyst was prepared by incipient wetness impregnation with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. The catalyst was dried at 423 K, calcined

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TABLE 1

Summary of Catalyst Compositions and Methods of Preparation

Catalyst	Pt loading (%)	Elemental analysis (wt%)					nM^{n+}/Al ratio	Preparation method
		Al	K	Na	Ba	Mg		
1% Pt/K–L	0.95	7.7	11.8	—	—	—	1.0	Impregnation
1% Pt/BaK–L	0.98	8.4	9.7	—	6.9	—	1.1	Impregnation
1% Pt/K(Ba)–L	0.98	7.6	9.4	—	7.0	—	1.2	Impregnation
1% Pt/K(0.6% Ba)–L	0.81	7.8	13.0	—	0.7	—	1.2	Impregnation
1% Pt/H–L	0.85	11.5	5.6	—	—	—	0.3	Impregnation
1% Pt/Na–Y	0.85	12.1	—	9.6	—	—	0.9	Impregnation
1% Pt/K–ZSM-5	0.86	1.4	2.2	—	—	—	1.1	Impregnation
1% Pt/K–SiO_2	0.89	—	0.1	—	—	—	—	Impregnation
1% Pt/SiO_2	1.22	—	—	—	—	—	—	Ion exchange
4% Pt/SiO_2	3.55	—	—	—	—	—	—	Ion exchange
7% Pt/SiO_2	7.18	—	—	—	—	—	—	Impregnation
1% Pt/MgAl(O)	0.56	7.4	0.6	—	—	39.1	—	Impregnation

at 573 K in flowing oxygen for 2 h, and reduced in flowing hydrogen at 723 K for 2 h.

The L- and Y-zeolite supports were obtained from Linde. The ZSM-5 sample was synthesized following published procedures (16). Platinum was loaded into the zeolites by impregnation using $Pt(NH_3)_4(NO_3)_2$ followed by drying at 393 K and calcination at 523 K.

The Si : Al molar ratio of the L-zeolite was ~3.5. Prior to use, excess potassium was reduced from the L-zeolite by a wash with water until the pH of the wash solution was 9.5. This support has a nM^{n+}/Al ratio of 1.0 and was used to prepare the 1% Pt/K-L sample. Approximately 15 g of the washed K–L-zeolite was impregnated with 0.17 g of $Ba(NO_3)_2$, dried and calcined at 773 K for 3 h. This support has a nM^{n+}/Al ratio of 1.2 and was used to prepare the 1% Pt/K(0.6% Ba)–L sample. A sample of K–L-zeolite was ion exchanged with a 0.5 *M* solution of $Ba(NO_3)_2$ at 353 K for 3 h and washed with 500 ml of cold deionized water, and dried and calcined at 773 K for 3 h. This support has a nM^{n+}/Al ratio of 1.2 and was used to prepare the 1% Pt/K(Ba)-L sample. A second K–L-zeolite sample was ion exchanged with a 0.3 *M* solution of $Ba(NO_3)_2$ and washed three times with hot deionized water. This support has a nM^{n+}/Al ratio of 1.1 and was used to prepare the 1% Pt/BaK–L sample. The H–L-zeolite was prepared by three exchanges of a K–L-zeolite sample with a 1.0 *M* solution of NH_4NO_3, followed by calcination at 773 K for 3 h. The H–L-zeolite support has a nM^{n+}/Al ratio of 0.3 and was used to prepare the 1% Pt/H-L sample.

The synthesized ZSM-5 catalyst was calcined at 813 K for 16 h, followed by two overnight ion exchanges with a 1.5 *M* solution of KNO_3 at 333 K. The exchanged zeolite was filtered and washed with 500 ml of cold deionized water. This sample was further washed a second time with a solution of dilute KOH at a pH of 9.5. The zeolite was filtered, dried, and calcined at 813 K for 3 h. This support has a nM^{n+}/Al ratio of 1.1 and was used to prepare the 1% Pt/K–ZSM-5 sample.

A magnesia/alumina support, MgAl(O), was prepared by coprecipitation following the procedure outlined by Schaper *et al.* (17). The precipitate was filtered and washed with hot deionized water, dried overnight in air at 403 K, and calcined in flowing oxygen at 573 K for 1.5 h. A 0.56% Pt/MgAl(O) catalyst was prepared by incipient wetness impregnation of the support with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. The catalysts was calcined and reduced prior to use in the manner described above for Pt/SiO_2.

Microcalorimetric measurements of the heats of adsorption were conducted using Tian–Calvet-type heat-flow microcalorimeters obtained commercially (Setaram C80) and constructed in our laboratory. Hydrogen and carbon monoxide were used as probe molecules, with gaseous pressures measured by a Baratron capacitance manometer. Doses of the probe molecules, typically 1–3 μmol, were admitted sequentially into the system to titrate the platinum surface. Detailed descriptions of these apparatuses can be found elsewhere (18, 19).

Hydrogen (Liquid Carbonic) was purified by passage through a Deoxo unit (Engelhard), followed by 4 Å molecular sieves (Davison) at 77 K. Carbon monoxide (Matheson, 99.9%) was purified by passage through a heated trap (573 K) packed with quartz wool and dried by passage through molecular sieves at 77 K. The purified hydrogen and carbon monoxide were stored in 5-liter bulbs attached to a volumetric adsorption system.

Prior to microcalorimetric adsorption experiments, each prereduced catalyst was heated to 543 K at 6 K/min under vacuum in the calorimeter cells and degassed at this temperature until the pressure reached 10^{-4}–10^{-5} Torr (ca. 0.5–1 h). After cooling the cells to room temperature, hydrogen was admitted into the system at ~760 Torr, and the cells were heated to 673 K for 2–3 h to reduce the catalyst. The gas in the cells was evacuated and replaced with fresh hydrogen several times during this treatment. Following reduction, the catalyst was outgassed at 673 K for 2–3 h, until the pressure was 10^{-5}–10^{-6} Torr. The calorimeter thermal block was subsequently raised around the cells and the system was allowed to equilibrate overnight. The cells were evacuated during this equilibration period to maintain a pressure of ca. 10^{-7} Torr within the cells. All adsorption measurements were conducted at 403 K.

RESULTS

The volumetric uptake results of hydrogen and carbon monoxide adsorption on the various catalysts at 403 K are summarized in Table 2. Values of platinum dispersions calculated from the hydrogen uptake data are also presented in this table, assuming a H/Pt ratio of unity. (This assumed adsorption stoichiometry is employed for convenience, but it is not necessarily correct since the adsorption measurements were conducted at 403 K instead of the more typically used temperature of ~300 K.) As will be discussed later, the L-zeolite samples are capable of adsorbing hydrogen in excess of the total metal loading of the samples; therefore, the hydrogen uptake values for the L-zeolite samples reported in Table 2 correspond to the amount of hydrogen adsorbed by the catalyst with a differential heat of adsorption greater than ca. 30 kJ/mol. This hydrogen is likely associated with adsorption sites on the metal particles. The dispersion values indicate that the zeolite-supported catalysts are well-dispersed and contain small platinum particles. Indeed, solid-state NMR (20) and EXAFS (21) studies on several of the L-zeolite-supported catalysts have shown that cluster-sized platinum particles predominate on these catalysts. The 4% Pt/SiO_2 catalysts prepared by the ion-exchange procedure is also well-dispersed.

TABLE 2

Summary of Hydrogen and Carbon Monoxide Adsorption Data

Catalyst	Coverage (μmol/g) Hydrogen	Coverage (μmol/g) CO	Pt dispersion (%)
1% Pt/K-L	21 ± 1	27 ± 1	86
1% Pt/BaK-L	20 ± 1	25 ± 1	80
1% Pt/K(Ba)-L	24 ± 1	34 ± 1	96
1% Pt/K(0.6% Ba)-L	19 ± 1	27 ± 1	92
1% Pt/H-L	21 ± 1	32 ± 1	96
1% Pt/Na-Y	20 ± 1	27 ± 1	92
1% Pt/K-ZSM-5	19 ± 1	25 ± 1	86
1% Pt/K-SiO_2	13 ± 1	12 ± 1	57
1% Pt/SiO_2	18 ± 1	22 ± 1	56
4% Pt/SiO_2	69 ± 3	130 ± 3	76
7% Pt/SiO_2	94 ± 3	162 ± 3	51
1% Pt/MgAl(O)	9 ± 1	18 ± 2	63

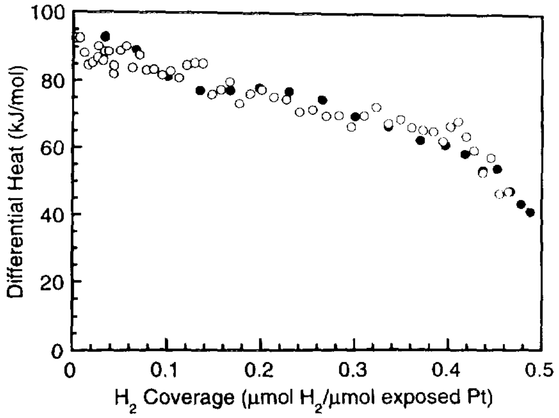

FIG. 1. Differential heats of hydrogen adsorption on (●) 4% Pt/SiO_2 and (○) 7% Pt/SiO_2 at 403 K.

Figures 1 and 2 show plots of the differential heats of hydrogen and carbon monoxide adsorption versus adsorbate coverage on Pt/SiO_2 catalysts having different metal dispersions. In these figures, the adsorbate coverage is normalized to the total amount of exposed platinum using the aforementioned values of platinum dispersion. This procedure facilitates comparison of catalysts with different metal loadings and dispersions. Similar values are obtained for the initial heat of hydrogen adsorption with values of 91 ± 5 and 92 ± 5 kJ/mol for the 4 and 7% Pt/SiO_2 samples, respectively. The initial heats of CO adsorption on these samples are also similar for the two catalysts, i.e., 140 ± 3 kJ/mol.

The initial heats of hydrogen and carbon monoxide adsorption measured in this study are in good agreement with previously published values for supported and un-

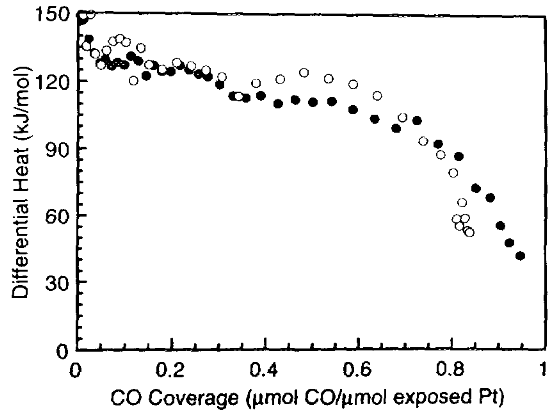

FIG. 2. Differential heats of carbon monoxide adsorption on (●) 4% Pt/SiO_2 and (○) 7% Pt/SiO_2 at 403 K.

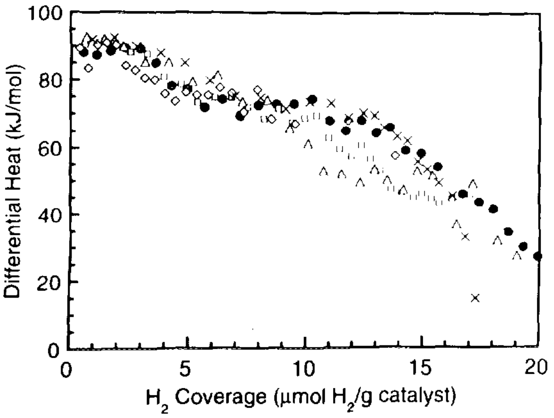

FIG. 3. Differential heats of hydrogen adsorption on (●) 1% Pt/K-L zeolite, (□) 1% Pt/BaK-L zeolite, (△) 1% Pt/Na-Y zeolite, (◇) 1% Pt/K-ZSM-5 zeolite, and (×) 1% Pt/SiO_2 at 403 K.

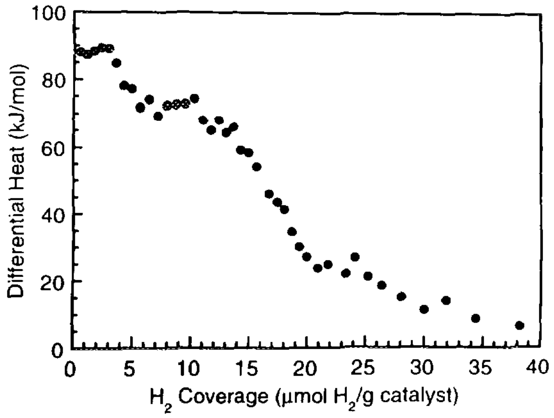

FIG. 5. Differential heat of hydrogen adsorption at high pressures on 1% Pt/K-L zeolite at 403 K.

supported platinum catalysts. For example, Cerny *et al.* (22) estimated an initial heat of 89 kJ/mol for hydrogen adsorption at room temperature on evaporated platinum films. Lantz and Gonzalez (23) reported a value of ca. 89 kJ/mol for hydrogen adsorption at 300 K on silica-supported platinum catalysts. Norton and Richards (24) found a value of ca. 90 kJ/mol for hydrogen adsorption at 77 K on unsupported platinum filaments. Goddard et al. (18) measured initial heat values of 85 and 126 kJ/mol for hydrogen and carbon monoxide adsorption at 308 K on silica-supported platinum catalysts, respectively. Gravelle and co-workers (25) reported values equal to 93 and 134 kJ/mol for hydrogen and carbon monoxide adsorption at 296 K on titania-supported platinum catalysts, respectively.

The microcalorimetric data for hydrogen and carbon monoxide adsorption on the zeolite-supported platinum catalysts are summarized in Figs. 3 and 4. The data in these figures are for zeolite samples in which the framework acidity has been neutralized by K^+, Ba^{2+}, and/or Na^+ cations such that the nM^{n+}/Al ratio is 1.1 or less (where M^{n+} represents an exchange cation with a valence of n). The results for the 1% Pt/SiO_2 sample are plotted in these figures for comparison. In all cases, the initial heats of hydrogen and carbon monoxide adsorption are ca. 90 kJ/mol and ca. 140 kJ/mol, respectively. The differential heats decrease continuously with increasing adsorbate coverage. The decrease in adsorption strength at higher coverage is indicative of a heterogeneous adsorption environment and/or the presence of lateral repulsive interactions between adsorbed species. Although there are differences in the distributions of adsorption strengths among the various catalysts, all catalysts have sites of similar strength regardless of the type of support.

The microcalorimetric results of hydrogen adsorption on the 1% Pt/K-L sample are shown in Fig. 5. The corresponding hydrogen adsorption isotherm is shown in Fig. 6. At high hydrogen coverages, weak adsorption sites are distinguishable at ca. 30 kJ/mol. These weak sites, however, are absent for the silica-supported platinum samples. It is possible that these weak adsorption sites

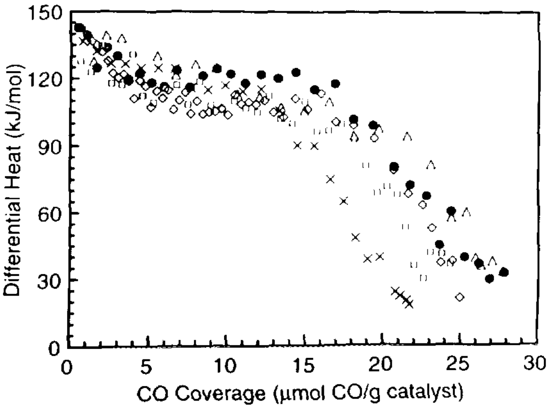

FIG. 4. Differential heats of carbon monoxide adsorption on (●) 1% Pt/K-L zeolite, (□) 1% Pt/BaK-L zeolite, (△) 1% Pt/Na-Y zeolite, (◇) 1% Pt/K-ZSM-5 zeolite, and (×) 1% Pt/SiO_2 at 403 K.

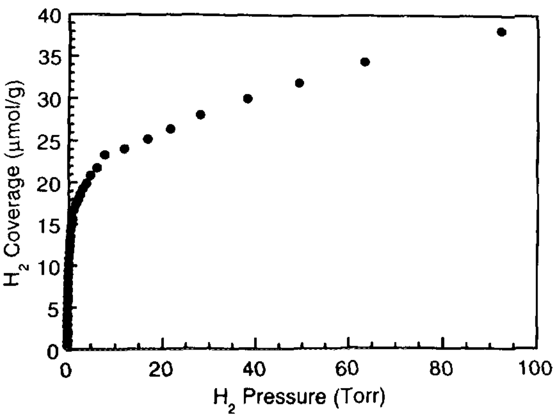

FIG. 6. Isotherm for hydrogen adsorption on 1% Pt/K-L zeolite at 403 K.

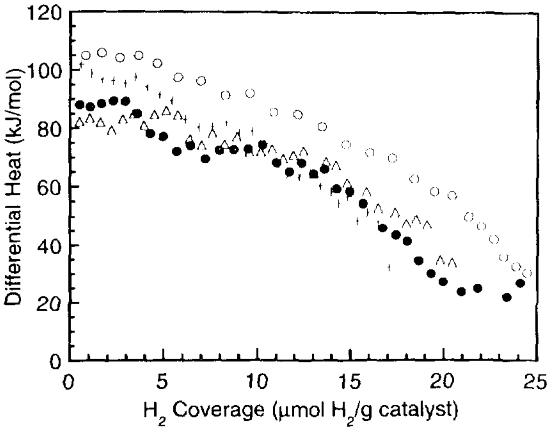

FIG. 7. Differential heats of hydrogen adsorption on L-zeolite-supported platinum catalysts at 403 K containing excess base-metal oxide. (○) 1% Pt/K(Ba)-L zeolite, (+) 1% Pt/K(0.6% Ba)-L zeolite, (●) 1% Pt/K-L zeolite, and (△) 1% Pt/H-L zeolite.

on the L-zeolite samples are associated with spillover hydrogen originating from the stronger adsorption sites on platinum. This suggestion is further supported by the observation that at similar conditions hydrogen adsorption does not occur on K-L-zeolite samples that do not contain platinum. Spillover hydrogen has been observed for L-zeolite catalysts by other researchers (26).

Figures 7 and 8 show the effect of basic-metal cations (K^+, Ba^{2+}) that are present in large excess of the ion-exchange capacity of the zeolite, at nM^{n+}/Al ratios greater than 1.2. The microcalorimetric results for the 1% Pt/K-L sample, shown previously, are also plotted in these figures for comparison. The initial heats of hydrogen and carbon monoxide adsorption are higher for catalysts that contain an excess of the exchange cations. This result suggests that the excess exchange cations may function to promote the adsorption properties of the metal particles.

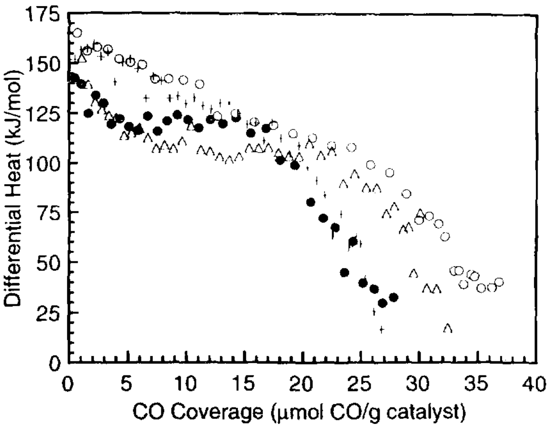

FIG. 8. Differential heats of carbon monoxide adsorption on L-zeolite-supported platinum catalysts at 403 K containing excess base-metal oxide. (○) 1% Pt/K(Ba)-L zeolite, (+) 1% Pt/K(0.6% Ba)-L zeolite, (●) 1% Pt/K-L zeolite, and (△) 1% Pt/H-L zeolite.

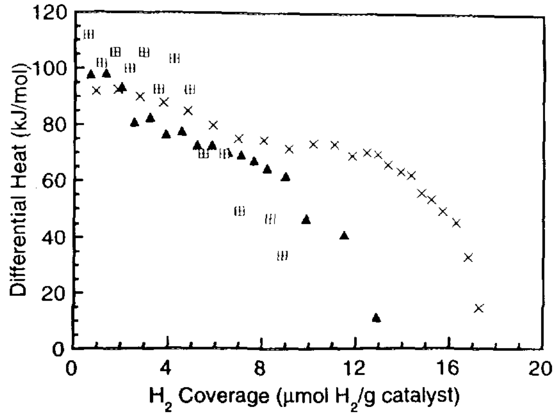

FIG. 9. Differential heats of hydrogen adsorption on alkali-promoted platinum catalysts at 403 K. (▲) 1% Pt/K-SiO_2, (⊞) 1% Pt/MgAl(O), and (×) 1% Pt/SiO_2.

Similar promotional effects by alkali metals and metal oxides have been reported for hydrogen and carbon monoxide adsorption on supported Pd catalysts by Gravelle-Rumeau-Maillot *et al.* (27). The microcalorimetric results for an acidic 1% Pt/H-L sample are also presented in Figs. 7 and 8. This sample shows similar adsorption features as the stoichiometrically exchanged 1% Pt/K-L sample.

The adsorptive properties of platinum particles supported on nonzeolitic, basic supports are shown in Figs. 9 and 10. The differential heats of hydrogen and carbon monoxide adsorption on 1% Pt/SiO_2 are shown in these figures for comparison. The addition of potassium to a silica-supported platinum catalyst increases the initial heat of carbon monoxide adsorption. The initial heats of hydrogen and carbon monoxide adsorption on magnesia/alumina-supported platinum are also higher than the corresponding values for the unpromoted Pt/SiO_2 sample. It is important to note that potassium is also present on the magnesia/alumina-support (see Table 1), remaining after the synthesis procedure used to prepare the support. Ac-

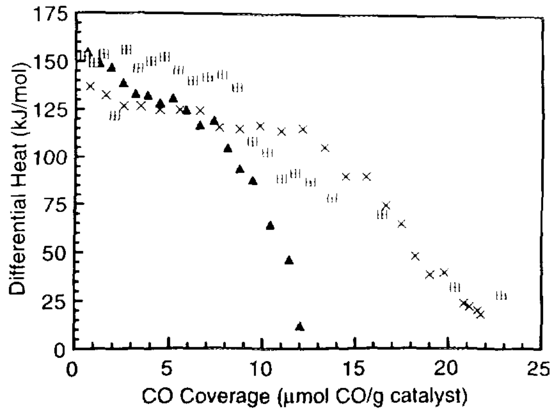

FIG. 10. Differential heats of carbon monoxide adsorption on alkali-promoted platinum catalysts at 403 K. (▲) 1% Pt/K-SiO_2, (⊞) 1% Pt/MgAl(O), and (×) 1% Pt/SiO_2.

cordingly, an increase in the initial heat of adsorption value observed for this catalyst may be related to the residual potassium from the support.

DISCUSSION

The microcalorimetric results obtained during this study show that particle size does not have a significant effect on the heats of hydrogen and carbon monoxide adsorption on platinum. For example, Figs. 1 and 2 show that similar adsorption sites exist on both silica-supported platinum catalysts. A similar conclusion for adsorption on platinum was reached by Lantz and Gonzalez (23) and Sen and Vannice (28).

The microcalorimetric results of hydrogen and carbon monoxide adsorption show that the cluster-sized platinum particles supported on neutralized L-zeolite have energetically similar adsorption sites as platinum particles supported on neutral supports such as silica. These results suggest that platinum particles supported on L-zeolite, exchanged to a nM^{n+}/Al ratio of 1.1, do not have unusual adsorptive properties. At these exchange levels, the exchanged cations only serve to neutralize the zeolite framework acidity and do not appear to alter the adsorption energetics of the platinum particles located within the zeolite.

L-zeolite samples containing alkali metal and/or alkali earth cations in large excess of the ion-exchange capacity of the zeolite (nM^{n+}/Al ratios greater than or equal to 1.2) have larger differential heats of hydrogen and carbon monoxide adsorption than the aforementioned samples in which the ion-exchange capacity has been stoichiometrically titrated. This promotional effect may result from electronic enrichment of the platinum particles by the excess base-metal cations located within the zeolite channels (29, 30) or by electrostatic effects associated with the base-metal cations on the platinum surface (31). The results presented in Figs. 7 and 8 suggest that the value of the differential heat of adsorption is related to the concentration of the excess exchange cations. Promotional effects of alkali metals and metal oxides on platinum are not unique to L-zeolite-supported catalysts, but have been documented in the literature for a variety of supported and unsupported metal catalysts (e.g., see Refs. (27, 32)).

The microcalorimetric results presented in Figs. 9 and 10 show that alkali metal cations added to the nonzeolite-supported platinum catalysts also increase the initial heats of hydrogen and carbon monoxide adsorption. The number of platinum adsorption sites on the 1% Pt/K–SiO_2 catalyst that are modified by the addition of potassium is approximately equal to the amount of potassium in the sample. Also, the basic 1% Pt/MgAl(O) sample shows stronger adsorption for both hydrogen and carbon monoxide. This sample, however, contains approximately 150 μmol/g of potassium, and it is unclear if this latter result is a consequence of the potassium or a result of metal–support interactions between the basic MgAl(O) support and the platinum particles, as has been suggested by Derouane and co-workers (11).

A small decrease in the adsorption strengths of hydrogen and carbon monoxide is possibly observed for the acidic 1% Pt/H–L sample compared to the Pt/SiO_2 samples. This result may suggest that platinum particles in the acidic L-zeolite catalysts are electron deficient in comparison to platinum particles supported on the base-exchanged zeolites. Electron-deficient, cluster-sized metal particles have been reported to exist in acidic, zeolite-supported catalysts (33, 34).

From the previous discussion it is clear that excess base-metal oxides can modify the heats of hydrogen and carbon monoxide adsorption on supported platinum catalysts. Platinum particles supported on stoichiometrically exchanged L-zeolite, however, are more stable and active for the aromatization reaction of normal paraffins than conventional silica-supported catalysts (14, 35), and yet the adsorptive properties of these catalysts are similar. These observations imply that the differences in catalytic activity and stability between L-zeolite-supported platinum catalysts and silica-supported platinum catalysts are not related solely to the adsorptive properties of platinum. Instead, we suggest that the activity and stability of L-zeolite-supported platinum catalysts may be influenced by other factors, such as the unidimensional channel system of L-zeolite (13) and/or the possibility that cluster-sized platinum particles in L-zeolite are particularly resistant to deactivation by carbonaceous species (14, 35). While it is likely that the addition of excess metal oxides is not necessary for good aromatization selectivity, catalyst promotion by metal oxides may still have beneficial effects on paraffin aromatization activity and selectivity.

CONCLUSIONS

Microcalorimetric measurements of the heats of adsorption versus adsorbate coverage for hydrogen and carbon monoxide on various supported platinum catalysts indicate that the adsorptive properties of platinum are not affected by particle size. Furthermore, cluster-sized platinum particles supported in L-zeolite samples, where the acidity has been stoichiometrically neutralized by basic metal cations, have similar heats of hydrogen and carbon monoxide adsorption as platinum supported on silica. The presence of basic metal oxide in excess of the amount required to neutralize the zeolite acidity increases the strengths of hydrogen and carbon monoxide adsortion on platinum. Similar effects of basic metal oxides are observed for platinum supported on silica and magnesia/alumina catalysts. The high dehydrocyclization activity and selectivity exhibited by platinum in L-zeolite do not appear to be caused solely by changes in the adsorptive properties of platinum. Instead, the novel catalytic properties of these materials may be caused by other factors such as the unidimensional channels of the zeolite or the possibility that cluster-sized platinum particles supported in L-zeolite may show greater resistance to deactivation by carbonaceous species.

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