Heterogeneous Catalysis

DOI: 10.1002/ange.200600830

Hydrated Dibromodioxomolybdenum(VI) Supported on Zn-MCM-48 for Facile Oxidation of Methane**

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Methane is the most abundant and low cost C_1 feedstock and is considered to be a clean substitute for dwindling petroleum resources. However, its efficient transformation to more valuable liquid products remains a great challenge.[1] The current route is a multistep and energy-intensive conversion that involves the incipient generation of syngas from methane.[2] With potentially many benefits, much effort has been directed towards the exploration of direct methods to partially oxidize and selectively functionalize one of the C–H bonds of methane, to convert it into valuable oxygenated and unsaturated compounds more efficiently, economically, and cleanly. As methane is an unreactive molecule, it reacts only under extreme conditions. Some methyl derivatives such as methanol,[3] methane sulfonic acid,[4] methane sulfonyl chlorides,[5] methyl bisulfate,[6] and acetic acid,[7] can be synthesized through the activation of methane in strong acid solvents with oxidants and radicals. Methane can also be activated over some solid catalysts with oxygen at high temperature, but selectivity towards valuable oxygenated products is poor. Catalytic methane-activation systems under mild conditions are all based on intricate metal complexes[8] and enzymes,[9] and their applications are limited to very small-scale syntheses.

Methane can be converted into oxygenates under mild conditions through a three-step catalytic recycling of the oxidation mediator by using oxygen as the ultimate oxidant: 1) oxidizing methane to methyl derivatives by an oxidation mediator; 2) converting the methyl derivatives into oxygenated compounds; 3) regenerating the oxidation mediator. We have reported a series of catalysts for the low-temperature vapor-phase conversion of methane to methanol via methyl bisulfate with supported concentrated sulfuric acid as the oxidation mediator.[10] Others have considered halogens as the oxidation mediator. Olah et al. described selective monohalogenation of methane over supported acid and platinum-metal catalysts followed by hydrolysis of methyl halides over γ-alumina-supported metal-oxide/hydroxide catalysts to convert methane into methanol and dimethyl ether.[11] Lorkovic and co-workers proposed a process for the functionalization of methane and ethane by using bromine as the mediator.[12] The process was carried out in a sequential zone-flow reactor (SZFR) that consisted of two serial reactors. In this process, the three-step conversions are actually carried out separately, and it is difficult to recycle the halogens.

Herein, we report the design and preparation of a novel multifunction methane-activation catalyst, hydrated dibromodioxomolybdenum(VI) supported on Zn-MCM-48 (a zinc-modified mesoporous silica), which integrates the three catalytic steps to transform methane into oxygenated products at a relatively low temperature ($<250\,^{\circ}C$). Bromine is derived from dibromodioxomolybdenum and can be recycled in the catalyst bed through bromine metathesis of metal bromide/metal oxide pairs. Bromine acts as the oxidation mediator and has advantages over other halogens; methane bromination is less exothermic than chlorination and proceeds spontaneously to completion. Bromine metathesis of metal bromide/metal oxide pairs can be accomplished under relatively mild conditions through the deoxidization of metal bromide with oxygen (the reduction potential of Br_2 (to Br^-) is 1.07 V versus a normal hydrogen electrode (NHE), and that of O_2 is 1.23 V).

MoO_2Br_2 is a useful precursor for the preparation of many excellent oxotransfer catalysts for chemical and biochemical processes.[13] Molybdenum in the MoO_2Br_2 core is on the borderline of stability between the V and VI oxidation states of the metal, which makes these compounds useful models for redox studies.[14] $MoO_2Br_2(H_2O)_2$ occurs in solutions of alkali molybdates, in concentrated hydrobromic acid, and it can be extracted with diethyl ether. Yellow crystals of $MoO_2Br_2(H_2O)_2\cdot 2\,(Et)_2O$, which is the precursor for the preparation of $MoO_2Br_2(H_2O)_2$ supported on Zn-MCM-48, are obtained by cooling a solution of $MoO_2Br_2(H_2O)_2$ in diethyl ether to $-5\,^{\circ}C$.[15]

The catalytic cycles for the partial oxidation of methane are initiated by the decomposition of $MoO_2Br_2(H_2O)_2$. MoO_2Br_2 reacts readily with O_2 to release Br_2, which oxidizes C–H bonds to form HBr and a C–Br bond with higher selectivity than O_2. MoO_3 then scavenges the bromine atoms from HBr and the C–Br functionality to yield the oxidized products and regenerate MoO_2Br_2. The ultimate oxidant is oxygen, and bromine acts as the oxidation mediator. Figure 1 shows the test results for the partial oxidation of methane with $MoO_2Br_2(H_2O)_2$ supported on Zn-MCM-48-*N* (where *N* is the molar ratio of Si/Zn). The time-on-stream data (Figure 1a) show that zinc content has a great influence on the stability of the catalyst. Moreover, the zinc content provides control over the product distribution (Figure 1b). The presence of ZnO in the support induces the formation of dimethyl ether, which indicates that the product of the catalytic cycle involving $ZnBr_2$/ZnO pairs is different from that of MoO_2Br_2/MoO_3 pairs. The former affords predominantly dimethyl ether and the latter proceeds to yield methanol. With increasing zinc content the propensity towards deactivation is reduced gradually and the selectivity

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[**] This work supported by Sopu Chemical Co. China.

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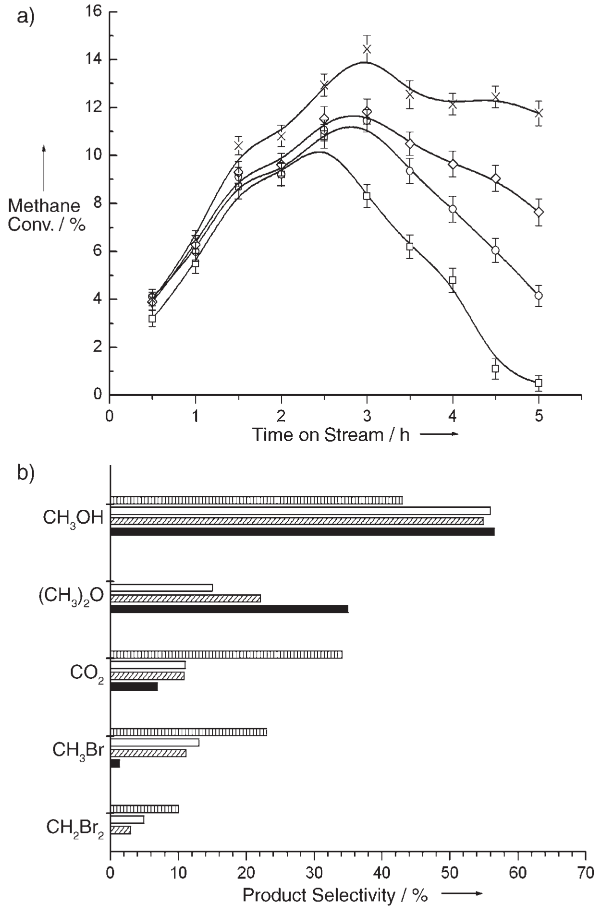

Figure 1. a) Time-on-stream data from catalytic-activity tests on $MoO_2Br_2(H_2O)_2$/MCM-48 (□), $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-60 (○), $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-40 (◇), and $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-20 (×). The data are one-pass methane conversions, with error bars indicated. b) Product distribution after 2.5 h on the reaction stream for $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-20 (black), $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-40 (diagonal stripes), $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-60 (white), and $MoO_2Br_2(H_2O)_2$/MCM-48 (vertical stripes).

towards the halocarbon species (CH_3Br and CH_2Br_2) dwindles. Bromine may leach from the catalyst column in the form of unconverted halocarbon species and bromine fumes, and this leaching is the main reason for the reduction in activity. Facile bromine metathesis of MoO_2Br_2/MoO_3 pairs increases the possibility of bromine leaching. The involvement of ZnO in the bromine metathesis of metal-bromide/metal-oxide pairs (Scheme 1) increases the chances of bromine being scavenged from HBr and the C–Br bond to yield the oxidized products. The moderate rate of bromine metathesis of the $ZnBr_2$/ZnO pair is an important factor for holding bromine in the catalyst column, and the promoting effects of $ZnBr_2$ on C–H bond bromination may also reduce the leaching of unconverted bromine.[16]

To obtain direct information about the role of bromine as mediator in the catalytic cycle, we have compared the catalytic conversion of methane by MoO_3 supported on Zn-MCM-48-20 and by MCM-48 before and after the introduction of bromine to the catalytic systems. Figure 2a shows that the catalytic systems have negligible methane conversion with the feed gas comprising methane, oxygen, and argon (Stage 1). After 2 h on the reaction stream, bromine is injected into the feed gas, which results in a sharp increase in methane conversion (Stage 2). This rise in activity clearly demonstrates the mediator role of bromine in the catalytic

$$CH_4 + Br_2 \xrightarrow{ZnBr_2} CH_3Br + HBr \quad (1)$$
$$CH_3Br + HBr + ZnO \longrightarrow ZnBr_2 + CH_3OH \quad (2)$$
$$2\,CH_3Br + 2\,HBr + 2\,ZnO \longrightarrow 2\,ZnBr_2 + CH_3OCH_3 + H_2O \quad (3)$$
$$ZnBr_2 + 1/2\,O_2 \longrightarrow Br_2 + ZnO \quad (4)$$

$$CH_4 + 1/2\,O_2 \longrightarrow CH_3OH$$

or

$$2\,CH_4 + O_2 \longrightarrow CH_3OCH_3 + H_2O$$

Scheme 1. Proposed mechanism for the role of the zinc species in the catalytic cycle.

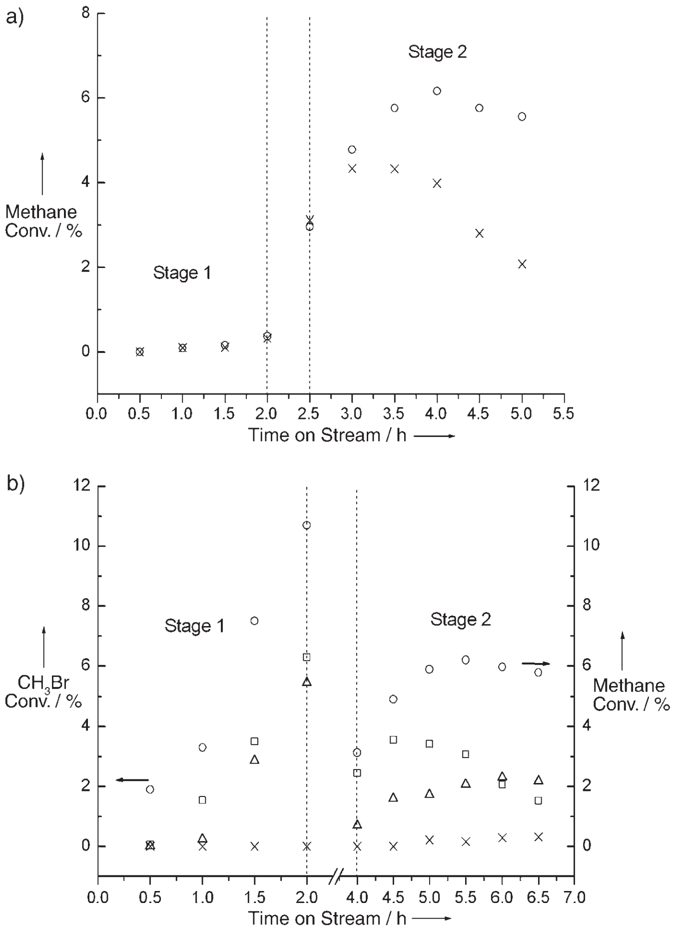

Figure 2. a) Time-on-stream data for MoO_3/Zn-MCM-48-20 (○) and MoO_3/MCM-48 (×), demonstrating the mediator role of bromine in the catalytic cycle. Stage 1: $CH_4/O_2/Ar$ (2:1:7) feed gas; Stage 2: after injection of bromine to the feed gas at 2 h. b) Control experiments on MoO_3/Zn-MCM-48-20 (○), MoO_3/MCM-48 (□), Zn-MCM-48-20 (△), and MCM-48 (×) to determine the bromine-metathesis activity of the catalyst components. Stage 1: $CH_3Br/HBr/Ar$ (1:1:8) feed gas; Stage 2: $CH_4/O_2/Ar$ (2:1:7) feed gas. After 2.0 h, the catalyst was gradually cooled in an argon flow.

cycle. In Figure 2b, we present data from a control experiment to determine the performance of bromine scavenging from HBr and C−Br bonds by four solid catalysts with different compositions. During Stage 1, the feed gas for the reactor consists of CH_3Br, HBr, and argon. MCM-48 shows no activity for bromine metathesis. MoO_3 supported on Zn-MCM-48 yields some CH_3Br. At 2 h on the reaction stream, the reactor is cooled under an argon flow, and the feed gas is changed to a mixture of methane, oxygen, and argon. Methane conversion is detected for the three samples that show activity for bromine metathesis during Stage 1. The MoO_2Br_2/MoO_3 pairs show high bromine-metathesis activity and the $ZnBr_2/ZnO$ pairs have a high rate of bromine scavenging, but a lower rate of re-oxidation of $ZnBr_2$ to release bromine, which is the main mechanism for holding bromine in the catalytic systems, thus improving catalytic stability.

Based on the above experimental observation, we conclude that the catalytic cycle involves reversible bromine metathesis of two types of metal-bromide/metal-oxide pairs: MoO_2Br_2/MoO_3 pairs and $ZnBr_2/ZnO$ pairs, which show different bromine-metathesis activity. An X-ray photoelectron spectroscopy (XPS) spectrum of $MoO_2Br_2(H_2O)_2$ on Zn-MCM-48-20 was taken after 3 h on a stream of methane, oxygen, and argon (Figure 3a); fitting the Mo 3d envelope identifies two chemical states of molybdenum, in MoO_3 ($3d_{5/2}$ 232.28 eV) and the MoO_2Br_2 core ($3d_{5/2}$ 233.65 eV). The full width at half maximum (FWHM) ratio of MoO_3/MoO_2Br_2 is 1.1:1 and the peak-area ratio is 0.876:1, which evidences MoO_2Br_2/MoO_3 pairs in the catalytic cycle. Fitting of Mo 3d envelope of the XPS spectrum of MoO_3/Zn-MCM-48-20 taken after 2 h on a stream of CH_3Br, HBr, and argon under the given reaction conditions (Figure 3b) also demonstrates the presence of two chemical states of molybdenum, in MoO_3 ($3d_{5/2}$ 232.5 eV) and the MoO_2Br_2 core ($3d_{5/2}$ 233.3 eV). The FWHM ratio of MoO_3/MoO_2Br_2 is 1.13:1 and the peak area ratio is 3.01:1. These results confirm that the key step in bromine metathesis of the MoO_2Br_2/MoO_3 pair is the scavenging of bromine from HBr and a C−Br bond to yield the oxidized products and regenerate dibromodioxomolybdenum. Figure 3c shows XPS survey spectra of Zn-MCM-48-20 and MCM-48 after 2 h on the reaction stream of CH_3Br, HBr, and argon. The presence of the Br^- peak (69.6 eV) in the spectrum of Zn-MCM-48-20 suggests that ZnO can scavenge bromine from HBr and a C−Br bond to yield the oxidized products and form $ZnBr_2$. This result confirms the involvement of $ZnBr_2/ZnO$ pairs in the bromine metathesis.

In summary, we have demonstrated that $MoO_2Br_2(H_2O)_2$ supported on Zn-MCM-48 readily converts methane into oxygenated products (methanol and dimethyl ether) with high selectivity at low reaction temperatures. The catalytic cycle proceeds by the reversible bromine metathesis of MoO_2Br_2/MoO_3 pairs and $ZnBr_2/ZnO$ pairs. Bromine acts as the oxidation mediator, and oxygen is the oxidant. However, many issues require further investigation, such as the bromine-metathesis efficiency of the metal-bromide/metal-oxide pairs and the product control provided by the catalyst components.

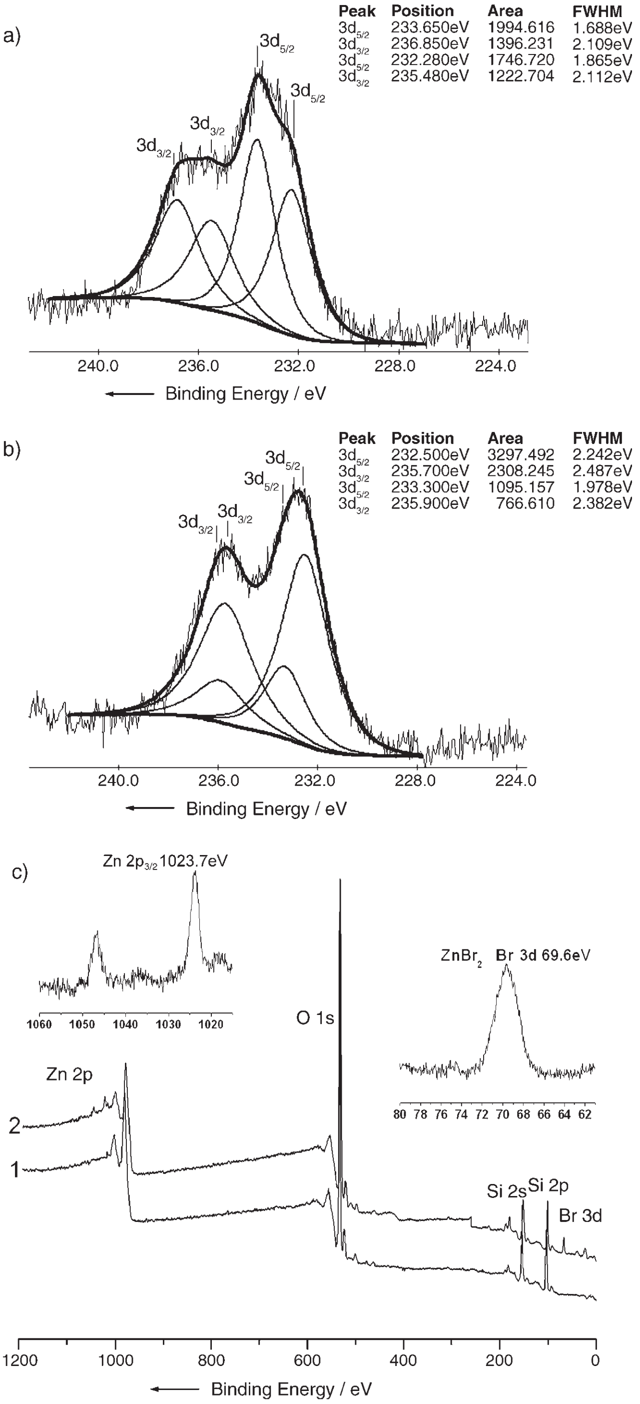

Figure 3. a) Mo 3d envelope in the XPS spectrum of $MoO_2Br_2(H_2O)_2$/Zn-MCM-48-20 after 3 h on a reaction stream of $CH_4/O_2/Ar$; peak fitting is indicated. b) Mo 3d envelope in the XPS spectrum of MoO_3/Zn-MCM-48-20 after 2 h on a reaction stream of $CH_3Br/HBr/Ar$; peak fitting is indicated. c) XPS survey spectra of MCM-48 (1) and Zn-MCM-48-20 (2) after 2 h on a reaction stream of $CH_3Br/HBr/Ar$; insets are enlargements of the Zn 2p and Br 3d envelopes.

Experimental Section

The Zn-MCM-48 materials were synthesized as follows. The required amount of silica (tetraethyl orthosilicate) and zinc precursors (zinc hydroxide) was added to a stirred solution of cetyltrimethylammonium hydroxide (CTAOH). The molar ratio of the incipient gel was $SiO_2/x\,Zn(OH)_2/0.28\,CTAOH/42\,H_2O$ (for which $x = 0.017$, 0.025, 0.05, 0.1, 0.2). After aging in a sealed autoclave at 150°C for 24 h, the resulting solid was collected by filtration, washed with a copious amount of deionized water, and then calcinated at 550°C for 6 h to yield Zn-MCM-48. Pure silica MCM-48 was prepared by using the synthesis gel with a ratio of $SiO_2/0.28\,CTAOH/42\,H_2O$.

A solution of $MoO_2Br_2(H_2O)_2$ in diethyl ether was synthesized by an established method.[15] $MoO_2Br_2(H_2O)_2$/Zn-MCM-48 catalysts were prepared by impregnating Zn-MCM-48 materials (dried at 300°C under vacuum before use) in a solution of $MoO_2Br_2(H_2O)_2$ in diethyl ether, then drying the materials at room temperature under high vacuum for several hours. The load of $MoO_2Br_2(H_2O)_2$ was 8 wt%. MoO_3/Zn-MCM-48 and MoO_3/MCM-48 were prepared by decomposing $MoO_2Br_2(H_2O)_2$/Zn-MCM-48 and $MoO_2Br_2(H_2O)_2$/MCM-48 in air at 150°C. The catalytic activity was measured in a conventional fixed-bed reactor at 220°C with a feed gas consisting of methane, oxygen, and argon (1.6 g of catalyst, $P_{total} = 1.0$ MPa, $P_{Ar}/P_{CH_4}/P_{O_2} = 7{:}2{:}1$, $W/F = 0.3\ \mathrm{g\,min\,cm^{-3}}$; P is pressure, W is the weight of catalyst, and F is the reactant flow rate). Product analysis was performed on a DB5 column (30 m × 0.25 mm) by using a VG Trio 200 spectrometer, with a thermal conductivity detector (TCD) or an MS detector. Conversion and selectivity are defined as (% conversion) = $[([CH_4]_{inlet} - [CH_4]_{outlet})/[CH_4]_{inlet}]\,100$ and (% selectivity to X) = $[[X]/([CH_4]_{inlet} - [CH_4]_{outlet})]\,100$.

The Zn-MCM-48 materials and the samples loaded with $MoO_2Br_2(H_2O)_2$ were characterized by powder X-ray diffraction, N_2 adsorption, and XPS. Detailed characterization data are presented in the Supporting Information.

Received: March 3, 2006
Revised: July 6, 2006

Keywords: heterogeneous catalysis · mesoporous materials · metathesis · molybdenum · oxidation

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