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Cr-doped Zr, Si-mesoporous molecular sieves as catalysts of CH_2Cl_2 oxidation

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Abstract

Zirconium-containing mesoporous silica of nominal Si/Zr ratio in the range 40–5 have been synthesized using dodecylamine as a structure-directing surfactant. The samples were characterized with PXRD, SEM/EDX, BET, CEC measurement and chemical analysis. The materials were used as supports for chromium species incorporated by means of cation exchange procedure. Gradual substitution of Si by Zr in the mesoporous framework results in an increasing structural disorder, increasing cation exchange capacity and increasing capacity for incorporation of Cr. All Cr-doped ZrMMS*x* catalysts are active in the deep oxidation of methylene chloride reaching 100% conversion at temperature ≥400°C. The catalytic performance depends strongly on the catalyst composition. The role of particular components in determining the catalytic activity and selectivities to various products is discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mesoporous molecular sieves; Chlorinated hydrocarbons; Chromium catalysts; Methylene chloride; Deep oxidation

1. Introduction

Chlorine-containing volatile organic compounds are commonly used as solvents in various chemical processes, and as a result, are present in the industrial flue gases. In view of their poisonous nature, they represent a serious environmental problem and in many countries legal limits have been set for emission of these substances [1–7]. Increasingly, one of the means of reducing the concentration of a chlorinated hydrocarbon pollutant is its removal in the course of catalytic combustion, with the ultimate goal being the conversion of chlorine present in the organic molecule to HCl, and oxidation of the organic component to CO_2 and H_2O.

It has been argued that the catalytic combustion of chlorinated organics requires both acid and redox centres. Indeed, the catalytic systems found active in this process include supported noble metals, bulk or supported transition metal oxides, transition metal doped zeolites or pillared clays, as well as classical acid catalysts such as Al_2O_3, zeolites, and TiO_2/SiO_2 [8–24].

The synthesis of various mesoporous molecular sieves with large diameter channels, following the report in 1992 by Mobil on M41S family, created new opportunities in the area of heterogeneous catalysis [25,26]. The solids are generally prepared from a solution of an inorganic precursor in the presence of ordered aggregates of surfactants acting as structure-directing agents. Formation of the

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mesoporous lattice occurs via attachment and polymerization of the precursor at the surfactant–solution interface. The mechanism of interaction involves either an electrostatic attraction between the quaternary ammonium cation surfactants and anionic inorganic precursor species (MCM-type materials), or hydrogen bonding between neutral amine surfactants and neutral inorganic precursors (HMS or MMS solids). Although unsubstituted mesoporous silicas do not show any considerable catalytic activity due to the lack of acid and/or redox functions, the addition of heteroatoms either by framework incorporation or by surface anchoring provides materials of significant catalytic potential [26–58]. In a recently published work, Kawi and Te [51] used an MCM-48 supported chromium catalyst for oxidation of trichloroethylene. The material was found to be very active in this process, but the paper did not provide any information about the nature of the reaction products.

In the present work, we use the neutral-amine–neutral-inorganic precursor mechanism to obtain Zr, Si mesoporous molecular sieves (MMSs) with various Si/Zr ratios. The resulting materials are then used as supports for chromium species and tested in the total oxidation of methylene chloride, one of the most resistant chlorinated hydrocarbons. The catalytic activity and selectivities to various oxidation products are interpreted in terms of the physico-chemical properties of the MMS samples.

2. Experimental

2.1. Materials

To obtain the Zr, Si mesoporous molecular sieves, referred to as ZrMMSx (x=Si/Zr ratio), 0.2 mol of tetraethylsilicate (TEOS) dissolved in 46 ml of absolute alcohol was added at room temperature to an appropriate amount of Zr(IV) propoxide (70 wt.% in 1-propanol, Aldrich), previously diluted in 40 ml isopropanol at 70°C. The mixture was heated with vigorous stirring at 70°C for 4 h to obtain the Zr–Si–O polymerized species. After cooling to room temperature the mixture was added, with stirring, to a 0.15 M solution of dodecylamine (DDA) in 60 vol.% alcohol. The resulting gel was aged at room temperature for 20 h, filtered, washed with ethanol, dried at room temperature and calcined in air at 650°C for 4 h.

All the ZrMMSx samples were doped with Cr(III) species by means of cation exchange. The exchange agent was prepared by refluxing aqueous solution of $Cr(NO_3)_3$ in the presence of Na_2CO_3 for 24 h. Under such conditions the oligomerization of mononuclear chromium species occurs [59]. The nature of the polymers is quite speculative but the final products in the alkaline solution are believed to be highly condensed species such as $[Cr_{12}(OH)_{28}(H_2O)_{12}]^{8+}$ [60,61]. Cationic exchange was carried out at 95°C for 1.5 h using 6 mmol of Cr(III) per gram of ZrMMSx material. The samples were washed, dried at 100°C and calcined for 4 h at 500°C in argon. The resulting materials are referred to as ZrMMSx_{Cr}. A reference Cr-doped sample with no Zr in the siliceous matrix, prepared in a similar manner, is denoted by ZrMMS∞_{Cr}.

2.2. Cation exchange capacity determination

The ZrMMSx materials were subjected to ion exchange with 1 M NH_4Cl for 16 h at room temperature, washed free of Cl^- and dried. A typical Kjeldahl method was used to determine the amount of ammonium ions retained by the samples. The materials were refluxed with 1 M NaOH, the ammonia produced collected in a known amount of 0.1 M HCl and the resulting solution titrated with 0.1 M NaOH, using phenolphtalein as an indicator.

2.3. Characterization techniques

The X-ray diffraction patterns were recorded with a Philips 1710 powder diffractometer using Ni-filtered Cu Kα radiation. A 0.020 step size and 2 s step time were used.

X-ray fluorescence (XRF) was used to determine the content of Si and Zr, while ICP AES method was used to determine the amount of Cr dopant after dissolution of the samples in concentrated HF/HNO_3 acids.

The XPS spectra were obtained with a VG-ESCA 3 photoelectron spectrometer using non-monochromatized Al K$\alpha_{1,2}$ radiation and calibrated against the C 1s line position assumed to be 284.8 eV.

Scanning electron micrographs were obtained using a PHILIPS XL 30 scanning electron microscope equipped with a LINK-ISIS EDS system. The scatter of the Si/Zr ratio for a given sample was evaluated by carrying out the EDS analysis for 10 points chosen at random on the sample surface. Then the standard deviation of the mean value was calculated and treated as a measure of compositional inhomogeneity. In order to evaluate the composition of individual, well-separated grains, the EDS analysis was carried out on samples which were suspended in ethanol and subjected to ultrasound disintegration prior to deposition on the sample holder.

BET specific surface areas were determined from nitrogen adsorption at −196°C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2400 apparatus. Prior to the measurement, the samples were outgassed at 200°C.

2.4. Catalytic reaction

Catalytic activity was measured in a conventional flow apparatus equipped with a glass reactor of 10 mm inner diameter. The volume of the catalytic bed was 1 ml. Oxidation of methylene chloride was studied in the temperature range 300–550°C. Methylene chloride was introduced into the hot stream of air in order to allow its rapid evaporation. The concentration of CH_2Cl_2 in air was 2.5 g/m^3 (STP). The GHSV was 10 000 h^{-1}. Chlorine-containing products, except HCl, were analysed by an on-line GC (SRI 86 10A) with DCQF column. In order to determine the HCl, a known volume of the reaction gas was passed through water and the amount of absorbed HCl was determined from the conductivity of the solution. CO and CO_2 were analyzed by Chrom-5 GC with TCD and two columns: molecular sieve 5A for CO analysis and HayeSep R for CO_2.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the XRD diagrams of the ZrMMS*x* samples. Each pattern consists of a single (1 0 0) reflection that can be assigned to a lattice with a short-range hexagonal symmetry. The peak broadens as the Zr content increases, indicating that incorporation of Zr is associated with an increasing MMS lattice disorder. Similar effect has been reported as a result of introducing Al into MMS [44]. Exchange with chromium has no significant influence on the appearance of the XRD diagrams.

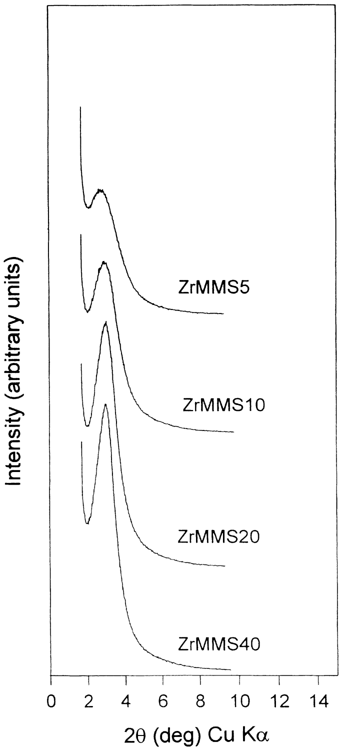

Fig. 1. PXRD patterns of ZrMMS*x* samples.

Chemical analysis of the samples has shown that the actual Si/Zr ratios within the samples differ from the intended ones, the amount of Zr being higher than its relative content in the inorganic precursor solution. The relevant data are gathered in Table 1 which also shows the lattice parameters, results of the CEC measurement, amount of incorporated Cr, and specific surface areas. The slightly increasing value of the lattice parameter as the Si/Zr ratio decreases is an indication that zirconium ions (ionic radius 0.72 Å) do enter the MMS structure and substitute part of Si^{4+} (ionic radius 0.26 Å). As the value of "*x*" decreases, the cation exchange capacities of the samples increase. This is understandable in view of the well-known property of the mixed zirconia–silica system to display higher surface acidity than either of the individual components [62]. The phenomenon is associated with the charge

Table 1
Chemical analysis, lattice parameters, CEC and specific surface areas of ZrMMS*x* samples before and after doping with Cr

Support	Si/Zr (real)	d_{001} (Å)	a_0 (Å)	S_{BET} (m^2/g)		CEC of ZrMMS*x* (meq/100 g)	Incorporated Cr(III) (at.%)
				Before Cr-doping	After Cr-doping		
ZrMMS∞	∞	30.5	35.2	966	1017	0	0.09
ZrMMS40	32.5	31.0	35.7	1064	1076	0	0.12
ZrMMS20	12.0	31.1	35.9	1012	862	6.7	0.48
ZrMMS10	7.5	31.3	36.2	905	748	16.7	0.81
ZrMMS5	3.7	32.6	37.7	713	679	31.7	1.13

redistribution around the bridging oxygens located between two heterometal centres (Zr–O–Si). Following the CEC increase, the amount of chromium attached to the ZrMMS*x* support also increases with the growing Zr content. It is, however, noted that the samples with no measurable cation exchange capacities, such as ZrMMS∞ and ZrMMS40, also bind certain amounts of chromium. This shows that the incorporation of Cr oligomers into MMS structures occurs not only by a pure cation exchange mechanism but also via formation of surface adsorbed species.

The SEM/EDX analysis was undertaken in order to get some insight into the degree of morphological and compositional homogeneity of the ZrMMS*x* samples. SEM micrographs reveal that the morphology of the MMS materials depends on the degree of Zr substitution (Fig. 2a–d). ZrMMS40 and ZrMMS20 samples are composed mainly of rounded

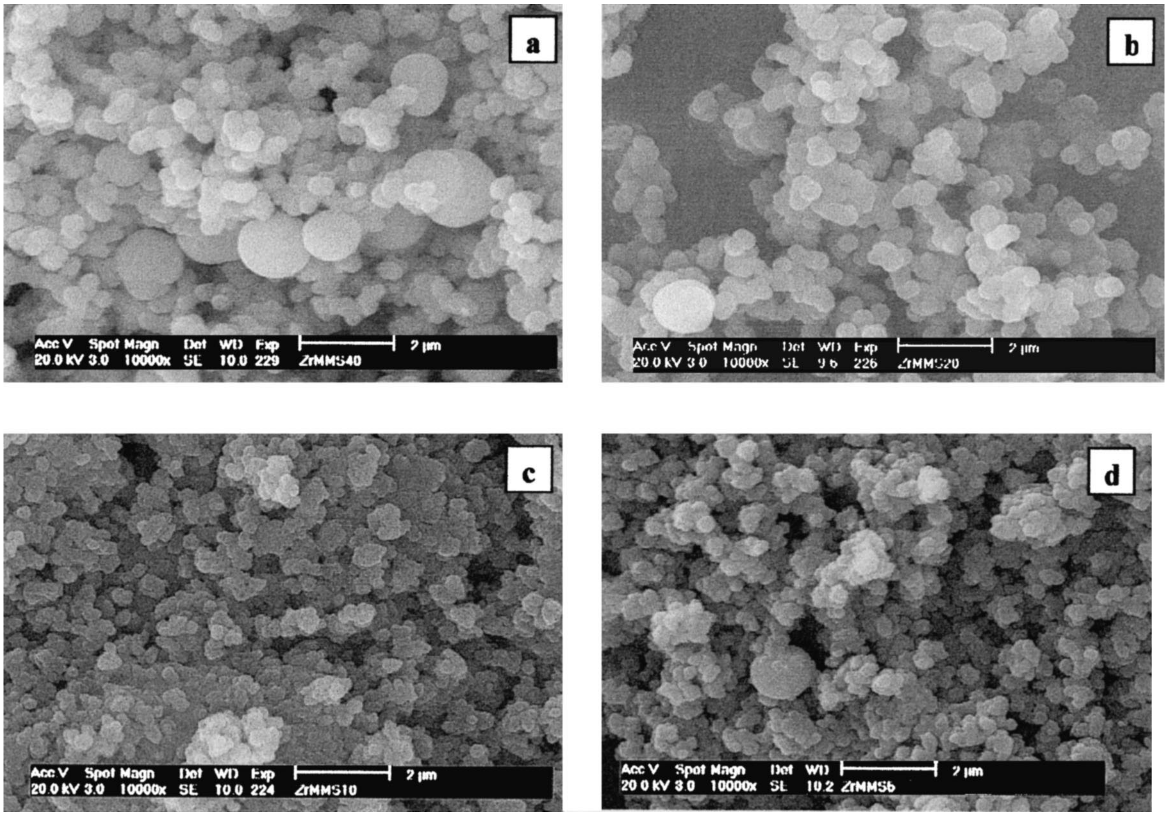

Fig. 2. SEM micrographs of: (a) ZrMMS40; (b) ZrMMS20; (c) ZrMMS10 and (d) ZrMMS5.

crystallites of varying sizes. Samples of ZrMMS10 and ZrMMS5 contain smaller, less regular crystallites of sizes in the range 0.1–0.3 μm. Slight fluctuations in the Si/Zr content were observed in a given sample when analysing crystallites of different dimensions, the smaller grains showing generally more zirconium than the larger ones. In order to assess whether the degree of substitution influences the Si/Zr fluctuations the standard deviations of the mean values determined for 10 randomly chosen points were determined for each sample. They were found to correspond to 7% (x=40), 10% (x=20), 8% (x=10) and 8% (x=5) of the mean Si/Zr value of a given sample. This result, although of no real statistical value, may nevertheless be taken as an indication that the increasing substitution with Zr does not result in an increasing compositional segregation.

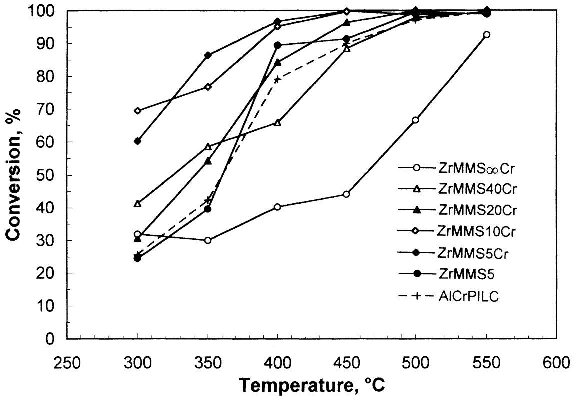

Fig. 3. Dependence of the CH_2Cl_2 conversion on the reaction temperature for MMS catalysts.

3.2. Catalysis

All the MMS samples are active in the oxidation of CH_2Cl_2, approaching 100% conversion at temperature $\geq$400°C (Fig. 3) (Table 2). Fig. 3 shows the dependence of CH_2Cl_2 conversion on the reaction temperature for all the ZrMMSx_{Cr} materials. It can be seen that the catalytic performance depends on the value of "x", the lower Si/Zr ratios favouring increased activity. It should be remembered that "x" influences the amount of Zr and the amount of Cr in a similar manner: both increase as "x" decreases. In order to determine the role of each of these elements separately, experiments with samples containing only one of these components were performed. As shown in Fig. 3, the ZrMMS∞_{Cr} sample with matrix based purely on silicon and Cr content comparable to that of ZrMMS40$_{\mathrm{Cr}}$ is much less active than any of the zirconium-containing samples. This indicates an important role of Zr in enhancing the catalytic performance. On the other hand, a Cr-free ZrMMS5 sample is quite active, although less than the sample after doping with chromium.

For the sake of comparison we have also prepared an Al, Cr-pillared montmorillonite catalyst, following the procedure described in [22] and using a Milowice (Poland) bentonite as a source of the smectite matrix. Such a material, obtained from Nador (Morocco) bentonite, was reported to give 100% conversion of methylene chloride in the temperature range 300–400°C [22]. Under the conditions of our experiment, the catalyst did not achieve a similar performance and showed intermediate activity. One has to bear in mind, however, that the catalytic properties of

Table 2
Catalytic performance in oxidation of methylene chloride at 450°C

Sample	Conversion (%)	Selectivity (%)				Σ_{Cl} (%)	Σ_{C} (%)
		HCl	Cl_2	CO_2	CO		
ZrMMS∞_{Cr}	44.1	1.6	0	11.4	11.8	1.6	23.2
ZrMMS40$_{\mathrm{Cr}}$	88.5	2.4	6.3	18.3	33.4	8.9	42.3
ZrMMS20$_{\mathrm{Cr}}$	96.4	30.5	12.0	20.0	44.0	42.5	64.0
ZrMMS10$_{\mathrm{Cr}}$	99.6	27.0	20.7	42.5	32.3	47.7	74.8
ZrMMS5$_{\mathrm{Cr}}$	99.8	32.4	25.1	61.0	20.4	57.5	81.4
ZrMMS5	91.3	57.2	2.9	12.2	47.1	60.1	59.3
AlCrPILC[a]	89.9	10.5	0	9.9	38.5	15.0	48.4

[a] CH_3Cl appears additionally with a selectivity of 4.5%.

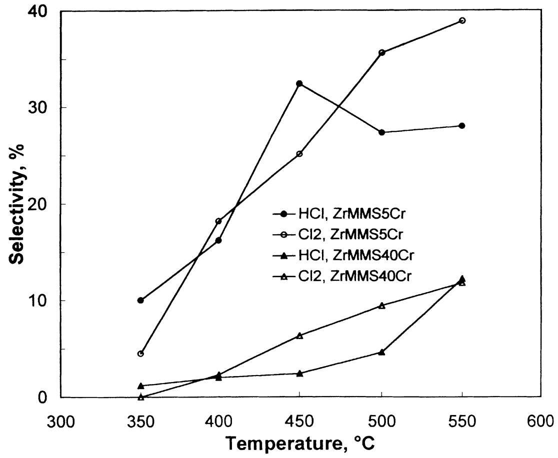

Fig. 4. Dependence of the selectivities to chlorine-containing products on the reaction temperature for ZrMMS40$_{Cr}$ and ZrMMS5$_{Cr}$ catalysts.

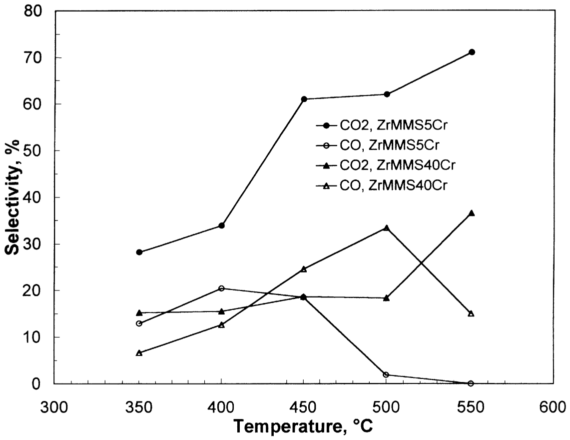

Fig. 5. Dependence of the selectivities to CO and CO_2 on the reaction temperature for ZrMMS40$_{Cr}$ and ZrMMS5$_{Cr}$ catalysts.

pillared clays may be affected by the origin of the montmorillonite matrix.

Important variations are apparent when analysing the reaction products (water, HCl, Cl_2, CO_2 and CO). Fig. 4 shows the selectivities to the chlorine-containing products for the two end-members of the ZrMMSx_{Cr} series. In all cases chlorine is produced in addition to HCl. The selectivities to both products increase with temperature but the overall balance between reactants and products is rather poor, indicating that additional processes, possibly retention of the products in the catalyst pore system or reactions of the products with the catalyst, occur. Of the two catalysts, the ZrMMS5$_{Cr}$ sample gives a better balance; at 550°C almost 70% of the expected products are detected. Selectivities to carbon-containing products for the same catalysts are shown in Fig. 5. Selectivity to CO_2 increases with temperature for both catalysts, while that of CO initially increases, passes through a maximum and then decreases. Again, there is a poor balance of carbon-containing products. Also here, a better agreement between the amount of expected and the amount of detected products is observed for the ZrMMS5$_{Cr}$ sample. The lack of balance suggests that carbon-containing products are partially retained by the catalyst, possibly due to the formation of coke deposits. Indeed, ESCA measurement confirmed that the surface of used catalysts contained increased amount of carbon. The EDX analysis of the spent ZrMMS5$_{Cr}$ catalyst showed that a small amount of Cl is retained by the catalyst after catalytic run (Table 3). The Si/Zr ratio in the used sample is smaller than in the fresh catalyst, pointing to the partial loss of silicon from the MMS framework due to the volatilization by chlorine and HCl. On the other hand, the amount of the Cr component, normalized to the Zr content, remained virtually unaffected. This points to the relative resistance of MMS materials against the loss of active chromium phase. For a comparison, the exposure of Cr-exchanged ZSM-5 catalysts to chlorinated volatile organics led to a gradual loss of chromium and, consequently, to the catalyst deactivation [20].

The role of particular elements can be further elucidated by comparing the data describing the catalytic performance of all the samples at 450°C (Table 2). One can see that parameters such as reaction conversion, selectivities to various products, chlorine and carbon balance are very sensitive to the catalyst composition. As already mentioned, substitution with Zr

Table 3
Si/Zr, Cr/Zr and Cl/Zr ratios determined by EDX analysis for the fresh and the spent ZrMMS$_{Cr}$ catalyst

Sample	Si/Zr	Cr/Zr	Cl/Zr
ZrMMS5$_{Cr}$-fresh	4.28	0.15	0.00
ZrMMS5$_{Cr}$-spent	3.65	0.14	0.02

is required for high catalytic activity of MMS materials. Comparison of the data for ZrMMS∞_{Cr} and ZrMMS40$_{Cr}$ shows that at the same level of doping with Cr the presence of zirconium improves both the Cl and the C balance. On the other hand, the data for ZrMMS5$_{Cr}$ and ZrMMS5 show that although the addition of chromium does not affect significantly the Cl balance, it has a beneficial effect on the carbon balance. As far as the nature of reaction products is concerned, addition of Cr suppresses the formation of CO and enhances Deacon process leading to oxidation of HCl–Cl_2. This is in agreement with the finding of Greene and co-workers [20] who, for a series of Cr-doped ZSM-5 materials, observed that high chromium catalysts always had higher CO_2 and Cl_2 selectivities than the low chromium ones.

Summarizing, the Cr-doped ZrMMS catalysts possess a significant catalytic potential in destruction of chlorinated volatile organics. The catalytic performance is very sensitive to the catalyst composition which opens possibilities for further tuning of the catalytic function of these materials, e.g. by introducing new heteroatoms into the MMS structure. Work along this line is currently being done in our laboratories.

4. Conclusions

The zirconium-containing mesoporous silicas have been prepared using a primary amine as a structure directing agent. The resulting materials possess hexagonal structure similar to that observed for aluminosilicate mesoporous catalysts prepared by a similar method. Gradual substitution of Si by Zr in the MMS framework results in materials of increasing structural disorder, increasing cation exchange capacity and increasing capacity for incorporation of chromium species. The Cr-doped ZrMMS*x* catalysts are active in the deep oxidation of methylene chloride, their performance improving as Si/Zr ratio decreases. Incorporation of zirconium is essential for high catalytic activity, and results in materials less susceptible to the corrosive action of chlorine-containing reaction products and is beneficial for the Cl and C balance. Addition of chromium suppresses formation of carbon oxide, increases the tendency to form Cl_2, and improves the reaction balance of carbon-containing products.

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