

Oxidative Catalysis of Chlorinated Hydrocarbons by Metal-Loaded Acid Catalysts

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Complete catalytic oxidation of methylene chloride in air was studied over concentration and temperature ranges from 1000 to 2000 ppm and 300 to 475°C, respectively. Three different supported zeolite catalysts, H–Y, Cr–Y, and Ce–Y, were prepared and their activities and selectivities investigated for the above reaction. Conversions varied from 17 to 99%, with catalytic activity decreasing in the order: Cr–Y > H–Y > Ce–Y. The oxygen chemisorption and the acidity values of the catalysts showed similar trends. Differences in oxidizability to higher valence states (Cr–Y > Ce–Y) and cation sizes ($Ce^{3+} > Cr^{3+}$), were probable reasons behind the higher activity of the Cr–Y. A dual site mechanism for the oxidation process, involving adsorption of chlorocarbon at Brønsted sites and adsorption of oxygen at cationic sites, was found feasible. The presence of water (about 27,000 ppm) in the feed stream reduced conversion between 10 and 60%, depending upon catalyst and temperature, and appeared to temporarily deactivate the catalysts. The selectivity among the catalysts was quite similar, with HCl and CO being the only major products. © 1991 Academic Press, Inc.

INTRODUCTION

The increased production and application of chlorinated VOCs (volatile organic compounds) such as methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), trichloroethylene (C_2HCl_3), have caused increased concerns over proper disposal and/or control of these hazardous waste materials. Among the available waste disposal processes, catalytic combustion may be the most economically advantageous method for dilute halocarbon destruction because of its low temperature (300 to 500°C) of operation, low energy consumption, and reduction in noxious by-product formation.

A large number of articles are available regarding catalytic oxidation of chlorinated hydrocarbons over various metal and metal oxide catalysts. The desired reaction is the complete oxidation of the chlorinated VOC to produce HCl and CO_2 ; however, an excess of chlorine over hydrogen atoms in the

parent molecule hinders complete oxidation, and Cl_2 gas is produced as a reaction by-product (1). Although noble metals have found widespread application as automotive exhaust catalysts (2) and as other industrial gas treatment catalysts (3), the deactivation and volatilization of the noble metals by chlorine and HCl renders them ineffective for chlorinated VOC oxidation (5–9). Transition metal oxide (TMO) catalysts, on the other hand, have been found highly active and much more resistant to chlorination and/or HCl poisoning. A detailed review of VOC oxidation catalysts and mechanisms was compiled by Spivey (10), who reported that the most active catalysts for a variety of complete oxidation reactions are usually the oxides of V, Cr, Mn, Fe, Co, Ni, and Cu. Further studies (11, 12, 14, 15) have suggested that the elemental Cl_2 produced by the classical Deacon reaction (13) during VOC oxidation can cause chlorination and hence deactivation of the TMO catalyst. Therefore, catalysts that are less efficient for the Deacon reaction (viz., Cr_2O_3) are

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more suitable for chlorocarbon oxidation. Addition of water to the reactants has also been found to inhibit the Deacon reaction and thus improve the catalyst stability by preventing direct chlorination.

Much less consideration has been given to investigating the suitability of cation-exchanged zeolites as potential catalysts for chlorinated VOC oxidation. The unique features of shape selectivity and high Brønsted acidity caused by their regular crystalline structures have made them essential for numerous industrial catalytic processes, while the presence of multivalent cations within the zeolite matrix has been found to increase the activity for various reactions by creating highly acidic centers through hydrolysis of charged cations (16).

Some investigations on the oxidation of hydrocarbons (viz., ethanol, propylene, toluene) over metal-loaded zeolite catalysts have been reported (17–23) in recent years. The high activity of transition metal-exchanged zeolites as catalysts for deep oxidation as well as partial oxidation reactions has been noticed. Kubo *et al.* (31) reported that oxygen chemisorption capacity and hence the activity of zeolite catalysts for CO oxidation increased with the presence of transition metal ions such as Cr^{3+} , Co^{3+} . Aparicio *et al.* (23) further suggested that the activity of a metal-loaded zeolite catalyst in CO oxidation increased with the ease of oxidation of the metal cation to higher valence states. They found that Cr–Y showed the maximum activity due to the ability of the Cr ion to be oxidized from +3 to +5. The application of zeolite catalysts for selective oxidation of chlorocarbons to form HCl and CO_2 was reported in a patent issued to Dow Chemical Co. (24). Even without the presence of any transition metal cations, zeolites of type Y as well as mordenite produced complete oxidation of CHCl_3 and CCl_4 between 200 and 300°C. The potential of metal-exchanged zeolites for chlorocarbon destruction was briefly suggested in several other existing patents (25).

In view of the notable activity of the zeo-

lite catalysts in oxidation reactions, the probability seems high that suitable cation-exchanged zeolites can be effective alternatives to the metal and metal oxide catalysts currently available for halocarbon destruction. The present study compares the effects of two different exchangeable cations (a transition metal (Cr), and a rare earth (Ce)) with the activity and product selectivity of an H–Y zeolite for vapor-phase oxidation of methylene chloride (CH_2Cl_2) in excess air between 300 and 500°C. The catalysts are compared with and without the presence of water in the feed.

The oxygen adsorption capacities of the catalysts were also measured using thermogravimetric methods. Since the oxygen adsorption capacity of a catalyst often determines its effectiveness in an oxidation reaction, the data obtained were used to analyze observed trends in reactor activity experiments. The acidity of the zeolites, measured by the NH_3 desorption procedure, was also used to compare the activities of the different catalysts.

EXPERIMENTAL

Reactions were carried out with either the cation-exchanged or as-received zeolite catalysts washcoated onto low surface area (0.5–1.0 m^2/g , 400 cells/in.²) honeycomb cordierite supports (each weighing approximately 14 g) obtained from Corning Co. The powdered H–Y zeolite was obtained from Union Carbide Co. as low soda ammonium exchanged LZ–Y82. H–Y was prepared by calcining the ammonium exchanged LZ–Y82 at 500°C.

Approximately 2 wt% of metal ions (Cr or Ce) were loaded onto the LZ–Y82 zeolite by well-known exchange procedures (26). Cation exchange was carried out in two steps. In the first step, NH_4^+ exchange of the LZ–Y82 was carried out by dissolving 89.77 g of NH_4Cl in 745 ml of distilled water (the ratio being 120.5 g of salt in 1 liter of water) and slurring 74.5 g of Linde LZ–Y82 powder in it. The slurry was heated to about 100°C and an even mixing was accomplished

by stirring it for 2 h. The exchanged powder was filtered hot, and washed with distilled deionized water during filtration.

The second step was the metal loading process. The NH_4^+ exchanged and filtered zeolite powder was slurried in approximately twice its weight of distilled deionized water (≈ 150 ml). For Cr^{3+} exchange, 6 wt% of $\text{Cr}(\text{NO}_3)_3$, ($\text{Ce}(\text{NO}_3)_3$ for Ce^{3+} exchange) based on the weight of zeolite powder, was dissolved in approximately 300 times its weight of distilled deionized water. The dilute solution of the exchanged salt was added to the zeolite slurry and the resulting mixture was continuously stirred. In order to establish an exchange equilibrium, stirring of the mixture was continued over a period of 12–15 h. After the required time period, the slurry was filtered and washed with distilled deionized water to remove all traces of soluble salts. The filtered zeolite powder was dried at 125°C for 2 h and then calcined at 550°C over a period of 10–12 h. The final metal loadings were obtained by analyzing the catalysts using a Philips PV9550 energy dispersive X-ray fluorescence (XRF) spectrometer. The loadings obtained were calculated to represent 2.39E + 20 Cr atoms per gram of Cr–Y and 0.743E + 20 Ce atoms per gram of Ce–Y.

The resulting exchanged zeolite agglomerate was crushed to a fine powder and washcoated onto the honeycomb cordierite support from a slurry of the zeolite in perhydrolyzed ethyl orthosilicate binder. Approximately 25 wt% (based on binder volume) of zeolite (exchanged or unexchanged) powder was slurried in 200 ml of silica binder. The slurry was kept well mixed by continuous stirring. Leached and dried cordierite cores were dipped into the slurry and then taken out. The cordierite channels were cleared by blowing compressed air through them. The above procedure was repeated three more times with the same core. Finally, the washcoated cores were dried at 200°C followed by calcination at 550°C for 12–15 h. Generally the cores showed a weight gain of about 15–20% after completion of the wash-

coating procedure. The actual exchanged or unexchanged zeolite constituted approximately 50–60% of the total washcoat after calcining. These procedures produced washcoated cores prepared from H–Y, Cr–Y, and Ce–Y. Further details regarding the preparation techniques are available elsewhere (27).

Catalyst activity and selectivity experiments were carried out by passing mixtures containing 1500–2000 ppm by volume of CH_2Cl_2 in dry air through the 7.62 cm long honeycomb catalyst situated inside a vertical Pyrex preheater/reactor tube (28 mm o.d., 25 mm i.d., and 1 m length) which was maintained between 300 and 500°C . Water was added as a co-feed in concentrations ranging from 22000 to 30000 ppm by volume. The reactor inlet air flow rate was adjusted to obtain a residence time in the catalyst section of 1.04 s at 400°C . Feed and product samples were collected from the reactor by Hamilton CR 700–200 constant rate syringes and analyzed by injecting into a H.P. 5890 GC with H.P. 5970B mass selective detector (GC/MS).

The GC/MS system was capable of both identifying and quantifying gas samples. The GC/MS had a dedicated 9133 Chem Station computer with a capability of identifying 40,000 chemical compounds by comparing mass spectra. Quantification of gas samples was carried out by calibrating the GC/MS with premixed calibration gas and then comparing the responses of the reactor samples to that of the calibration gas mixture. The GC/MS was capable of detecting most of the organic components with a detection limit as low as 10 ppm. However, two major products of catalytic oxidation CO and HCl could not be detected in the GC/MS. The general purpose column (HP Altra I) used in the GC was unable to produce a distinct peak for HCl. HCl was analyzed by passing the reactor effluent through a bubbler containing water followed by titration of the dissolved HCl. In the case of CO, as the mass of both CO and N_2 were identical (28), it was not possible to distinguish be-

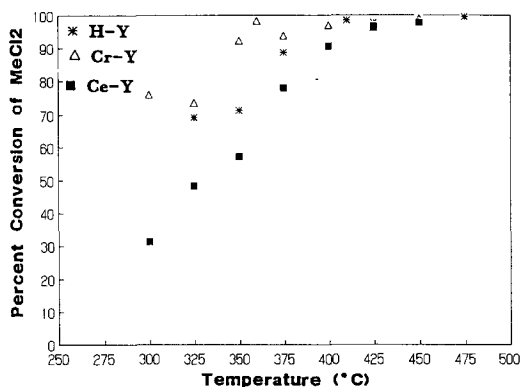


FIG. 1. MeCl₂ conversion vs temperature for runs without water addition.

tween the CO and N₂ peaks in the GC/MS. Therefore, CO analysis was carried out by using MSA detector tubes. The CO tubes were capable of detecting CO samples in the range of 50–3000 ppm. Further details concerning reactor operation and pertinent analytical techniques are discussed elsewhere (27, 28).

The oxygen adsorption (pickup) capacities and acidity values of the test zeolite catalysts (H–Y, Cr–Y, and Ce–Y) were determined by using a DuPont Model 2100 thermal analyst system with 951 thermogravimetric analyzer (TGA). The oxygen pickup capacities of the catalysts at 450°C were determined in the TGA, in two separate steps. In the first step the powdered zeolite sample was first equilibrated in ultrahigh purity helium at 450°C and then dry grade air was passed over it. The change in weight during gas switching was caused by a combination of both oxygen pickup and a buoyancy effect. Since the molecular weight of N₂ (28) is close to that of air (29), the above experiment was repeated with the same sample, using helium and nitrogen to obtain the buoyancy effect associated with the gas change from helium to air. The weight gain in gas switching from He to N₂ was subtracted from that obtained in gas switching from He to air to obtain the actual oxygen pickup capacity of each zeolite catalyst.

For acidity determinations, the powdered zeolites were subjected to NH₃ adsorption at 25°C, at an NH₃ partial pressure of approximately 60 Torr for about 8 h. The adsorbed NH₃ was then desorbed and quantified in the DuPont 951 TGA by using a 10°C/min temperature ramp. Only the amount of NH₃ desorbed above 100°C was considered as chemisorbed NH₃ (29) and subsequently used for acidity determination.

RESULTS

The results from the catalytic reactor experiments with the three zeolite washcoated catalysts (H–Y, Cr–Y, and Ce–Y) are summarized in Table 1. "Feed conc." in the table refers to MeCl₂ inlet concentration. Each product selectivity is calculated based on either chlorine or carbon atoms present in that product divided by the total chlorine or carbon atoms present in the feed (expressed as %).

The catalytic experiments with the H–Y, Cr–Y, and Ce–Y catalysts, without water addition to the feed, were carried out at reaction temperatures varying from 300 to 475°C. As shown in Fig. 1 and listed in Table 1, MeCl₂ conversion with all three catalysts showed a progressive increase with increasing temperature. However, at temperatures above 425°C, the feed conversions with all three catalysts remained above 90%. At

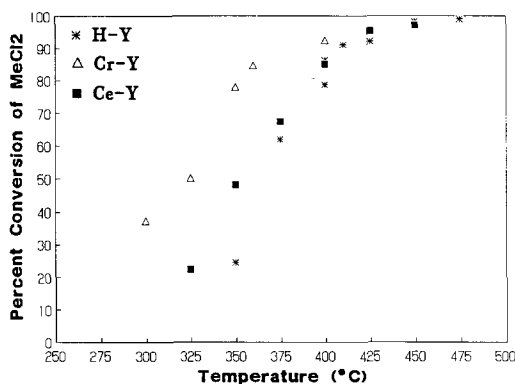


FIG. 2. MeCl₂ conversion vs temperature for runs with ~27000 ppm water addition.

TABLE I
Results of Catalytic Experiments Along with Their Chlorine and Carbon Balances

Run No.	Feed conc. (ppm)	Water conc. (ppm)	Temp (°C)	Conv. (%)	% Cl to HCl	% Cl to Cl ₂	% C to CO	% C to CO ₂	Chlorine balance	Carbon balance
H-Y Catalyst										
574	1297		350	71.6	65.9	ND	23.1	5.8	94.4	57.4
575	1225	30611	350	24.8	1.6	ND	8.2	3.4	76.9	86.9
576	1380		400	91.6	81.9	ND	58.0	3.2	90.3	69.7
577	1637	29676	400	79.0	89.7	ND	36.7	1.8	110.8	59.5
578	1599		425	99.2	118.1	ND	50.0	6.6	118.9	57.4
579	1322	30849	425	92.5	72.7	ND	60.5	1.3	80.2	69.2
580	1497		450	99.1	93.5	ND	53.4	7.7	94.5	62.0
581	1485	27803	450	98.5	53.5	ND	53.9	1.9	55.0	57.3
582	1482		475	99.7	81.7	ND	54.0	7.0	82.0	61.4
583	1600	27934	475	99.3	53.4	ND	50.0	0.2	54.2	50.9
584	1667		375	89.0	74.8	ND	48.0	2.2	85.9	61.2
585	1610	28713	375	62.2	32.3	ND	24.8	5.4	70.1	68.0
586	1772		410	98.8	81.0	ND	56.4	5.7	82.2	63.4
587	1517	32742	410	91.4	95.9	ND	52.7	2.6	104.5	63.9
588	1433		325	69.4	63.4	ND	42.3	6.4	94.0	79.4
589	1104	24588	325	25.3	6.5	ND	9.1	3.8	81.2	87.6
590	1440		400	96.7	103.5	ND	55.6	6.6	106.7	65.5
591	1662	25613	400	86.6	65.7	ND	48.1	0.5	79.0	62.0
608	1728		400	98.1	86.2	ND	69.5	0.9	88.1	72.3
609	1388		400	98.0	70.4	ND	72.1	7.2	72.4	81.3
610	1493		425	98.0	84.9	ND	67.0	6.2	86.9	75.2
611	1806		450	98.4	70.5	ND	55.4	6.4	72.1	63.3
Cr-Y Catalyst										
592	1454		325	73.5	78.8	1.5	55.0	3.5	106.8	85.0
593	1336	23247	325	50.1	32.4	ND	44.9	1.9	82.3	96.8
594	1601		350	92.2	107.8	1.6	75.0	4.3	117.2	87.2
595	1375	23825	350	77.8	86.7	ND	72.7	5.2	108.9	100.2
596	1829		375	93.7	97.4	ND	65.6	10.1	103.7	82.0
597	1749	23300	375	79.5	71.8	0.3	57.2	6.2	92.6	83.9
598	1794		400	97.0	106.7	5.0	66.9	10.8	114.7	80.7
599	1606	24048	400	92.3	90.4	1.2	74.7	8.8	99.3	91.2
600	1785		425	96.2	103.4	6.2	67.2	15.1	113.4	86.1
601	1574	22854	425	94.6	93.8	1.0	76.3	9.1	100.1	90.8
602	1735		300	76.0	69.9	ND	46.1	3.1	93.9	73.2
603	1603	28440	300	37.4	27.1	ND	24.9	0.3	89.7	87.9
604	1769		360	98.2	93.8	ND	67.8	7.8	95.6	77.4
605	1736	27649	360	84.5	67.5	ND	69.1	2.6	83.1	87.3
606	1550		450	98.9	97.3	ND	77.4	14.5	108.8	93.2
Ce-Y Catalyst										
643	1939		300	31.7	20.8	ND	20.6	2.8	89.1	91.8
644	1680	25440	300	23.0	4.7	ND	11.9	1.2	81.7	90.1
645	1779		325	48.6	27.8	ND	22.5	1.4	79.3	75.3
646	1485	25637	325	22.5	13.1	ND	13.5	0.5	90.6	90.0
647	1919		350	57.5	32.6	ND	42.1	3.5	74.8	87.7
648	1665	26097	350	48.4	26.9	ND	48.0	0.4	78.6	100.1
649	1899		375	78.3	57.1	ND	63.2	1.2	78.8	86.1
650	1541	26227	375	67.6	55.5	ND	51.9	0.6	87.9	84.9
651	1771		400	90.9	82.4	ND	79.0	5.5	91.5	93.6
652	1382	26124	400	85.2	67.1	ND	72.4	0.9	81.9	88.0
653	1774		425	96.9	92.9	ND	78.9	7.7	96.0	89.7
654	1760	27536	425	95.6	13.5	ND	68.2	0.6	17.9	73.2
655	2100		450	98.0	80.5	ND	76.2	7.9	82.5	86.0
656	1573	27295	450	97.4	101.9	ND	76.3	2.7	104.5	81.5

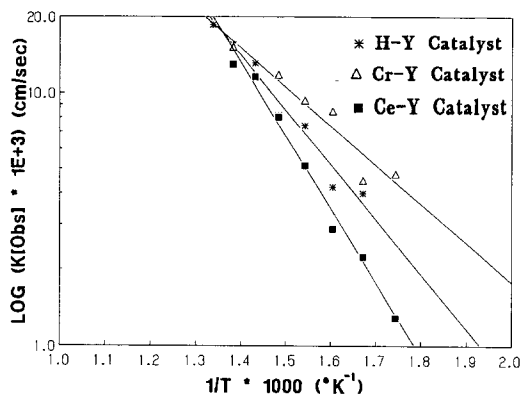


FIG. 3. Arrhenius plot for runs without water.

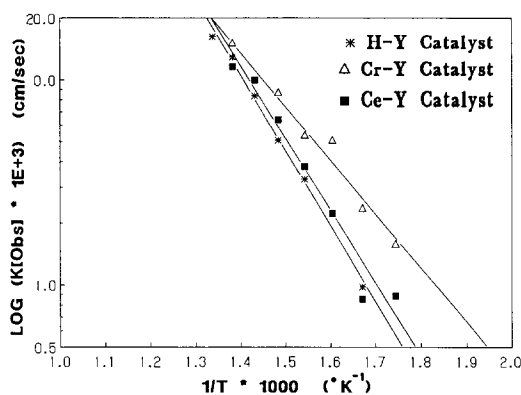


FIG. 4. Arrhenius plot for runs with water.

temperatures below 425°C, MeCl₂ conversions with the three catalysts showed the following trend: Cr-Y > H-Y > Ce-Y.

As shown in Fig. 2, with addition of about 27,000 ppm of water to the feed, MeCl₂ conversions with all three catalysts were significantly reduced for temperatures below 400°C. For example, at 350°C conversion for the H-Y catalyst went from about 70 to 20%; for Cr-Y from about 91 to 78%; and for Ce-Y from about 56 to 48%. Thus, the effect of water addition on conversion was variable, being greatest for the H-Y and least for the Ce-Y catalyst.

A previously developed integral reactor model (30) for a porous walled reactor was used to fit the data to a pseudo-first-order rate equation, from which the observed reaction rate constants (K_{obs}) and activation energies (E) were determined. K_{obs} was defined as the product of the effectiveness factor (η) and the true rate constant (K). The true reaction rate constants based on surface area could not be separated out due to well-known inaccuracies in determining appropriate surface areas for zeolitic wash-coated catalysts by standard BET methods. Therefore, during modeling calculations, the geometric surface area of a single cordierite channel (3.05 cm²) was used instead. Figures 3 and 4 show the Arrhenius plots for all three catalysts, with or without water

being present as a co-feed. The activation energies as calculated from these plots are listed in Table 2.

For runs without water addition, the results showed that the observed rate constants (K_{obs}) of the catalysts increased in the order of Cr-Y > H-Y > Ce-Y while the activation energies followed the reverse trend Cr-Y < H-Y < Ce-Y, corroborating the fact that Cr-Y was the most active catalyst while Ce-Y was the least active one.

However, with water addition and corresponding reduction in activity, the trend in rate constants was modified to Cr-Y > Ce-Y > H-Y. The resulting losses in activity are confirmed by the observed increases in activation energies. The effect of water addition was found to be temporary how-

TABLE 2
Activation Energies of Zeolite Catalysts for MeCl₂ Oxidation

Water addition	Catalyst name		
	H-Y	Cr-Y	Ce-Y
Activation Energies (K cal)			
Without water	9.92	7.08	13.28
With water	19.92	12.01	16.16

TABLE 3

Comparison of Feed Conversion, Oxygen Pickup, and Acidity of the Different Zeolite Catalysts

Catalyst	Feed conversion (%) [at 350°C]	O ₂ Pickup (μg/g) [at 450°C]	Acidity (mmole/g of NH ₃) [at 25°C]
H-Y	71.6	62.37	5.42
Cr-Y	92.2	104.7	6.49
Ce-Y	57.5	43.68	5.09

ever, for as soon as water was removed from the feed, the catalysts regained their prior activity.

The product selectivity data for the zeolite catalysts without water addition to the feed did not show any detectable formation of undesirable higher chlorinated compounds as a result of partial oxidation reactions, as shown in Table 1. Only oxidation products such as HCl, CO, and CO₂ were obtained in the product spectrum. However, small amounts of Cl₂ (1–6%) were formed with the Cr-Y catalyst, suggesting the occurrence of the Deacon reaction (13), whereby HCl and oxygen are converted to Cl₂ and H₂O. The low CO₂/CO product ratios (about 0.1), for all three catalysts, suggest that the zeolites generally favor the formation of CO over CO₂.

Water addition to the feed appeared to substantially reduce the catalytic selectivity toward CO₂ in the case of H-Y and Ce-Y, but only modestly with Cr-Y. Water addition also almost completely eliminated Cl₂ formation with the Cr-Y catalyst.

Table 3 lists the oxygen adsorption (or pickup) capacities of the three catalysts at 450°C along with their no-water feed conversions (at 350°C) and acidity values. Unfortunately, comparisons of oxygen pickup with feed conversions for each catalyst at 450°C would be meaningless since all conversions were >95%. The comparisons in Table 3 suggest that feed conversion is possibly en-

hanced by an increase in catalyst oxygen pickup and/or acidity (based on mmole of desorbed NH₃ per gram of catalyst). However, this is not conclusive and will be further investigated.

The "fractional cation availability," defined as the ratio of metal cations that are active for chemisorbing oxygen to the total number of metal cations present, was calculated by combining the oxygen pickup data and the catalyst metal loading obtained from X-ray fluorescence (XRF) data. The number of cations available for oxygen pickup was obtained from the oxygen adsorption data, arbitrarily assuming a 1 : 1 ratio between cations and adsorbed oxygen atoms. The total number of metal cations present in the zeolite was calculated from the metal loading (about 2%) of the chromium and cerium zeolites as measured by the XRF. The results showed that the fractional cation availability (FCA) for Cr-Y was 0.017 while for Ce-Y it was 0.022. This fraction implies that only about 2 of every 100 metal cations present in the zeolite structure are nominally accessible for 1 : 1 oxygen pickup.

The acidity values of the zeolite catalysts, based on mmole of desorbed NH₃ per gram of catalyst, followed the same trend as the oxygen pickup capacities. Cr-Y, the most active catalyst showed the highest acidity; next was the H-Y, followed by the least active Ce-Y.

DISCUSSION

The results indicate that the catalytic activity of the different zeolites was largely determined by the respective cations present in the Y zeolite matrix. The transition metal ion Cr³⁺ was present in Cr-Y while the rare-earth ion Ce³⁺ occupied the cationic sites within the Ce-Y. By contrast, only H⁺ ions (with small amounts of unexchanged Na⁺) and no metal ions, were present in the H-Y. It is probable that these cations influenced the acidity, oxygen adsorption capacity, and ultimately the activity of the catalysts by virtue of properties

including electronic structure, ionization potential, atomic radius, cation-zeolite bond strength, and site occupancy (or accessibility) within the zeolite.

The primary catalytic property for predicting activity in oxidative reactions is usually the oxygen adsorption capacity of the catalyst. In the case of cation-exchanged zeolites, the oxygen adsorption capacity of a zeolite is believed to increase with the highest available oxidation state change (31, 23). Thus, comparing Cr-Y and Ce-Y, the Cr ion could be oxidized to a valence state (Cr^{3+} to Cr^{5+} to Cr^{6+}) (32, 23) higher than that of the Ce (Ce^{3+} to Ce^{4+}) ion (33).

Also unfavorable for Ce-Y activity, it is noted that to an incoming ligand, the rare-earth Ce^{3+} ion presents essentially a noble gas atom outer electronic arrangement with the 4f orbitals and the electrons occupying them being effectively unavailable, whereas the partially filled d orbitals of the Cr^{3+} transition metal ion make Cr-Y much more reactive. Furthermore, the larger size of the Ce^{3+} ion ($\cong 1.03 \text{ \AA}$) vs Cr^{3+} ($\cong 0.63 \text{ \AA}$) minimizes the covalent interaction with ligands and thus electrostatic interactions are reduced (34) over what they might be for a typical 3+ charge. As a result, the Ce^{3+} ion is susceptible to form far fewer addition complexes than the Cr^{3+} .

In addition to the poor reactivity of the Ce cations, their inaccessibility due to migration from zeolite supercages toward the smaller β cages (35) at elevated calcination temperature (550°C) could also have caused lower oxygen pickup and activity of Ce-Y as compared to the Cr-Y. It should be noted here that even though the FCA for the Ce-Y was higher than for the Cr-Y, its oxygen pickup capacity was substantially less. This is reasonable since the FCA was calculated based on the total number of metal ions present in the zeolites and Cr-Y had almost three times the number of exchangeable metal ions than Ce-Y did. Hence it could be argued that the ions exchanged on the Ce-Y occupied fewer sites

which were on average more accessible to oxygen atoms than with the Cr-Y, where cation exchange continued even after oxygen accessible sites were filled.

In contrast to the Cr-Y and the Ce-Y catalysts, the H-Y catalyst did not have an exchanged metal ion, yet showed slightly higher oxygen pickup than did the Ce-Y. At this point, it is not clear whether the adsorbed oxygen was directly associated with the framework Al atoms or somehow bonded to the Brønsted acid sites in the H-Y catalyst. It seems evident however, that cerium exchange must have blocked or interfered with more original H-Y sites than were created during the exchange process.

Even though the absence of any exchanged metal ions in the H-Y could make it appear to be a blank catalyst and lead us to accept the results obtained with the H-Y as baseline experiments, it was apparently not the case. Under the existing conditions, no detectable homogeneous reactions of MeCl_2 occurred at temperatures below 400°C. This, therefore, suggests that in spite of the absence of any exchanged metal ions, the H-Y catalyst did have some activity which was considerably higher than the homogeneous conversion results.

As suggested by Gentry *et al.* (18), oxidation of a hydrocarbon with a cation-exchanged zeolite can involve two primary steps: (a) hydrocarbon adsorption as a secondary carbonium ion at the Brønsted acid sites, (b) oxygen adsorption at cationic sites. In subsequent steps, this adsorbed oxygen reacts with the carbonium ion to yield final oxidation products. Therefore, both the acidity and the oxygen pickup can influence the catalytic activity for hydrocarbon oxidation with zeolite catalysts.

The catalyst acidity values showed the same trend as oxygen pickup ($\text{Cr-Y} > \text{H-Y} > \text{Ce-Y}$). It is known that replacement of monovalent ions by polyvalent ones in Y zeolites improves activity by creating highly acidic centers through hydrolysis of charged cations (16). This is represented by the scheme



Thus, Cr-Y would show acidity higher than that of H-Y due to enhanced cation hydrolysis of the trivalent chromium ion. Further, the above reaction equilibrium is known to move toward the right with decreasing cation radius and increasing electrostatic field potential of the cation (36, 37). Therefore, in the present experiment, the lower electronegativity and larger ionic radius of cerium ions would be expected to produce lower acidity in the Ce-Y than in the Cr-Y or the H-Y. Hence, both the oxygen adsorption and the acidity results tend to support the observed catalytic activity for MeCl_2 oxidation in the absence of water.

Water addition (≈ 27000 ppm) during vapor phase MeCl_2 oxidation with all the zeolite catalysts resulted in a sudden significant reversible drop in activity. Similar results were also reported by Petunchi and Hall (38) during CO oxidation with Cu-Y. The possible reason for such an occurrence could have been the blockage of cationic sites by water molecules. As explained by Breck (39), when water molecules enter inside the Y zeolite cavity they are localized near the cationic sites. Non-framework water and cations behave as a concentrated electrolyte. At higher temperatures, this localization is prevented and the zeolite does not undergo any structural changes during this process. Results obtained during the present experiments tend to support this approach. Thus, as the reaction temperature was gradually increased from 300 to 400°C, the deactivation effect of water addition diminished accordingly.

The following kinetic scheme can be proposed for the present reaction system:

(Note that { } and [] represent two different catalytic sites.)

1. $\text{CH}_2\text{Cl}_2 + \{ \} \rightleftharpoons \{\text{CH}_2\text{Cl}_2\}$
2. $\text{O}_2 + [] \rightleftharpoons [\text{O}_2]$
3. $[\text{O}_2] + [] \rightleftharpoons 2[\text{O}]$
4. $\{\text{CH}_2\text{Cl}_2\} + [\text{O}] \rightleftharpoons [\text{CO}] + 2\{\text{HCl}\}$
5. $2\{\text{HCl}\} + [\text{O}] \rightleftharpoons [\text{H}_2\text{O}] + \{\text{Cl}_2\}$
6. $[\text{CO}] + [\text{O}] \rightleftharpoons [\text{CO}_2]$

7. $[\text{CO}] \rightleftharpoons \text{CO} + []$
8. $\{\text{HCl}\} \rightleftharpoons \text{HCl} + \{ \}$
9. $[\text{CO}_2] \rightleftharpoons \text{CO}_2 + []$
10. $\{\text{Cl}_2\} \rightleftharpoons \text{Cl}_2 + \{ \}$

As depicted in the above mechanism, the first three steps involve reactant adsorption either at Brønsted acid sites (CH_2Cl_2) or at the metal ion sites (O_2). Step 4 is the probable dual site reaction of the feed while Step 5 shows the Deacon by-product reaction proceeding between the product HCl and the adsorbed oxygen. Step 6 represents the formation of product CO_2 . Steps 7, 8, 9, 10 represent desorption of products (CO_2 , CO, HCl, Cl_2).

Additional experiments are obviously needed to ascertain the validity of the dual-site reaction mechanism in this case. However, since HCl, Cl_2 , CO, and CO_2 were the only compounds present (other than unconverted MeCl_2) in the product spectrum from the three zeolite catalysts, the oxidation of MeCl_2 did not appear to violate the above mechanism. Even if any intermediate chlorinated by-products were formed, they were converted to these final products and thus remained undetected.

Although the effects of diffusion might be expected to become significant at higher conversions in the case of a zeolite catalyst, the Arrhenius plots for the H-Y, Cr-Y, and Ce-Y catalysts did not show any curvature at high temperatures suggesting diffusion limitations. If this effect were true, the small size of the MeCl_2 molecule (4.75 Å) as compared to the entrance (≈ 8 Å) to the large faujasite supercages was playing a significant role. However, a detailed investigation of the potential for diffusion limitations has not yet been carried out.

The presence of Cl_2 only in the product spectrum of the Cr-Y suggested the occurrence of the Deacon reaction only with this catalyst. Addition of water retarded the Deacon reaction on this catalyst and competed for sites occupied by Deacon reactants (i.e., HCl and oxygen).

The reduction in CO_2/CO ratio with water

addition for all three catalysts suggests that CO (which may need to be desorbed and then re-adsorbed in order to form CO₂) receives increased competition for active sites from the added water. If we speculate that the active site is an adsorbed oxygen, this is consistent with the concomitant loss in CH₂Cl₂ oxidative activity, which we believe also requires adsorbed oxygen to proceed.

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