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Carbon Molecular Sieves as Catalysts and Catalyst Supports

Gerald C. Grunewald and Russell S. Drago*

*Contribution from the Department of Chemistry, University of Florida,
Gainesville, Florida 32611.* *Received May 29, 1990*

Abstract: Ultrahigh surface area (>2500 m^2/g) carbon molecular sieves (CMS's) are shown to be very effective catalysts and catalyst supports for the oxidative dehydrogenation and dehydration of a variety of substrates. Studies of methanol, ethanol, 1- and 2-propanol, and propanal provide mechanistic insight concerning the reactivity of these materials. The activities are superior to many inorganic oxide based systems. As catalysts, CMS systems are shown to have the ability to function via hydride or hydrogen atom abstraction mechanisms, depending on the nature of the substrate. As catalyst supports, a synergism is demonstrated between the CMS support and metal dopants, which enables the system to have greater activity than that of either of the constituents alone. The highly reactive surface, the ability to disperse and stabilize metal clusters, and the extraordinary adsorption capabilities of the CMS materials are the key contributors to their high activity. One of the catalysts studied (a 15% MoO_3/CMS system) has pronounced activity toward methanol oxidation: 70% of the substrate is converted to methyl formate in a single pass with over 95% selectivity. A further significant finding involves the metal-catalyzed conversion of the carbonaceous support itself to small molecular weight products via reactions with methanol fragments. This finding has fundamental implications in heterogeneous catalyzed CO reductions and in the conversion of methanol to gasoline in zeolites.

Introduction

The introduction of synthetic zeolites in the early 1960s sparked a great deal of research in materials science and catalysis.[1] In the ensuing years, hundreds of patents, books, and papers have described the application of zeolites to a plethora of molecular sieve separation processes and shape-selective catalysis systems. Currently a new class of materials has been discovered that has the potential to equal or surpass the novel properties and reactivity of aluminosilicate compounds. Carbon molecular sieves (CMS's)[2] with extraordinarily high surface areas (>2500 m^2/g) and relatively uniform pore sizes have recently been synthesized.[3] Initial investigations have shown these materials to be very effective in gas-separation studies,[4-6] in pressure-swing absorption experiments,[7] and in a variety of catalytic systems.[8-11] Despite these encouraging preliminary results, there have been surprisingly few fundamental studies of the reactivity and properties of the CMS-based materials as catalyst supports.[12-17]

We have recently reported the reactivity of CMS catalysts in the oxidative dehydrogenation of ethylbenzene to styrene.[18] We are particularly interested in obtaining information to characterize the CMS catalyst as both a reactive species and a support with possible synergistic interactions in catalytic processes. In this light, our major focus is on factors that affect how the catalyst adsorbs and transforms various substrates, how the chemical structure of the substrates affects the reactivity shown by the support, and how various promoters interact with the CMS to give rise to novel synergism. For this purpose, we have chosen the oxidation of alcohols and aldehydes as substrates for study because their mechanisms of oxidation are reasonably well understood. In the process, a low-temperature oxidation of methanol to methyl formate was found. Methyl formate is becoming increasingly important as a starting material for the preparation of acetic acid,[19-21] dimethylformamide,[22] and ethylene glycol.[23]

Table I. Reactivity of C_3 Oxygenated Substrates over CMS Catalyst[a]

substrate	products	selectivity[b] (%)	conversion[c] (%)
1-propanol	propene	63	40
	propanol	13	
2-propanol	propene	70	46
	acetone	20	
propanal	acetaldehyde	69	48
	ethanol	10	
	ethylene	8	
acetone			<1

[a] Conditions: reaction temperature, 230 °C; carrier flow, 5 mL/min; substrate flow, 0.2 mL/h. [b] Percentage of stated product among all products. [c] Other products include small amounts of ethers and esters.

Experimental Section

The CMS sample (Type AX 21) is purchased from Anderson Development Co. The carbon is made by a direct chemical activation route in which petroleum coke is reacted with excess KOH at 500 °C to produce an intermediate product that is subsequently pyrolyzed at 900 °C to produce activated carbon-containing potassium salts. These salts are removed by successive water washings. More detail on the preparation of this material and extensive characterization studies are reported elsewhere.[24] The surface area of the final product measured by the Brunauer-Emmett-Teller (BET) method is consistently in the range of 3000-3300 m^2/g. This value underscores the extraordinary nature of CMS materials. The theoretical maximum for surface area based on a

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(2) The name carbon molecular sieve is broadly applied to a wide range of carbon-based adsorbants, which vary greatly in their molecular sieving ability. As one reviewer pointed out, these materials are perhaps better described as ultramicroporous carbons to distinguish them from crystalline inorganic molecular sieves such as zeolites.

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Table II. Methanol Reactivity over Molybdenum-Doped Catalysts[a]

sample	major product	conversion (%)	selectivity (%)
SiO_2		0	
CMS	dimethoxymethane	10.0	98.0
MoO_3[b]	methyl formate	22.8	98.0
MoO_3/SiO_2	methyl formate	12.2	98.4
MoO_3/CMS	methyl formate	70.0	96.4
$(NH_4)_2MoO_7$/CMS	methyl formate	70.0	96.0
Na_2MoO_4/CMS	dimethoxymethane	3.0	82.0
MoO_3/CMS(N_2)[c]	dimethoxymethane	2.2	90.9
MoO_3/CMS (350)[d]	formaldehyde	90	<60
CMS/MoO_3[e]	dimethoxymethane	23.5	43.0
	methyl formate		57.0

[a] Conditions: reaction temperature, 230 °C; air feed, 5 mL/min; substrate feed, 0.2 mL/h; reaction time, 10 h. [b] 0.5 g of bulk MoO_3 used for this experiment. [c] Product formation ceases after 3 h. [d] Reaction temperature is 350 °C for this experiment. Conversion and selectivity numbers are not as exact because not all products are calibrated. [e] 0.5 g of CMS placed on top of 0.10 of MoO_3 in the reactor tube.

monolayer of carbon, including the area on both sides of the plane, is 2620 m^2/g.[25] Exposure of both sides of every carbon atom is an impossibility for a solid with any physical integrity. Thus, these compounds are on the thresholds of sensitivity for surface area measurement techniques and are among the most porous materials ever synthesized.

Since the material is supplied as a dust-free moist powder, it is dried in vacuo at 100 °C prior to use. Complete elemental analysis is performed on the dry sample, and the material is found to contain 6.18% oxygen. Of the other non-carbon constituents, N, S, and H total less then 1% and K, present as ash, is measured at 1.8%. The various Mo-doped catalysts (15% by weight molybdenum trioxide, ammonium dimolybdate, and sodium molybdate) are prepared by refluxing the appropriate mixtures of Mo species and CMS in water for 6 h. The heating and mixing provide an excellent dispersion of the metal species as shown in scanning electron microscopy (SEM) studies. The H_2O is removed by rotary evaporation, and the sample is dried in vacuo at 100 °C. For the molybdenum trioxide system, 0.45 g of MoO_3 and 2.55 g of CMS are used. Since ammonium dimolybdate is essentially an 85% assay of MoO_3, 0.53 g of the dopant is used in order to keep the molar quantities of Mo the same (3.13×10^{-3} mol). Analogously, 0.64 g of Na_2MoO_4 is employed for the final system.

Typically, 0.5 g of catalyst was used for each catalytic run. The reactor is a fixed-bed flow reactor. The substrate is delivered via a syringe pump at a constant rate of 0.2 mL/h. All substrates are dried over 4A molecular sieves prior to use. Carrier flow rate (either air of N_2) is 5 mL/min. Catalyst bed height is 1 in. A 5-in. bed of glass beads is added above the catalyst to allow complete vaporization and mixing of substrates before contact with the catalyst.

Products are analyzed via gas chromatography with a Varian 940 GC fitted with a Hayesep Q column and a flame-ionization detector (FID). Samples are taken both in the gas phase at the exit of the reactor oven and from the liquid phase after the effluent is condensed in a cold trap. The data reported in Tables I and II are from gas-phase samples. Since FID instruments do not have appreciable sensitivity for formaldehyde, the sulfite titration method[26] was employed to quantify this product. Additional product analysis for trace quantities of CO and CO_2 is performed on a Hewlett-Packard 5700A GC with a Hayesep DB column and a thermal conductivity detector. Further product identification was afforded through the use of GCIR and GCMS techniques. The former is accomplished by a Hewlett-Packard 5890A GC with a DB 130 column in conjunction with a Nicolet 5DXB FTIR. The latter technique was performed on a Varian 3400 GC attached to a Finnigan 700 ion-trap mass spectrometer.

Scanning electron microscopy is performed with a JEOL JSM 35C electron microscope with an acceleration voltage of 25 kV. Samples are initially examined at 300× in order to ensure the regions to be studied at higher magnification are representative of the whole. Micrographs are taken at 6000× and 40 000×.

Results and Discussion

Undoped CMS Catalysts. Our initial experiments involve studying the reactivity of CMS as oxidants for ethanol. When the alcohol vapor is passed over the catalyst in a N_2 flow at 230 °C, small amounts of products are initially formed, with the major one being ethylene. This reactivity ceases within a couple of hours; however, the system regains activity, essentially immediately, when the carrier flow is switched to air. The CMS system is very active toward this substrate—in an air flow, 70% of the ethanol is converted in a single pass. The major products are acetaldehyde and ethyl acetate (57% and 36% of all products, respectively). When the gas flow is again returned to N_2, oxidation slows almost immediately and within 2 h no appreciable amounts of products are observed. These carrier gas cycling experiments reveal that the active sites are reduced by alcohol and regenerated by air to effect a catalytic cycle. In order to further investigate the nature of the active sites in the CMS catalyst, a series of C_3 substrates were studied. The results for the oxidation of 1-propanol, 2-propanol, propanal, and acetone are shown in Table I. It is evident that the alcohols were quite susceptible to both dehydration and dehydrogenation. The aldehyde substrate was equally reactive; however, the products are significantly different—they are all C_2 species. Acetone is virtually unreactive as a substrate. Analogous to the ethanol system, the reactivity for the C_3 substrates is dependent on the nature of the carrier flow. When N_2 is used in place of air, product formation ceases.

Several important implications about the mechanism of oxidation by CMS catalysts can be drawn from these results. In typical alcohol dehydrogenation and dehydration schemes over inorganic oxides, the mechanism usually invoked is acid catalysis in which the catalyst either abstracts a hydride via a Lewis site or protonates the alcohol OH via a Bronsted site to generate a carbocation or a protonated alcohol.[27,28] The route to products is then straightforward: Loss of a proton from the former moiety generates the aldehyde and loss of water and a proton from the latter species generates the alkene. For either mechanism, the first step involves coordination of the substrate via the oxygen.[29-32] Though carbonaceous species are not commonly thought of as being strongly acidic, both hydride and hydrogen atom abstraction processes are proposed for pyrolyzed poly(acrylonitrile) catalysts, depending on the nature of the substrate.[33,34] For the alcohol substrates over the CMS materials, the products formed indicate a mechanistic route that involves typical Lewis acid catalysis via a carbocation species. For ethanol, this leads directly to the acetaldehyde product. The other major product observed (ethyl acetate) is the result of a secondary condensation reaction with another ethanol molecule or surface fragment. The products observed with the propanol substrates are similarly formed. Dehydration to form propylene and dehydrogenation to the respective carbonyl compounds are the usual products of acid-catalyzed reactions of C_3 alcohols.[35,36]

It is of interest to note that, in the 1-propanol system, there are small amounts (<2%) of acetaldehyde and ethylene. These can be explained as the result of secondary reactions of the propanal primary product (vida infra).

When propanal is used as the substrate, all of the products are C_2. In this case, a hydrogen atom abstraction mechanism is better suited to account for these observations. Abstraction of the aldehydic hydrogen atom gives rise to an $RCO^{\bullet}$ species.[36a] This $RCO^{\bullet}$ species can then decarbonylate to produce the C_2 fragment ($R^{\bullet}$), which further reacts to form the observed products. Thus, the results indicate that the nature of the substrate determines whether hydride or hydrogen atom abstraction prevails. Hydrogen atom abstraction is relatively easy for an aldehydic species such as propanal, whereas hydride abstraction is more facile on alcohol

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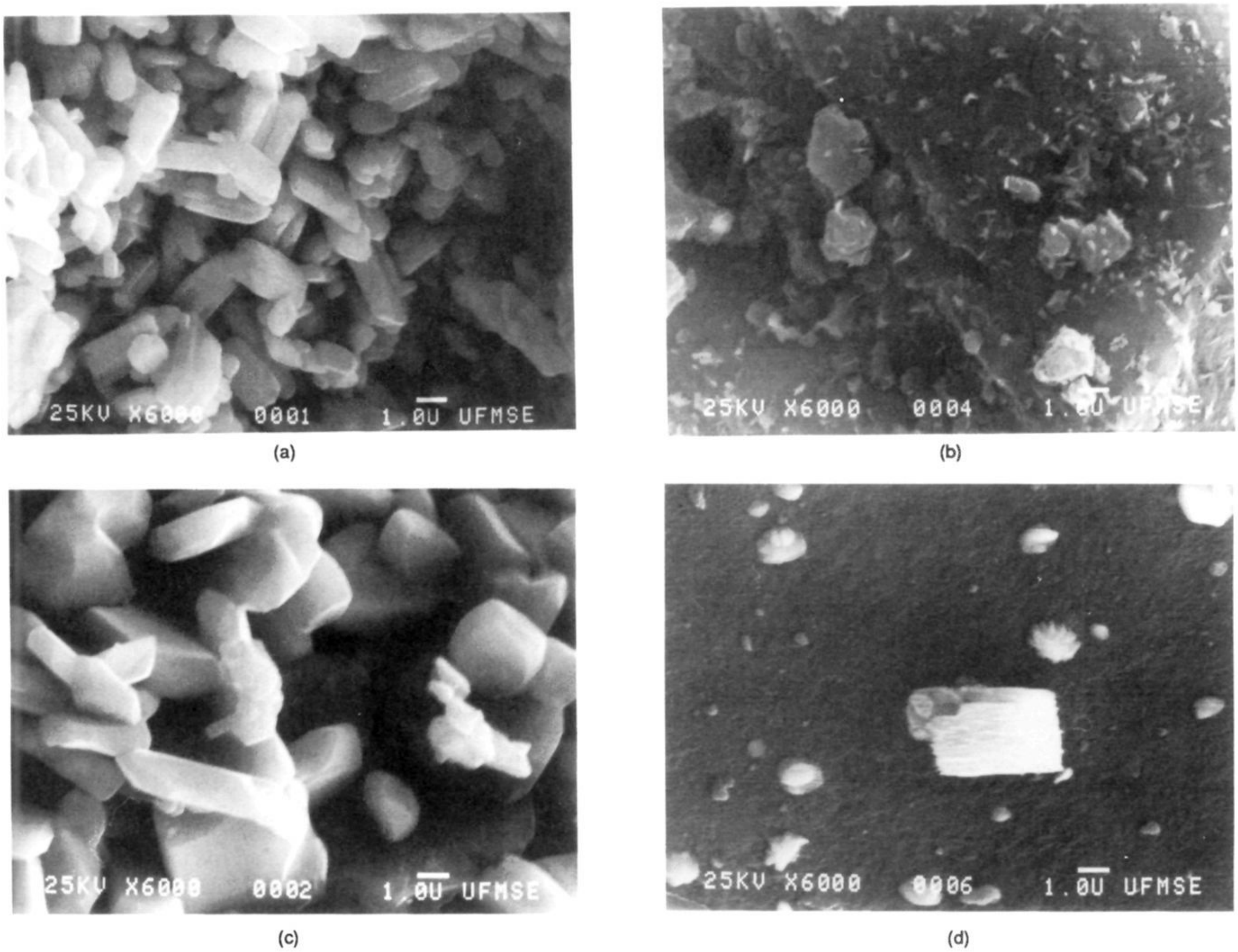

Figure 1. SEM micrographs (6000×): (a) bulk MoO_3 before reaction, (b) bulk MoO_3 after reaction, (c) MoO_3/CMS after reaction, and (d) MoO_3/SiO_2 after reaction.

substrates. In the case of acetone, neither hydride nor hydrogen atom abstraction occurs readily. This substrate is expected to be unreactive, and the results concur. Virtually no products are formed.

In light of the significant activity of the CMS catalyst toward alcohols, methanol was investigated as a substrate. It is a much more difficult substrate to transform than the higher alcohols studied above. Typical systems for the oxidative dehydrogenation of methanol to formaldehyde involve reaction temperatures of 600–800 °C over iron molybdate or bulk silver catalysts.[37-40] Systems have been reported that can transform methanol to methyl formate at lower temperatures (160–250 °C).[41-46] Under the conditions of the previous studies, the CMS system was active for methanol oxidation, forming dimethoxymethane selectively—10.0% conversion with virtually 100% selectivity. This product, which is often observed in mixed-oxide-catalyzed systems when operating at low conversions,[47] is the full acetal of formaldehyde formed via secondary reactions of two methanol molecules with one formaldehyde. Since dimethoxymethane is readily hydrated back to formaldehyde and 2 equiv of methanol, studies were done with cofeeds of methanol and water to prevent the secondary reactions and thus generate formaldehyde directly. The addition of any significant amount of H_2O (>10%) in the feed, however, greatly decreases the overall conversion. The hydrophilic nature of the CMS evidently enables H_2O to compete more efficiently for adsorption sites and thus inhibits methanol oxidation.

Doped CMS Catalysts. The fact that any activity is observed toward methanol with a nonmetalated catalyst is very interesting and of particular interest to our objective, for it provides a substrate that is difficult to oxidize and leads to different products, depending on conditions. Thus, it can be used as an indicator of reactivity and synergism in doped catalysts. The CMS catalyst was doped with various molybdenum species because molybdenum oxide moieties are active catalysts for methanol oxidation.[48-50] For an initial activity test, the MoO_3/CMS catalyst was first studied with ethanol as substrate. It is extremely active for dehydrogenation. Essentially 100% of the ethanol substrate is converted in a single pass at 230 °C with more than 85% selectivity to acetaldehyde.

The results for methanol oxidation are shown in Table II. It is evident that the 15% MoO_3/CMS catalyst is far more active than either a similarly prepared MoO_3/SiO_2 catalyst or a bulk MoO_3 sample. It is further observed that, among molybdenum-

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doped CMS systems, the Lewis acid species MoO_3 is necessary for any significant activity. Ammonium dimolybdate (nominally $(NH_4)_2MoO_4$) evolves ammonia and water on heating and is an 85% assay of MoO_3 (the doping level is altered accordingly so that the weight percentage of MoO_3 is the same for both systems). This system is shown to have reactivity identical with that of the MoO_3/CMS catalyst. Na_2MoO_4, on the other hand, is a chemically different molybdenum species in which the Lewis acidity of MoO_3 has been neutralized by coordination of oxide. Enhancement in activity is not observed with this dopant.

The major product formed in the molybdenum-doped CMS systems is methyl formate, which is produced by dimerization of formaldehyde units in the so-called Tischenko reaction. The activity of the MoO_3/CMS system is significantly greater than those recently reported.[32-35] In order to probe the possible synergistic effect between MoO_3 and CMS, both of which are active on their own, several experiments are done with both species present but not intimately mixed and with the bed height held constant. In the first system, 0.5 g of CMS is layered on top of (0.10 g) MoO_3 in the reactor tube (this is labeled as CMS/MoO_3 in Table II) and the experiment is run as usual by feeding substrate from the top of the reactor. Only 23.5% conversion results, with a large amount being dimethoxymethane. In the second system, the MoO_3 is on top and CMS's are on bottom. The same products result, and the conversion rate is about 8%. Experimental difficulties associated with evenly layering the MoO_3 in the second experiment could account for the difference in the conversion of these layering experiments. The layering experiments clearly show that the MoO_3/CMS catalyst, which has the constituents intimately mixed, is best able to utilize the advantages of the respective components.

Further characterization of the CMS materials as a support is done via SEM of the MoO_3-doped materials. Figure 1 shows the micrographs (at 6000×) of bulk MoO_3 before (a) and after (b) catalysis, MoO_3/CMS after catalysis (c), and MoO_3/SiO_2 after a catalytic reaction (d). The bulk MoO_3 and MoO_3/SiO_2 samples illustrate the sintering that occurs during the course of reaction. It is apparent that the CMS support inhibits crystallite growth. Inhibition of sintering is clearly one of the reasons for the much superior activity of the CMS-based catalyst. Dispersion of MoO_3 is particularly important in the conversion of methanol to methyl formate. A recent study concluded that the degree of metal dispersity was the key parameter to high selectivity for methyl formate over the other possible oxidation products.[51]

Our next concern in characterizing CMS supports is their oxidative stability. At the reaction temperature employed for the studies in Table II (230 °C), methyl formate is the expected product. Since MoO_3 is also a catalyst for formaldehyde formation (at higher reaction temperatures), experiments were done at 275, 300, 330, and 360 °C with the MoO_3/CMS catalyst. As temperature increases, methanol conversion increases; however, selectivity decreases sharply. At temperatures above 300 °C, the major product is formaldehyde. By 360 °C, virtually 100% of the methanol is converted but the selectivity to formaldehyde is less than 60%. Among the numerous other products observed are several hydrocarbons (ethane and propane being present in the greatest quantity), which are apparently formed in part from degradation of the CMS itself. We observe a 50% weight loss of the catalyst after a 20-h experimental run at this high reaction temperature.

The breakdown of the carbonaceous material is not too surprising considering the conditions of this reaction. High temperature, an oxidizing atmosphere, and the addition of MoO_3, a good oxidizing agent, make degradation processes probable occurrences. Several points should nonetheless be noted. Measurable catalyst weight loss is not observed with the same MoO_3/CMS system for methanol oxidation at 230 °C. The pre- and post-reaction weights are virtually identical after 48-h runs. Furthermore, CMS systems without MoO_3 doping can tolerate high reaction temperatures. In the CMS-catalyzed conversions of ethyl benzene to styrene,[18] no significant loss in weight (or activity) is observed after 120 h of continuous operation at a reaction temperature of 350 °C.

Our finding of hydrocarbon products that arise in part from the breakdown of the CMS support under high reaction temperature has significant implications for several heterogeneous catalyzed reactions. Although this is obviously counterproductive, for a catalytic oxidation it is somewhat novel that the support material would react with adsorbed methanol fragments to make new products. When the system is run at these high temperatures (i.e., >350 °C) with a H_2O feed (i.e., in the absence of methanol as a substrate), no hydrocarbons are formed. The degradation product is simply CO_2. Thus, the CMS fragments actually form new bonds with the surface methanol moieties. Similar processes may be involved with carbonaceous deposits formed on the surface of heterogeneous catalysts in the conversion of methanol to gasoline with ZSM-5 and in heterogeneous CO reduction systems for Fischer–Tropsch processes.

Conclusions

Ultrahigh surface area CMS materials have been shown to possess novel reactivity capable of hydride and hydrogen atom abstractions in the oxidative dehydrogenation and dehydration of a variety of substrates. These materials have also been shown to be excellent supports for metal dopants. The dopant/support catalytic system is a synergistic one, which exhibits an activity greater than the sum of those of the constituents. The highly reactive nature of these materials, together with their excellent dispersion and adsorption properties, is shown to make them quite attractive supports for catalytic applications. Novel reactivity of the support with an intermediate generated from methanol oxidation has implications for both Fischer–Tropsch and methanol to gasoline reaction mechanisms.

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Registry No. C, 7440-44-0; EtOH, 64-17-5; PrOH, 71-23-8; *i*-PrOH, 67-63-0; H_3CCH_2CHO, 123-38-6; MeOH, 67-56-1; $(MeO)_2CH_2$, 109-87-5; MoO_3, 1313-27-5; $(NH_4)_2MoO_7$, 131685-38-6; Na_2MoO_4, 7631-95-0; HCO_2Me, 107-31-3.

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