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Comparison of Modified Transition Metal-Exchanged Zeolite Catalysts for Oxidation of Chlorinated Hydrocarbons

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Complete catalytic oxidation of low-molecular-weight chlorinated hydrocarbons, such as methylene chloride, trichloroethylene, and carbon tetrachloride, was studied in air over several cation-exchanged Y zeolite catalysts. The reactions were carried out under atmospheric pressure with temperatures varying from 150 to 400°C and in presence of ≈13000 ppm of water. Primarily, three different cordierite-supported (washcoated) zeolite catalysts (Co–Y, Cr–Y, and Mn–Y) were prepared and their activities and selectivities were investigated for the above reactions, with Co–Y appearing to be superior. Although complete conversions of methylene chloride and carbon tetrachloride could be obtained at temperatures of 350 and 200°C, respectively, no significant conversion of trichloroethylene was noted at temperatures below 400°C. Incorporation of a transition metal oxide within the zeolite matrix by Cr_2O_3 impregnation of the cation-exchanged zeolites produced a substantial improvement in trichloroethylene conversion with over 90% destruction obtained at only 325°C. An unsupported chromia-impregnated $\frac{1}{16}$-in. pelletized Co–Y catalyst showed even better activity results for chlorocarbon oxidation than the supported catalysts. No detectable partial oxidation products were noted in the product spectra, with HCl, CO, and CO_2 being the only major products. Catalytic behavior was explained in the view of catalyst composition and properties such as acidity and oxygen adsorption capacity. Probable mechanistic details based on the activity and selectivity data were suggested.

INTRODUCTION

Chlorinated volatile organic compounds (CVOCs), such as methylene chloride (CH_2Cl_2 or $MeCl_2$), trichloroethylene (C_2HCl_3 or TCE), and carbon tetrachloride (CCl_4), constitute a major portion of the hazardous solvent wastes produced by industry. Among the various disposal/destruction methods applicable for these chlorocarbons, catalytic destruction has been more recently considered. The desired reactions, which have been the subject of many detailed investigations, over various metal and metal oxide catalysts (*1–4*) are the complete oxidation of the CVOCs to produce HCl and CO_2. Transition metal oxides such as Cr_2O_3, Co_3O_4, and MnO_2 have been found generally to be the most active among the metal and metal oxide catalysts for this oxidation process (*5*).

In a previous study (*6*), we reported the high activity and excellent selectivity of metal-exchanged zeolites as potential catalysts for oxidation of CVOCs. In a comparative study among the chromium-exchanged (Cr–Y), cerium-exchanged (Ce–Y), and regular Y (H–Y) zeolite catalysts for $MeCl_2$ oxidation, the Cr–Y proved to be far superior to the other two by producing over 90% conversion at temperatures of 350°C and above. It appeared that the oxidation of $MeCl_2$ involved both the acidic property as well as the oxygen adsorption capacity of the zeolite catalysts. It is believed that the presence of a transition metal ion (Cr^{3+}) with low ionization potential and higher available oxidation state (Cr^{5+} and Cr^{6+}) resulted in higher acidity and increased oxygen adsorption capacity of the exchanged Y zeolite, thereby producing higher activity.

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In recent years, transition metal-exchanged zeolites have been used as catalysts for several oxidation processes. The bulk of these studies (*7–11*) involved investigation of the redox properties of the cation-exchanged zeolites for CO oxidation. The ease of oxidation to higher valence states, as well as the highest available valence states among the various exchanged metal cations, appeared to play the most significant role in determining the activity for CO oxidation. Several studies were also carried out to investigate the properties of transition metal-exchanged zeolite catalysts in partial oxidation (*12, 13*) and deep oxidation processes (*14–17*). Results reported in these studies indicated that the oxidation of hydrocarbons in zeolite-catalyzed reactions depended on both the acidity and the oxygen adsorption capacity of the catalysts. Transition metal cations improved the zeolite activity for hydrocarbon conversion by increasing both zeolite acidity (by cation hydrolysis) and oxygen chemisorption.

In further pursuance of our catalytic studies with chlorinated hydrocarbons, several transition metal-exchanged Y zeolite catalysts were investigated for their activity and selectivity during oxidation of three different chlorinated feeds: $MeCl_2$, TCE, and CCl_4. Co, Cr, and Mn were selected as the exchangeable cations due to the reported high activity of Y zeolite catalysts exchanged with these ions in several oxidation reactions, as well as their high oxygen adsorption capacities. However, possible structural and reaction mechanistic differences among the CVOCs led to differences in the conversion levels. It was noted that complete conversion of CCl_4 could be easily achieved, with the cation-exchanged Y catalysts, at temperatures as low as 250°C while the same catalysts required a temperature increase to 350°C for $MeCl_2$. By contrast, almost no significant conversion of TCE could be obtained at temperatures below 400°C.

The poor reactivity of TCE with the transition metal-loaded Y zeolite suggested either a probable size exclusion or a mechanism for which the cationic sites available were relatively ineffective. This led us to further modify the cation-exchanged zeolite catalysts by metal oxide impregnation. Following such an impregnation with chromium oxide (Cr_2O_3), the cation-exchanged zeolites showed a remarkable improvement in TCE conversion, which increased from as low as 10% to almost 90% at 300°C. However, this impregnation causes a loss of surface area accompanied by a drop in $MeCl_2$ and CCl_4 conversions at the lower temperatures, suggesting either partial structural loss or blockage of zeolite sites responsible for the complete conversion of these feeds.

In this paper, we present a study of the activity and selectivity of several transition metal-exchanged Y zeolite catalysts for complete vapor phase oxidation of the above-mentioned chlorinated hydrocarbons. Particular emphasis is given to analyzing the properties of the bifunctional exchanged/impregnated catalysts. Surface areas and oxygen adsorption capacities of the different catalysts are compared to analyze the catalytic behavior of the exchanged and exchanged/impregnated bifunctional catalysts. X-ray analyses to determine the compositions of the various catalysts are also reported.

EXPERIMENTAL

Catalytic experiments were carried out with cation-exchanged Linde LZ-Y82 zeolite washcoated onto low-surface-area (0.5–1.0 m^2/g, 400 cells/$in.^2$) honeycomb cordierite supports obtained from Corning Co. Cation exchange of the base Y zeolite was carried out in two steps. First, LZ-Y82 powder was NH_4^+ exchanged with 2 *M* NH_4Cl solution. Then, the NH_4^+-exchanged zeolite was slurried in approximately twice its weight of distilled deionized water and a dilute solution of the exchanged transition metal salt ($Cr(NO_3)_3$, $Co(NO_3)_2$, etc.) was added to this slurry. The resulting mixture was continuously stirred over a period of 12–15 h and then filtered and washed. The filtered zeolite powder was dried at 200°C for 2 h followed by calcination at 500°C over a period of 10–12 h.

In some experiments, $\frac{1}{16}$-in.-diameter LZ-Y62 extrudates were used instead of washcoated catalysts. Cation exchange of these zeolite pellets was carried out in the same way except without the filtration step. Cation loading of the zeolites was determined by analyzing the catalysts using a Philips PV9550 energy dispersive X-ray fluorescence (XRF) spectrometer.

The exchanged zeolite powder was washcoated onto the honeycomb cordierite support from a slurry of approximately 20 wt% zeolite in perhydrolyzed ethyl orthosilicate binder (Silbond H-5). The washcoating was carried out by dipping the cordierite cores in the well-mixed slurry about four times, with in-between clearing of the channels. Finally, the washcoated cores were dried at 200°C followed by calcination at 500°C for 12–15 h. Generally, the cores showed a weight gain of about 15–20% following the washcoating. The zeolite content of the washcoat was approximately 50–60% after calcination.

After completion of the washcoating, some of the zeolite washcoated cores were further impregnated with Cr_2O_3 to enhance their catalytic properties. Cr_2O_3 impregnation was carried out with a solution of a chromium salt containing about 10 wt% of Cr_2O_3. The washcoated cores were kept immersed in the Cr_2O_3 solution for 2–4 h and then dried at 200°C for 2 h followed by calcination at 500°C for 10–12 h. This resulted in approximately 1–1.5% Cr_2O_3 loading on the washcoated catalyst. The cation-exchanged $\frac{1}{16}$-in. LZ-Y62 pellets were also impregnated with Cr_2O_3 in a similar way. Further details regarding catalyst preparation techniques were mentioned in a previous paper (*6*).

Catalyst activity and selectivity experiments were conducted by passing mixtures of 1000–1500 ppm by volume of CVOC ($MeCl_2$ or TCE or CCl_4) and dry air through the 7.62-cm-long washcoated honeycomb catalyst core situated inside a vertical Pyrex preheater/reactor tube (28 mm o.d., 25 mm i.d., and 1 m length). For the $\frac{1}{16}$-in. catalyst pellets, a narrower (19 mm i.d., and 1 m length) Pyrex reactor with a bed height of 5.2 cm was used. The temperature of the reactor was varied between 250 and 400°C. Water was added as a cofeed in concentrations ranging from 13000 to 16000 ppm by volume. The reactant space velocity was maintained at 1367 h^{-1} (calculated at 25°C) for the cordierite-supported catalysts and 2300 h^{-1} for the $\frac{1}{16}$-in. pellets. Feed and product samples were collected from the reactor by Hamilton CR 700-200 constant rate gas syringes and were analyzed by injection into an H.P. 5890 GC with an H.P. 5970B mass selective detector (GC/MS). Details about reactor operation and pertinent analytical techniques are mentioned elsewhere (*6*).

The oxygen adsorption (pickup) capacities of the zeolite catalysts were determined by using a DuPont Model 2100 thermal analyst system with a 2950 thermogravimetric analyzer (TGA). Since the oxygen pickup capacities of the catalysts varied with temperature, 300°C was chosen as the optimum temperature at which the O_2 pickups of all the catalysts were determined. During thermal analysis, the catalyst sample was preheated to 500°C in N_2 for an hour for degassing and then exposed to dry oxygen at 300°C for another hour. This process was repeated thrice and the weight change during oxygen adsorption was noted. However, this weight change measurement was affected by instrument buoyancy effects associated with temperature change from 500 to 300°C, as well as gas change from N_2 to O_2. Therefore, an identical volume of crushed glass beads was used as the inert sample, and the experiment was repeated in the TGA to quantify the weight change from buoyancy effects. This weight change was incorporated in the actual oxygen adsorption experiments to obtain the final net O_2 pickup data.

Surface areas of all the supported and unsupported catalysts were determined by using a Quantachrome Quantasorb Jr. BET surface area analyzer.

Acidity of the zeolite samples was determined by NH_3 desorption in the TGA. First the powdered catalyst sample was degassed by heating at 250°C for 2 h. The degassed sample was then subjected to NH_3 adsorption at 25°C for about 8 h. The adsorbed NH_3 was then desorbed and quantified in the TGA. For NH_3 desorption, the sample was first equilibriated at 100°C for 90 min to remove any physisorbed NH_3, then the rest of the NH_3 was desorbed by using a 10°C/min temperature ramp to heat the sample from 100 to 550°C. The NH_3 desorbed above 100°C was considered as chemisorbed NH_3 and used for acidity determination.

RESULTS

The catalytic experiments were carried out with 10 different catalysts. Three of these catalysts were metal-exchanged zeolites washcoated on cordierite cores. The metals selected for exchange were cobalt (Co), chromium (Cr), and manganese (Mn). In this paper, these catalysts are referred to as Co–Y, Cr–Y, and Mn–Y respectively. Three more catalysts were prepared by chromia impregnation of the previously washcoated metal-exchanged zeolites. These are listed here as Co–Y/CA, Cr–Y/CA, and Mn–Y/CA, respectively. A separate catalyst was prepared by washcoating the cordierite with Silbond alone (no zeolite) and then impregnating it with chromia. This is referred to as the Silbond/CA catalyst. Two separate washcoated Co–Y and Co–Y/CA catalysts were prepared with an alumina-based binder (Chlorhydrol) instead of silica-based Silbond. These catalysts were used to compare the effects of binders on catalyst properties. Finally, another Co–Y/CA catalyst was prepared from $\frac{1}{16}$-in.-diam Na–Y extrudates. This catalyst, listed here as Co–Y/CA pellets, was prepared by Co exchange of the Na–Y extrudates followed by chromia impregnation.

After completion of catalyst preparation, the compositions of the washcoated cores as well as the pellets were determined using XRF techniques. In addition to the actual catalyst cores, the base metal-exchanged powdered zeolites (viz. Co–Y, Cr–Y, and Mn–Y) were also analyzed to obtain information about levels of metal exchange. To determine the effect of chromia impregnation on washcoated cores, the Silbond binder and the Chlorhydrol binder were calcined to powder form and then impregnated with chromia and calcined. These catalyst forms, referred to as Silbond/CA powder and Chlorhydrol/CA powder, respectively, were also analyzed in the XRF. Table 1 lists the results of the X-ray analyses.

The cordierite support used for washcoating metal-exchanged zeolite was mostly made up of alumina (≈35%), magnesia (≈13%), and silica (≈50%). In addition to these, trace amounts (<1%) of oxides of iron, calcium, and titanium were also present.

Cobalt exchange with the LZ-Y82 powder produced 0.74 wt% cobalt loading on the unsupported Co–Y zeolite. After washcoating with Silbond, the resulting Co loading on the washcoated core was only 0.15%. The cobalt content was this low as a result of the large quantity of inert support material (≈80%) that then made up the total catalyst. The Co loading corresponded to approximately 60% zeolite in the final calcined washcoat. However, the alumina-based Chlorhydrol-washcoated Co–Y produced higher Co loading (0.22%) partly as a result of increased zeolite content of the final washcoat. Chromia impregnation of the two different washcoated catalysts also showed a difference in Cr_2O_3 loading. While the Chlorhydrol-washcoated Co–Y/CA showed 2.20% Cr_2O_3 content, the Silbond-washcoated Co–Y/CA contained only 1.46% Cr_2O_3.

XRF analysis of the chromia-impregnated Co–Y/CA cores also showed a drop in Co concentrations following the impregnation step. With both the Silbond and Chlorhydrol

TABLE 1

The Chemical Composition of Various Catalysts

Catalyst	Composition (wt%)						
	Al_2O_3	MgO	Fe_2O_3	SiO_2	Co_3O_4	Cr_2O_3	MnO_2
Co–Y (powder)	23.56	0.00	0.00	75.67	0.74	0.00	0.00
Co–Y (core)	26.73	8.68	0.30	63.72	0.15	0.00	0.00
Co–Y (core) Chlorhydrol	44.17	7.30	0.27	47.74	0.22	0.00	0.00
Co–Y/CA (core)	24.64	8.57	0.35	64.67	0.09	1.46	0.00
Co–Y/CA (core) Chlorhydrol	38.22	8.20	0.33	51.02	0.15	2.20	0.00
Co–Y/CA (pellet)	34.24	0.00	0.03	58.10	1.05	5.98	0.00
Cr–Y (powder)	25.66	0.14	0.05	72.89	0.00	1.20	0.00
Cr–Y/CA (core)	25.98	8.96	0.34	63.18	0.00	1.30	0.00
Mn–Y (powder)	27.91	0.42	0.07	64.07	0.00	0.00	7.50
Mn–Y (core)	29.54	9.69	0.34	59.44	0.00	0.00	0.64
Mn–Y/CA (core)	28.56	9.87	0.40	59.42	0.00	1.56	0.30
Silbond/CA (core)	27.72	10.14	0.34	60.26	0.00	1.04	0.00
Silbond/CA (powder)	2.09	0.00	0.00	92.30	0.00	5.58	0.00
Chlorhydrol/CA (powder)	85.59	1.44	0.00	2.95	0.00	9.69	0.00

washcoats, a 50–80% drop in Co concentration was noted. This reduction was much more than that expected as a result of 1–2% Cr_2O_3 loading, suggesting a probable structural loss due to Cr_2O_3 impregnation.

The $\frac{1}{16}$-in.-diam Co–Y/CA pellets, conversely, showed higher cobalt ($\simeq$1%) and chromia ($\simeq$6%) loading than both the washcoated catalysts. The Silbond and Chlorhydrol washcoated catalysts also showed differences in silica and alumina content. The silica-based Silbond catalyst showed higher overall silica content ($\simeq$64%), while alumina-based Chlorhydrol catalyst showed increased overall alumina content ($\simeq$38%).

Cr and Mn exchange of the LZ-Y82 zeolite produced 1.2 and 7.5% loading of the respective metals in the powdered zeolite. As with the Co–Y cores, the approximate 50–60% powdered zeolite content of the calcined washcoat produced less than 1% overall Cr_2O_3 or MnO_2 content of the washcoated cores. Since the bulk of the washcoated catalyst was made up of the inert cordierite core, the diluent effect of the core produced the lower overall Cr_2O_3 or MnO_2 content. Cr_2O_3 impregnation further reduced the exchanged metal concentration in the washcoated catalysts and this was much more severe than that expected by the addition of 1–2% of impregnated Cr_2O_3. This effect was more prominent in the case of Mn–Y/CA than Cr–Y/CA, since in the later case, both impregnated and exchanged metal salts were Cr_2O_3.

The chromia-impregnated Silbond washcoated (no zeolite) cordierite-supported catalyst showed approximately 1% overall chromia loading which was similar (1.4%) to that obtained with the earlier Silbond-washcoated Co–Y/CA core. The unsupported Silbond/CA and Chlorhydrol/CA powders, prepared by CA impregnation of calcined Silbond and Chlorhydrol binders, respectively, showed a significant difference in Cr_2O_3 content between the two bind-

TABLE 2

Comparison of the Properties of the Various Catalysts

Catalyst	Cation loading (as wt% TMO)	Surface area (M^2/g)	O_2 Pickup (mg/g)	FCA
H–Y (pellet)	—	574	—	—
Co–Y (powder)	0.74	540	1.27	0.86
Co–Y (pellet)	3.00	576	2.78	1.05
Co–Y/CA (pellet)	1.05	325	1.37	—
Co–Y (core) Silbond	0.15	116	—	—
Co–Y/CA (core) Silbond	0.09	21	—	—
Co–Y (core) Chlorhydrol	0.22	109	—	—
Co–Y/CA (core) Chlorhydrol	0.15	15	—	—
Cr–Y (powder)	1.2	564	1.52	0.60
Cr–Y/CA (core)	—	31	—	—
Mn–Y (powder)	7.5	619	2.04	0.15
Mn–Y (core)	0.64	86	—	—
Mn–Y/CA (core)	0.30	40	—	—
Silbond/CA (powder)	—	2	0.15	—
Chlorhydrol/CA (powder)	—	160	3.45	—

ers. As seen earlier with the Co–Y/CA cores, alumina-based Chlorhydrol/CA gave higher Cr_2O_3 loading (9.6%) than the Silbond/CA (5.5%).

The BET surface areas of the various washcoated cores and the metal-exchanged zeolite powders are shown in Table 2. As can be seen, all the metal-exchanged zeolite powders had much higher surface area (500–600 m^2/g) than the washcoated cores (85–115 m^2/g). The inherent low surface area (0.5–1 m^2/g) of the inert support material (cordierite) that comprised almost 80% of the total washcoated catalyst was primarily responsible for this decrease in surface area. Conversely, it was the high surface area of the zeolite present in the washcoat that determined the total surface area of the washcoated catalysts. Following Cr_2O_3 impregnation, the surface areas of the washcoated cores were further reduced to about 15–40 m^2/g. Similar to the washcoated catalyst cores, the exchanged and impregnated $\frac{1}{16}$-in. pellets also showed a drop in surface area following the chromia impregnation. The original surface area of about 570 m^2/g with the Co–Y was reduced to 325 m^2/g with approximately 6% of chromia loading.

As mentioned above, the surface areas of the washcoated catalysts were mostly dependent on the zeolite content and hence the differences between the two different types of washcoats could not be distinguished from these data. However, the pure Silbond/CA and Chlorhydrol/CA powders were completely free from any zeolite and were able to show a clear difference in the surface area between these two binders. Chlorhydrol appeared to be of much higher surface (160 m^2/g) area than Silbond (2 m^2/g).

Table 2 shows the oxygen pickup capacities of the metal-exchanged zeolite powders and the metal-exchanged $\frac{1}{16}$-in.-diam zeolite pellets. The unit mg/g signifies milligrams of oxygen adsorbed per gram of catalyst used. Among the various metal-exchanged zeolites, O_2 pickup increased from Co–Y to Cr–Y to Mn–Y. The "fractional cation availability," defined as the ratio of metal cations active for chemisorbing oxygen to the total number of metal cations present, was calculated by combining the oxygen pickup data and the metal loading of the zeolites. Among the metal-exchanged zeolites, Co–Y showed the highest FCA of 0.86; i.e., 86% of the cobalt ions present within the zeolite matrix were available for oxygen adsorption in a one-to-one ratio. The FCA ratios for the other two metal-exchanged zeolites were relatively lower, with 0.60 for Cr–Y and 0.15 for Mn–Y. However, it is possible that, since both Cr–Y and Mn–Y had larger concentrations of respective metal ions than Co–Y (Mn–Y, 10 times more metal atoms than Co–Y; Cr–Y, 2 times as many as Co–Y), so that even if the total number of sites for O_2 adsorption were similar, different FCA numbers would be obtained with Cr–Y and Mn–Y.

The effect of Cr_2O_3 treatment on oxygen adsorption capacity of the zeolite catalysts is evidenced by comparing the $\frac{1}{16}$-in.-diam Co–Y and Co–Y/CA pellets. The O_2 pickup capacity of the Co–Y pellet dropped sharply from 2.78 to 1.37 mg/g following the Cr_2O_3 impregnation. This could have been a consequence of the combination of drop in surface area and loss of Co from the zeolite, caused by Cr_2O_3 impregnation. Conversely, comparing the oxygen adsorption of the Cr_2O_3-impregnated calcined Silbond and Chlorhydrol powders reveals that the higher surface alumina binder produced much better oxygen adsorption than the silica-based one. Normalizing the O_2 pickup based on Cr_2O_3 content, it can be seen that the Chlorhydrol/CA picked up 0.355 g of oxygen per gram of Cr_2O_3 while the same for the Silbond/CA was only 0.027 g per gram of Cr_2O_3. This difference in results suggests a much better dispersion of Cr_2O_3 sites on the alumina-based binder than the silica one.

The catalytic activity data for the various zeolitic catalysts are presented in Figs. 1 through 4. The activities of the different catalysts are compared on the basis of actual feed conversion obtained with several chlorinated VOCs. Each graph shows the conversion of a particular VOC with various catalysts as a function of temperature. Unless mentioned as pellets, all the catalysts used were washcoated cordierites. Space velocities shown on the graphs were calculated at ambient temperature and based on the catalyst bed volume.

As shown in Fig. 1, among all the washcoated catalyst cores, $MeCl_2$ conversion was highest with the Co–Y catalyst. More than 90% conversions of $MeCl_2$ could be obtained with the Co–Y at temperatures at and above 350°C. Generally, all the metal-exchanged and washcoated catalysts without chromia impregnation produced higher $MeCl_2$ conversions than the impregnated ones. For example, Co–Y/CA produced 10–20% lower $MeCl_2$ conversion than the Co–Y under identical conditions. Similar results were obtained with Cr–Y/CA and Mn–Y/CA catalysts. The Co–Y/CA pellets and the washcoated Silbond/CA catalysts were at the extremes of the conversion spectrum; while zeolite-rich Co–Y/CA pellets produced the highest conversion among all the catalysts, the zeolite-free Silbond/CA was the worst. The Co–Y/CA pellets produced over 90% conversion of $MeCl_2$ at temperatures as low as 300°C. This represents about 40°C drop in reaction temperature for similar conversion level as compared to the washcoated Co–Y core. By contrast, the Silbond/CA catalyst needed a minimum temperature of 400°C to produce 90% conversion of $MeCl_2$.

Activities of the various catalysts for TCE conversion are compared in Fig. 2. The drastic difference between the reactivity of $MeCl_2$ and TCE is indicated by the extremely low conversion of TCE with the Co–Y, Cr–Y, and Mn–Y catalysts. Whereas non-chromia-impregnated catalysts produced higher $MeCl_2$ conversions than their chromia-impregnated counterparts, the case was completely reversed with TCE. Without chromia impregnation all three metal-exchanged catalysts showed less than 50% conversion at temperatures below 350°C. However, among the cation-exchanged washcoated catalysts, Cr–Y appeared to show better activity for TCE destruction at 300°C and above. Following impregnation, the same catalysts produced 80% and above conversions at temperatures as low as 300°C. The order of activity among the three chromia-impregnated zeolite catalysts was Co–Y/CA > Cr–Y/CA > Mn–Y/CA. The difference in activity was primarily noticeable at temperatures below 300°C, where the Co–Y/CA was much superior to the other two.

In the case of TCE, the Silbond/CA-washcoated catalyst cores showed higher activity than the non-chromia-impregnated zeolite cores. However, its activity was still considerably lower than the similar chromia-impregnated zeolite cores.

Co–Y/CA pellets, as expected, produced higher activity for TCE conversion compared to the supported washcoated ones. This catalyst was able to produce 90% and higher conversions from 250°C upward. For TCE conversions over 90%, this meant almost 60°C reduction of the minimum reac-

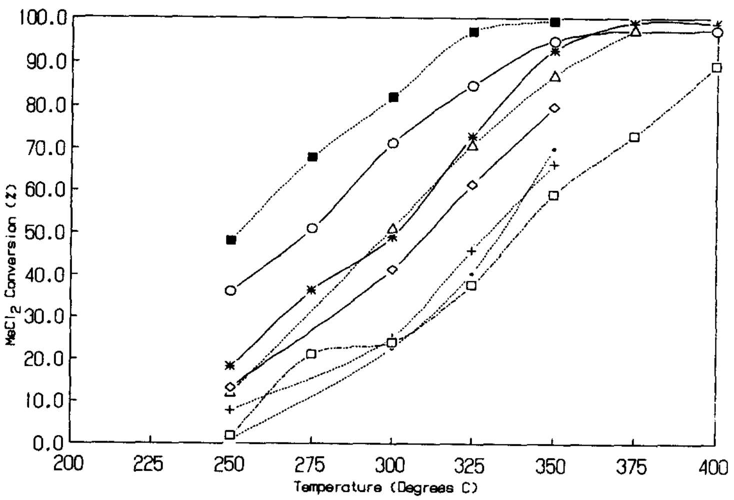

FIG. 1. MeCl$_2$ conversion vs temperature plot with various catalysts (○) Co–Y; (△) Co–Y/CA; (□) Silbond/CA; (◇) Mn–Y; (•) Mn–Y/CA; (✱) Cr–Y(3000 ppm water); (+) Cr–Y/CA; (■) Co–Y/CA pellets. Space velocity: monoliths = 1367 (h^{-1}), pellets = 2361 (h^{-1}).

tion temperature as compared to the wash-coated Co–Y/CA catalyst.

The activity of the various zeolite catalysts for decomposition of CCl$_4$ is shown in Fig. 3. The nonimpregnated zeolite catalysts (Co–Y, Cr–Y, etc.) gave much higher conversion of CCl$_4$ than their chromia-impregnated versions (Co–Y/CA etc.). The Co–Y catalyst was the best, producing almost complete conversion of CCl$_4$ at temperatures of 175°C and above. The chromia-impregnated Silbond/CA catalyst showed the worst activity with CCl$_4$. The Co–Y/CA pellets, conversely, showed activity as high

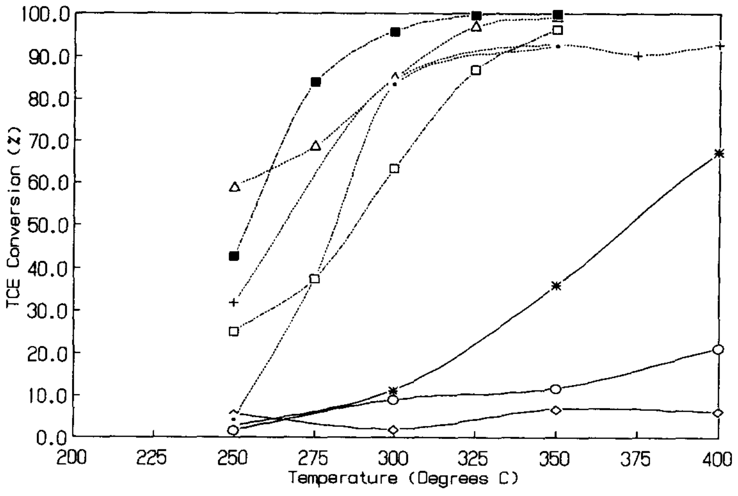

FIG. 2. TCE conversion vs temperature plot with various catalysts (○) Co–Y; (△) Co–Y/CA; (□) Silbond/CA; (+) Cr–Y/CA; (✱) Cr–Y; (◇) Mn–Y; (•) Mn–Y/CA; (■) Co–Y/CA pellets. Space velocity: monoliths = 1367 (h^{-1}), pellets = 2361 (h^{-1}).

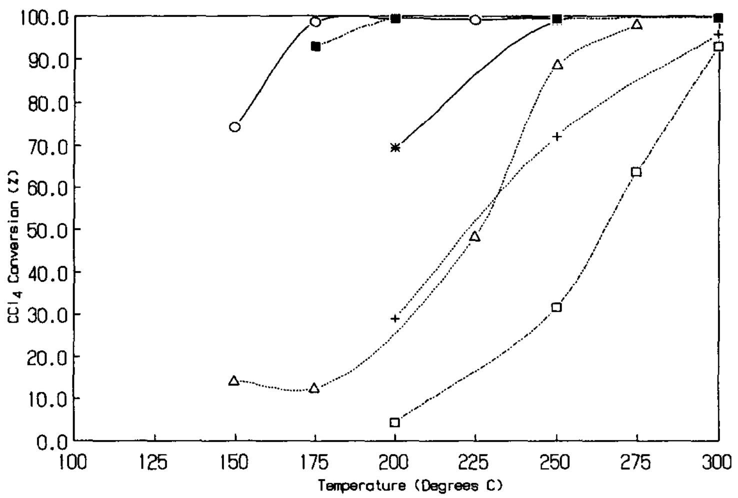

FIG. 3. CCl_4 conversion vs temperature plot with various catalysts. (O) Co–Y; (△) Co–Y/CA; (□) Silbond/CA; (✻) CR–Y(3000 ppm water); (+) Cr–Y/CA; (■) Co–Y/CA pellets. Space velocity: monoliths = 1367 (h^{-1}), pellets = 2361 (h^{-1}).

as the Co–Y catalyst and produced complete conversion of CCl_4 at temperatures as low as 200°C. It should be noted here that even though CCl_4 conversions between Cr–Y and Cr–Y/CA should not be compared due to the difference in water concentrations, additional unpublished data with Cr–Y and other such catalysts do show that the activity of the exchanged catalyst is significantly higher for CCl_4 conversion than similar exchanged/impregnated ones (Cr–Y/CA).

Since this study incorporated several washcoated metal-exchanged zeolite catalysts, the properties of the washcoat and its effect on the overall catalytic activity was also of paramount importance. As mentioned earlier, two different binders, one silica-based (Silbond) and the other alumina-based (Chlorhydrol), were used to washcoat the zeolite powder on the cordierite supports. The loading level of the active zeolite phase on the washcoated support (which depended on the volatility of the binder precursor) significantly affected the activity of the catalyst. Moreover, during chromia impregnation of the washcoated catalysts, the surface area of the washcoat directly affected the loading of Cr_2O_3. Therefore, it was necessary to compare the activity of washcoated catalysts prepared from these binders for CVOC destruction.

Figure 4 compares the TCE oxidation activity of the washcoated Co–Y and Co–Y/CA catalysts, made from these two different binders. Even though both surface area and oxygen pickup capacity of the chromia-impregnated calcined Chlorhydrol powder were much higher than the Silbond/CA powder, Co–Y and Co–Y/CA catalysts prepared with these two binders showed very similar results. Between the two Co–Y catalysts, the Chlorhydrol-washcoated one showed modest but slightly higher activity for TCE oxidation than the Silbond-washcoated one. Conversely, comparing the Co–Y/CA catalyst cores showed the Silbond-washcoated one producing slightly higher conversion than the Chlorhydrol one. However, the unsupported Co–Y/CA pellets, as expected, were still by far the best catalyst for TCE conversion.

As far as product selectivity was concerned, CO, CO_2, and HCl were the major products obtained during the oxidation of the chlorinated VOCs with the zeolite cata-

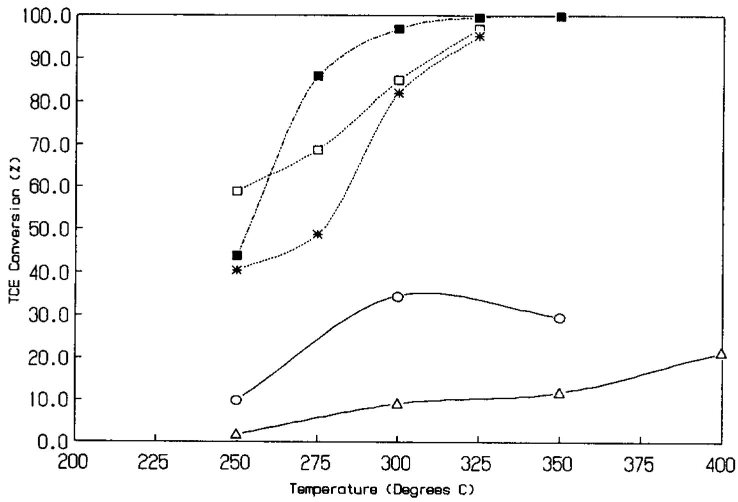

FIG. 4. TCE conversion vs temperature plot with various catalysts. (△) Co–Y Silbond/CA; (□) Co–Y/CA (Silbond); (○) Co–Y (Chlorhydrol); (✻) Co–Y/CA (Chlorhydrol); (■) Co–Y/CA pellets. Space velocity: monoliths = 1367 (h^{-1}), pellets = 2361 (h^{-1}).

lysts. The CO_2/CO ratio in the product spectrum was quite similar between $MeCl_2$ and TCE. The CO_2/CO ratio was approximately 0.02–0.05 for non-chromia-impregnated catalysts, such as Co–Y, while it increased to 0.2–0.3 following chromia impregnation (Co–Y/CA, Cr–Y/CA, etc.). It appeared that this increase in CO_2 production was a direct effect of chromia impregnation, since even the Silbond/CA catalyst produced a CO_2/CO ratio similar to the Co–Y/CA and Cr–Y/CA catalysts. In contrast, CO_2 was the only carbon-containing product formed during CCl_4 oxidation, with all the catalysts; no detectable amounts of CO were observed.

During oxidation of the chlorinated VOCs, the bulk of the chlorine was converted to HCl, utilizing excess hydrogen from the added water. Small amounts of elemental Cl_2 (1–10%) were detected with chromia-impregnated catalysts in the temperature range 300 to 350°C, suggesting the occurrence of the Deacon reaction. With CCl_4 experiments below 200°C, about 5–10% $COCl_2$ was detected. No other undesirable higher chlorinated partial oxidation products could be detected in the product spectra of the various catalysts.

The results from the acidity determination experiments are plotted in Figs. 5 and 6. While the abscissa denotes temperature, the normalized NH_3 desorbed per degree temperature increment is indicated in the ordinate. Ammonia is reported to be an excellent probe molecule for acidity determination of zeolites due to its small size and strong basicity. As plotted in Figs. 5 and 6, the position of the temperature maximum of the ammonia desorption versus temperature graph is a qualitative indication of the magnitude of the NH_3 desorption activation energy and consequently the relative acid strength of the particular sites (*26*). As can be seen in these graphs, all the curves displayed a major desorption peak between 150 and 200°C. This peak was indicative of the weak Brønsted sites present in the zeolite catalysts, which were easily accessible to the adsorbing NH_3. Among the three cation-exchanged zeolites (Fig. 5), the relative acid strength increased in the order of Mn–Y (167°C) < Co–Y (170°C) < Cr–Y (174°C). Similarly, in the case of the pelletized catalysts (Fig. 6), the acidity increased from H–Y (167°C) to Co–Y (170°C) to Co–Y/CA (187°C). This suggested that the acidity of

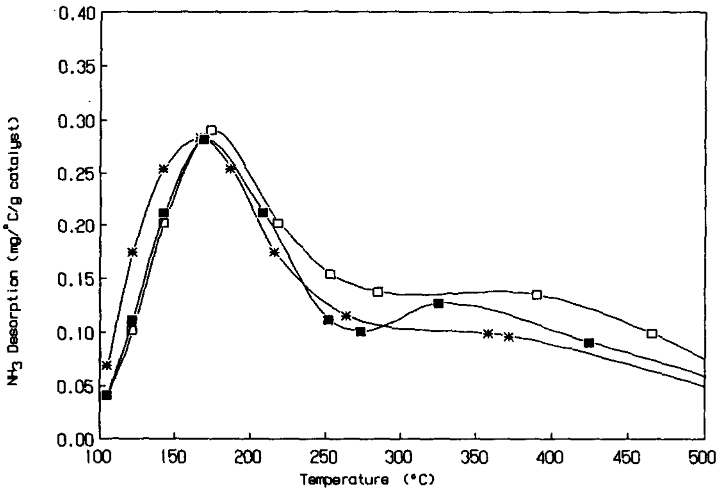

FIG. 5. NH_3 desorption vs temperature plot with cation-exchanged zeolite powders. (■) Co–Y powder; (□) Cr–Y powder, (✻) Mn–Y powder.

the zeolites increased by cation exchange from the base H–Y value (except with Mn–Y) with Co–Y/CA producing the maximum acid strength among all of them.

Apart from the temperature maximum of the NH_3 desorption curve, the area under the desorption peak is also indicative of the relative number of acid sites present. Comparing the desorption curves of the different catalysts, it is found that the apparent number of weak Brønsted sites was almost similar among the three cation-exchanged zeolite powders (Fig. 5). However, Fig. 6 indicates that there was a significant drop in the number of acid sites in going from H–Y to Co–Y. But, chromia impregnation did not appear to influence the site availability for NH_3 adsorption on the Co–Y/CA, as com-

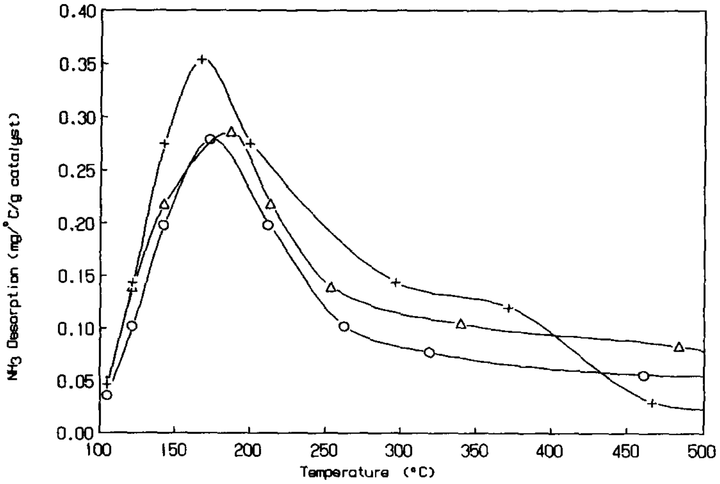

FIG. 6. NH_3 desorption vs temperature plot with various zeolite pellets. (○) Co–Y pellets; (△) Co–Y/CA pellets; (+) H–Y pellets.

pared to the Co–Y. This suggested that although the strength of the acid sites was increased by cation exchange, this also produced a loss of the total number of acidic sites.

A second much smaller desorption peak was obtained with the powdered cation-exchanged zeolites in the range 300 to 400°C, indicating the presence of small amounts of strong Brønsted acid sites. Among these stronger acidic sites, a distinct and significant peak was noted only with Co–Y. The other two zeolites (Cr–Y and Mn–Y) showed much smaller inflection in this region. Although, peak tailing could have affected the results in this region, the data seemed to indicate the presence of a significant amount of stronger Brønsted sites with the Co–Y which were less noticeable with Cr–Y and Mn–Y. Although the relative strength of these strong acid sites could not be clearly distinguished due to tailing of the desorption peaks, it appeared that, similar to the weaker sites, the strength of these strong Brønsted acid sites was also maximum with the Cr–Y.

DISCUSSION

As indicated in the results, the properties of these zeolite/TMO bifunctional catalysts were determined by both the cations present within the zeolite as well as the TMO impregnated on the washcoat. The three different transition metal ions, Co^{2+}, Cr^{3+}, and Mn^{2+}, when exchanged into the Y zeolite matrix, played a major role in influencing the catalytic properties for complete oxidation of the chlorinated hydrocarbons.

It is probable that addition of these transition metal ions improved the catalytic properties in two ways. First, since the cationic sites are responsible for oxygen adsorption (*6*), the presence of transition metal cations with higher available oxidation states and lower ionization potential improved the O_2 pickup capacity of the exchanged zeolite. Second, cation hydrolysis of the bi- or trivalent transition metal ions, in the presence of water vapor, increased the Brønsted acidity of the zeolite (*18*). However, the differences in electronic structure, ionization potential, cation oxygen bond strength, etc., among the three exchanged cations could be expected to produce variations in catalyst activity.

The oxygen pickup capacity of the three cation-exchanged zeolites was found to decrease from Mn–Y > Cr–Y > Co–Y. However, the total amount of cations present in the respective zeolites also decreased in the same order. Since the transition metal cations are assumed to be primarily responsible for the increased oxygen adsorption capacity of the zeolites at elevated temperatures, the lower cation content could have produced lower O_2 pickup with the Co–Y.

However, the activity of a cation-exchanged zeolite for the complete oxidation process is believed to be determined not only by its oxygen adsorption capacity but also by the ionization potential of the cation and the cation oxygen bond strength. Total oxygen adsorption is controlled by the ease of oxidizability of the cation to higher valence states and, therefore, in the present study Cr (+3 to +5 to +6) and Mn (+2 to +4) could have produced higher oxygen pickup capacity than Co (+2 to +3). However, the ability of an oxide for total oxidation increases with lower ionization potential (*19*) and with lower heat of formation of cation oxygen bond (*15*). Suzuki *et al.* (*15*) reported earlier that Co–Y showed lower heat of formation for cation oxygen bonds during ethanol oxidation than either Cr–Y or Mn–Y. Furthermore, the cation oxygen bond strength is smaller (*21*) with Co (92 kcal/mol) than with Cr (102.6 kcal/mol) or Mn (96.3 kcal/mol). This could have led to the formation of a less stable and weakly bound oxygen species with cobalt, which in turn produced the higher activity of the cobalt-exchanged Y zeolite, so noticeable with $MeCl_2$ and CCl_4 oxidation, despite its lower total oxygen pickup.

In addition to oxygen pickup and cation oxygen bond strength, acidity of the zeolite also plays a major role in controlling the activity for chlorocarbon oxidation (*6, 20*). The acidity results obtained during this study showed a slight increase in the strength of the weak Brønsted sites in the order Mn–Y < Co–Y < Cr–Y, but the relative amounts of these sites were almost similar among the three catalysts. Although the differences in acidity strength were quite small (3–4°C), the validity of this trend was indicated by similar results obtained with several repetitions of the experiments. It has been reported (*22, 23*) that acidity due to cation hydrolysis of the cation-exchanged zeolites increases with decreasing ionic radius and increasing electronegativity of the cation. In this case, the ionic radius decreased in the order $Mn^{2+} > Co^{2+} > Cr^{3+}$ while the electronegativity increased as $Cr^{3+} < Mn^{2+} < Co^{2+}$. At this point, it appears that the strength of the weak Brønsted sites was primarily influenced by the size of the exchanging cation with little or no observable effect of the cation electrongegativity. Conversely, a different trend was noted with the stronger Brønsted sites, which contributed toward the NH_3 desorption peaks at temperatures above 300°C. The data suggested the presence of larger amounts of the stronger Brønsted sites with the Co–Y than both the Cr–Y and the Mn–Y. These critical stronger acidic sites could have played a major role in determining the catalyst activity for CVOC oxidation, thereby producing higher activity with the Co–Y.

Apart from the composition of the catalysts, the efficiency of the catalytic oxidation process was directly related to the size, structure, and composition of the chlorinated VOC used. The presence of four chlorine atoms bonded to a single carbon atom in CCl_4 gives it a perfectly symmetric structure. $MeCl_2$ is also a symmetric molecule with two hydrogen atoms and two chlorine atoms bonded to a single carbon. Unlike these two, TCE is an unsaturated double-bonded compound (carbon–carbon double bond) with three chlorine and one hydrogen bonded to two carbon atoms. Therefore, it seems probable that the activity of the cation-exchanged zeolites depended directly on the structure of the VOC feed with the rate-limiting process being linked to the breaking of the strongest bond within the compound.

TABLE 3

CVOC Adsorption Results on Catalysts over Half an Hour

Feed	VOC Adsorbed at different temps. (mmol/g catalyst)		
	250°C	300°C	350°C
	Co–Y powder		
TCE	0.004	0.003	
$MeCl_2$	0.020	0.018	0.015
CCl_4	0.025	0.008	
	Co–Y/CA pellets		
TCE	0.025	0.018	
$MeCl_2$	0.037	0.037	
CCl_4		0.019	

To clarify this effect, adsorption of the three chlorinated VOCs on the powdered Co–Y zeolite in a nitrogen atmosphere was carried out using the TGA. Table 3 compares the relative adsorption of the feeds on the Co–Y catalyst after half an hour of exposure to the $CVOC/N_2$ mixture at different temperatures. It can be seen that, for the Co–Y powder, TCE adsorption was only about 20% of the values obtained for the other two feeds. Conversion trends of the three chlorinated feeds with the Co–Y zeolite exactly followed their adsorption patterns. CCl_4 (with maximum adsorption on Co–Y) was easily converted at temperatures as low as 200°C. $MeCl_2$, which showed less adsorption than CCl_4, required a temperature rise to 350°C for complete conversion, while TCE showed the least adsorption and also minimum conversion with the cation-exchanged zeolites.

In addition to its higher adsorption within the cation-exchanged zeolite, the relative ease of complete conversion of CCl_4 at lower temperatures (in contrast to either

$MeCl_2$ or TCE) could also be related to the differences in bond strengths among these molecules. In the chlorinated hydrocarbons, the carbon–chlorine bond is the weakest compared to the carbon–hydrogen or the carbon–carbon double bonds (*21, 24*). Bond strength for C—Cl at 25°C in the CCl_4 molecule is only about 73 kcal/mol whereas for the C–H in $MeCl_2$ and the C═C bond in TCE it is about 100 and 172 kcal/mol, respectively. If one considers breaking of the strongest bond within the VOC as a probable rate-controlling process (provided rapid and sufficient adsorption is possible), it is evident that higher conversion of CCl_4 would be favored as compared to the other two feeds at a given temperature. Similarly comparing between $MeCl_2$ and TCE, the higher adsorption of $MeCl_2$ in the nonimpregnated cation-exchanged zeolites (Co—Y, Cr—Y, etc.) along with the lower bond strength of the C—H bond, produced higher conversion of $MeCl_2$ than TCE, with Co—Y, Cr—Y, and Mn—Y.

The considerably lower adsorption of TCE within the Co–Y catalyst led to the initial assumption of probable size exclusion of TCE from the zeolite supercages. However, comparing the reported kinetic diameters for these molecules (*27, 28*) it was found that the size of the molecules increased in the order TCE (3.2 Å) < $MeCl_2$ (4.75 Å) < CCl_4 (5.6–5.9 Å). With TCE apparently having the smallest kinetic diameter, this difference in adsorption did not appear to be caused by a probable size exclusion but perhaps by a difference in adsorption mechanism or due to lack of proper adsorption sites.

The probable size-exclusion theory for TCE was further disproved by the VOC adsorption experiments on the Co–Y/CA pellets. It was noted that although the zeolite surface area went down as a result of chromia impregnation (576 to 325 m^2/g), adsorption of TCE showed significant (about 50 to 70% of $MeCl_2$ adsorption) improvement. This further suggested that instead of size exclusion, TCE adsorption was limited by the type of adsorption sites present in the zeolite matrix.

In addition to the adsorption changes, catalytic conversion of TCE was also substantially improved (Fig. 2) following chromia impregnation of the washcoated cation-exchanged zeolite catalysts (Co–Y/CA, Cr–Y/CA, etc.). This change was highly desirable and apparently brought about by the presence of the nonframework Cr_2O_3 along with the metal-exchanged cation. Since earlier results (*5, 25*) have shown good potential for Cr_2O_3 as a deep oxidation catalyst for chlorinated VOCs, this *p*-type oxide was chosen to form a bifunctional zeolite/TMO catalyst. The chromia impregnation of Co–Y and Cr–Y zeolites appeared to produce a catalyst which had both the acidic properties of the zeolite required for high conversions of CCl_4 and $MeCl_2$, as well as a nonframework deep oxidation catalytic site probably required for the initial adsorption and subsequent oxidation of TCE.

During the initial experiments with the chromia-impregnated zeolite catalysts, it appeared as if the nonframework Cr_2O_3 was supported solely on the Silbond washcoat. When later experiments with a plain Silbond/CA catalyst showed significantly less TCE conversion than Co–Y/CA or Cr–Y/CA, it seemed probable that the impregnating cation (or the TMO) was also present inside the zeolite cavities, thus producing higher conversions. This was further evidenced by a drop in surface area and O_2 pickup after chromia impregnation of the cation-exchanged catalysts. This result is consistent with a process whereby the impregnated TMO not only may reside inside the zeolitic supercages but also may block some of these supercages and/or the connecting channels. However, another possibility for the surface area loss following the Cr_2O_3 impregnation might have been partial structural collapse of the zeolite during the impregnation process. Some dealumination trends were indeed noted in comparing the silica/alumina weight percentage ratios of the Co–Y and Co–Y/CA cores. In going from Silbond washcoated Co–Y to Co–Y/CA cores, the ratio changed from 2.3 to 2.6 and again with Chlorhydrol washcoated ones it changed from 1.0 to 1.3. However, even though this apparent blockage or structural loss caused some reduction in $MeCl_2$ and CCl_4 conversions over nonimpregnated counterparts at lower temperatures, the corresponding improvement in TCE conversion was much more significant.

Compared to the washcoated Co–Y/CA catalyst (≃10–15% zeolite content), the unsupported $\frac{1}{16}$-in.-diam Co–Y/CA catalyst pellets were only made out of H–Y zeolite (with small amounts of alumina binder). This additional amount of zeolite in the Co–Y/CA pellets more than compensated for the adverse effects of chromia impregnation and thus produced improved $MeCl_2$, TCE, and CCl_4 conversions as compared to the washcoated Co–Y/CA. It is also to be noted that this additional zeolite amount was significant enough to produce higher activity with the Co–Y/CA pellets in spite of the higher space velocity ($\simeq$2300 h^{-1}) used with the catalyst pellets.

The drop in Co content of the Co–Y catalysts that was noted after Cr_2O_3 impregnation was probably due to some loss of Co during immersion in the chromic acid solution over a period of 8–10 h. This again could be an additional indication of structural loss due to Cr_2O_3 impregnation.

On initially comparing the BET results (Table 2) between the calcined chromia-impregnated Chlorhydrol powder (Chlorhydrol/CA) and the calcined chromia-impregnated Silbond powder (Silbond/CA), the former appeared to be superior based on its much higher surface area ($\cong$160 m^2/g). With this increased surface area, the Chlorhydrol/CA powder was able to incorporate almost twice the amount of Cr_2O_3 loading during impregnation. Further, the additional Cr_2O_3 sites resulted in significantly higher O_2 (more than 20 times) pickup with the Chlorhydrol/CA powder compared to the Silbond/CA.

However, despite these differences between the two chromia-impregnated powders, washcoated Co–Y or Co–Y/CA cores prepared from the two binders did not show any significant difference in surface area (Table 2). Similar trends were also found by comparing the activities for TCE conversion between the Co–Y and Co–Y/CA catalysts prepared from the two different binders. No remarkable difference in activity was noted between catalysts prepared from the different binders (Fig. 4). This similarity in activity between the two washcoated catalysts suggests that the bulk of the catalytic surface area was contributed by the zeolite and not by the binder. Consequently, much of the impregnated Cr_2O_3 was probably present inside the zeolite cages rather than on the outside binder. Therefore, the difference in binder surface area did not affect the catalyst properties in any significant way.

Comparing the product selectivities between the nonimpregnated and the chromia-impregnated zeolite catalysts for TCE and $MeCl_2$ conversion, a significant difference in the CO_2/CO ratio was noted, with chromia impregnation apparently causing a doubling of the CO_2/CO ratio with the washcoated zeolite catalysts. This suggested that the impregnated Cr_2O_3 sites which could be situated either inside the zeolite structure or in the binder were responsible for the further reaction of CO to CO_2. This was consistent with our previous suggestion (*6*) that for further conversion to CO_2, CO may need to be desorbed and then readsorbed on another active site. In the present case, this second active site was probably obtained from the additional impregnated Cr_2O_3 which thus enhanced CO_2 production.

A peculiar difference between CCl_4 and the other two CVOCs was the complete absence of any CO formation during CCl_4 oxidation. Irrespective of nonimpregnated Y zeolites or Cr_2O_3-impregnated ones, no detectable CO was ever observed during CCl_4 oxidation. This indicated a definite difference in the reaction mechanism or the intermediates formed during CCl_4 oxidation as compared to TCE or $MeCl_2$. This was further supported by the presence of $COCl_2$ and significant Cl_2 in the CCl_4 product spectrum at temperatures below 300°C. Most of the Cl_2 production with $MeCl_2$ and TCE feeds, for the chromia-impregnated catalysts, occurred at temperatures between 300 and 350°C, apparently as a result of the Deacon reaction (*25*).

As mentioned in the case of CCl_4, molecular Cl_2 in the amount of 2–6% of the total chlorine balance was noted at temperatures below 300°C, i.e., where the Deacon reaction is not thermodynamically favored. Similarly, small amounts of $COCl_2$ were noted as a by-product only with CCl_4 and were not detected with either $MeCl_2$ or TCE feeds. Therefore, it could be speculated that the oxidation of CCl_4 involves an intermediate step producing $COCl_2$ and Cl_2, and this $COCl_2$ (on further reaction with adsorbed oxygen or water vapor) produces CO_2. Conversely, the hydrogen atoms present in $MeCl_2$ and TCE could lead to the formation of intermediates such as COHCl (*29*). Such an unstable intermediate would immediately dissociate to produce CO and HCl. In this way, CO could be produced from the hydrogen containing CVOCs as a direct oxidation product. On further oxidation, this CO can form CO_2. Since this type of reaction does not lead to direct Cl_2 production and the only Cl_2 could be formed from Deacon reaction with HCl, the amount of Cl_2 formed with either $MeCl_2$ or TCE is usually negligible at temperatures below 300°C.

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