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Research Note

Dissociative adsorption of HCOOH, CH_3OH, and CH_2O on MCM-41

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Abstract

Adsorption and surface reactions of HCOOH, CH_3OH, and CH_2O on siliceous mesoporous MCM-41 have been investigated by Fourier-transform infrared spectroscopy. CH_2O decomposes on the surface to form adsorbed CH_3O and HCOO (an analog of Cannizzaro disproportionation) which are identified by dissociative adsorption of CH_3OH and HCOOH. In addition, CH_3OH is sequentially oxidized to CH_2O and HCOO on MCM-41. These types of reactions for CH_2O and CH_3OH on MCM-41 have not been observed on amorphous SiO_2 without a mesoporous structure.

Keywords: HCOOH; CH_3OH; CH_2O; Adsorption; MCM-41

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1. Introduction

Fully hydroxylated SiO_2 surfaces are generally catalytically inert [1,2]. SiO_2 surface activities can been enhanced by chemical modifications or thermal treatment. In the former case, surface active sites are created by incorporating heteroatoms [3,4] or surface functional groups [5–8]. Thermal treatment for SiO_2 activation results from loss of silanol groups which may exist in isolated, geminal, or hydrogen-bonded forms [9]. The active sites generated thermally are capable of dissociative chemisorption reactions of CH_3OH and C_2H_5OH forming the alkoxides [10,11], hydrogen–deuterium exchange [12], dehydrogenation of n-heptane into heptene and heptadienes and dehydrocyclization into toluene [13], and ammoximation of ketones to oximes [14], etc. In addition, mesoporous siliceous FSM-16 catalyzes α-pinene isomerization and methylamine synthesis after thermal activation [15].

Here, we examine the dissociative chemisorption of CH_3OH, CH_2O, and HCOOH on mesoporous siliceous MCM-41 by Fourier-transform infrared spectroscopy. It is found that CH_3OH and HCOOH are dissociatively adsorbed to form CH_3O and HCOO on the surface at 35 °C, respectively. Most interestingly, as CH_2O is adsorbed on the surface at 35 °C, both CH_3O and HCOO are generated. This is an analog of the Cannizzaro reaction in which aldehydes containing no α-hydrogens undergo self-oxidation and reduction to yield a mixture of an alcohol and a carboxylate in strong, basic solutions [16].

2. Experimental

MCM-41 used in the present study was prepared using a procedure as described previously [17], with an average particle size of ∼ 70 nm, a pore size of 2.23 nm, a pore volume of 2.01 $cm^3\,g^{-1}$, and a surface area of 1216 $m^2\,g^{-1}$. The MCM-41 powder was dispersed in deionized water (18.3 MΩ cm) and then sprayed onto a tungsten fine mesh (∼ 6 cm^2) held in a pair of stainless steal clamps which were attached to the power leads of a power/thermocouple feedthrough [18]. After that, the SiO_2/W sample was mounted inside an IR cell [19], with two CaF_2 windows for IR transmission, which was connected to a gas manifold and pumped by a 60 $L\,s^{-1}$ turbomolecular pump with a base pressure of $\sim 1 \times 10^{-7}$ Torr. The SiO_2/W sample in the cell was heated to 500 °C un-

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der vacuum for 24 h resistively by passing electric current through the tungsten mesh. The temperature of SiO_2/W sample was measured by a K-type thermocouple spot-welded on the tungsten mesh. Before each run of the experiment, the SiO_2/W sample was heated to 350 °C for 20 min in 3 Torr O_2 and then heated to 500 °C in a vacuum for 2 h. After the heating treatment, 10 Torr of O_2 was introduced into the cell as the sample was cooled to 70 °C. When the SiO_2 temperature reached 35 °C, the cell was evacuated for gas dosing. O_2 (99.998%, Matheson) was used as received in compressed states. CH_3OH (99.8%, Merck), CH_2O (37% aqueous solution, J.T. Baker), and HCOOH ($>$ 98%, Merck) were purified by several cycles of freeze–pump–thaw. CH_2O was introduced to the cell as the solution was cooled to $\sim$ 3 °C to reduce the solubility of CH_2O in water and the evaporation of water molecules. Pressure was monitored with a Baratron capacitance manometer and an ion gauge. Infrared spectra were obtained with a 4 cm^{-1} resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO_2-free dry air. The spectra presented here have been ratioed against a clean SiO_2 spectrum providing the oxide background.

3. Results and discussion

We present the infrared spectroscopic results of dissociative adsorption on MCM-41 in the order of HCOOH, CH_3OH, and CH_2O. Fig. 1 shows the infrared spectra of a MCM-41 surface after being in contact with $\sim$ 0.5 Torr of HCOOH at 35 °C, followed by evacuation at the indicated temperatures for 1 min. In the 35 °C spectrum, the infrared bands appear at 1362, 1375, 1609, 1721, 2721, 2821, and 2947 cm^{-1}. The 1721 cm^{-1} is assigned to carbonyl (C=O) stretching vibration, revealing the presence of molecularly adsorbed HCOOH. This C=O stretching frequency is 19 cm^{-1} lower than that of HCOOH in the gas phase [20] and is ascribed to the interaction between surface acidic sites with the lone-pair electrons on the carbonyl oxygen atom or with the π-bond electrons. The surface formic acid molecules are completely removed after heating the surface to 300 °C in a vacuum, as indicated by the disappearance of the 1721 cm^{-1} band in the 300 °C spectrum, presumably due to desorption and/or dissociation. The other bands at 1362, 1375, 1609, 2721, 2821, and 2947 cm^{-1} are still barely observable in the 400 °C spectrum, although their intensities decrease simultaneously after heating the surface higher than 150 °C. These bands are attributed to formate species (HCOO) adsorbed on the MCM-41 surface, based on the similar absorptions of HCOO on various metal-oxide surfaces as shown in Table 1. Furthermore, because the difference between the antisymmetric and symmetric –COO– stretching vibrations of HCOO on MCM-41 is 236 cm^{-1} which is larger than that of ionic HCOO ($\sim$ 200 cm^{-1}), it suggests that HCOO is adsorbed on MCM-41 with a unidentate or bridging configuration [23].

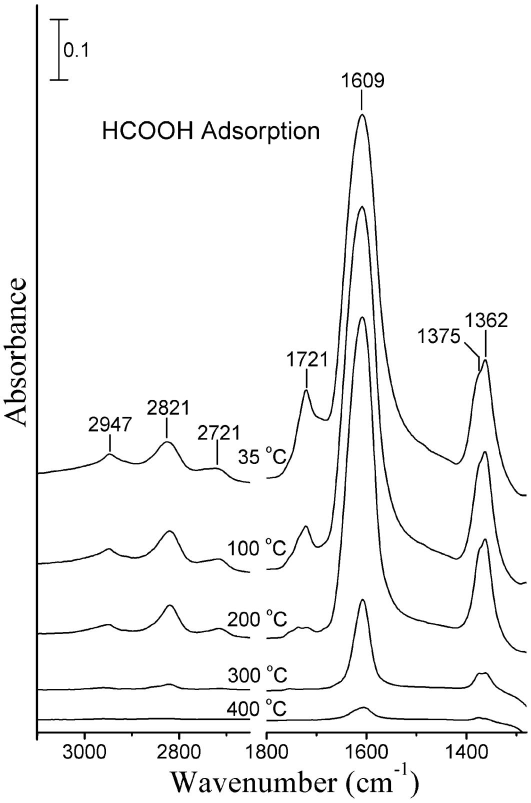


Fig. 1. Infrared spectra of a MCM-41 surface exposed to $\sim$ 0.5 Torr HCOOH and then evacuated at the indicated temperatures for 1 min. All the spectra were recorded with 50 scans at 35 °C.

Fig. 2 shows the infrared spectra of a MCM-41 surface after being in contact with $\sim$ 0.9 Torr of CH_3OH at 35 °C, followed by evacuation at the indicated temperatures for 1 min. In the 35 °C spectrum, the infrared bands appear at 1388, 1453, 1466, 1609, 1716, 2836, 2856, 2922, 2959, and 2994 cm^{-1}. The 1716 cm^{-1} band attributed to the carbonyl stretching mode shows that oxidation of methanol occurs upon its adsorption. The result of CH_2O adsorption on MCM-41, shown later, reveals that CH_3OH is oxidized to form CH_2O on the surface. On the other hand, the bands at 1388 and 1609 cm^{-1} agree with $HCOO_{(a)}$ absorptions, as demonstrated in Fig. 1. The 1609 cm^{-1} band grows at the expense of the 1716 cm^{-1} band after heating the surface to 100 °C, suggesting the transformation of $CH_2O_{(a)}$ into $HCOO_{(a)}$. This sequential oxidation process of $CH_3OH \rightarrow CH_2O \rightarrow HCOO$ on MCM-41 is distinct from CH_3OH adsorption on other SiO_2 without a mesoporous structure [10,24]. For example, CH_3OH is dissociatively adsorbed to form CH_3O on nonmesoporous SiO_2 (Degussa, Aerosil) at room temperature [10]. In Fig. 2, the adsorbed HCOO does not exist on the surface after raising the temperature to 400 °C, as indicated by the disappearance of the 1609 cm^{-1} band. In the 400 °C spectrum, the infrared bands are located at 1387, 1465, 1487, 2859, 2932, 2960, and 2999 cm^{-1} which are similar to the previously observed infrared frequencies from CH_3OH dissociative adsorption on nonmesoporous SiO_2 [10,24], as shown in Table 2. There-

Table 1
Comparison of the infrared frequencies (cm^{-1}) of HCOO on various oxide surfaces

Al_2O_3 [a]	ThO_2 [a]	ZrO_2 [a]	TiO_2 [a]	TiO_2 [b]	MgO [a]	Fe_2O_3 [a]	SiO_2 [c] (MCM-41)	Mode
2970	2950	2965	2970	2977	2930	2960		$\nu_a(CO_2) + \delta(CH)$
			2950	2952			2947	
2905	2850	2865	2885	2872	2860	2880	2821	$\nu(CH)$
			2880		2810			
2750	2740	2755	2730	2754	2770		2721	$\nu_s(CO_2) + \delta(CH)$
		2740			2735			
1595	1580	1570	1575	1552	1630	1565	1609	$\nu_a(CO_2)$
	1565		1560		1605			
1395	1375	1390	1390	1413	1395			$\delta(CH)$
			1380	1386	1383	1378		
1380	1365	1375	1372	1370	1370	1350	1375	$\nu_s(CO_2)$
			1360	1359	1340		1362	

δ, deformation; ν_s, symmetric stretching; ν_a, antisymmetric stretching.

[a] Ref. [21].

[b] Ref. [22].

[c] This work.

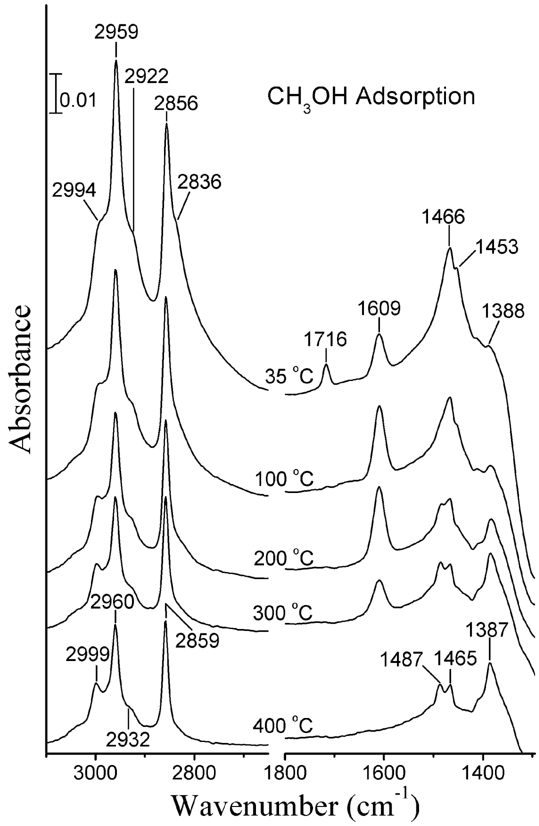


Fig. 2. Infrared spectra of a MCM-41 surface exposed to ~ 0.9 Torr CH_3OH and then evacuated at the indicated temperatures for 1 min. All the spectra were recorded with 50 scans at 35 °C.

Table 2
Comparison of the infrared frequencies (cm^{-1}) of CH_3O on nonmesoporous SiO_2 and on MCM-41

Nonmesoporous SiO_2		MCM-41	Assignment
Ref. [10]	Ref. [24]	(this work)	(Ref. [25])
3001		2999	$\nu_a(CH_3)$
2961	2956	2960	
2937		2932	$2\delta(CH_3)$
2859	2852	2859	$\nu_s(CH_3)$
2838			
1481	1470	1487	
1466	1452	1465	$\delta(CH_3)$
	1390	1387	

δ, deformation; ν_s, symmetric stretching; ν_a, antisymmetric stretching.

fore these bands are attributed to CH_3O on MCM-41. It is concluded that CH_3OH decomposes to form CH_3O, CH_2O, and HCOO on MCM-41 at 35 °C.

Fig. 3 shows the infrared spectra of a MCM-41 surface after being in contact with ~ 1 Torr CH_2O at 35 °C, followed by evacuation at the indicated temperatures for 1 min. In the 35 °C spectrum, the infrared bands appear at 1376, 1406, 1455, 1610, 1718, 2820, 2839, 2854, 2919, 2952, and 3002 cm^{-1}. The carbonyl 1718 cm^{-1} band demonstrates the presence of adsorbed CH_2O which is removed from the surface after heating to 150 °C. Compared to the C=O stretching absorption at 1744 cm^{-1} for free CH_2O molecules [20], it suggests that CH_2O on MCM-41 interacts with the surface via its carbonyl group, resulting in the C=O red shift. In fact, two more infrared bands at 1501 and 1725 cm^{-1} were also observed as the MCM-41 was in contact with ~ 1 Torr CH_2O vapor, but they disappeared after evacuation. The previously reported infrared bands of CH_2O on nonmesoporous SiO_2 (Degussa, Aerosil), preheated to 873 K in a vacuum, appeared at 1501, 1717, 1725, 2732, 2830, 2894, and 2995 cm^{-1} at 180 K [21]. The bands at 1376, 1610, and 2820 cm^{-1} in the 35 °C spectrum of Fig. 3 are attributed to $HCOO_{(a)}$, as supported by the HCOOH dissociative adsorption shown in Fig. 1. Another set of bands at 1455, 2854, 2952, and 3002 cm^{-1} is consistent with $CH_3O_{(a)}$ absorptions as shown in Fig. 2. CH_2O on MCM-41 oxidizes and reduces simultaneously to form $HCOO_{(a)}$ and $CH_3O_{(a)}$ at 35 °C. This is a heterogeneous Cannizzaro-type disproportionation which has been observed on the ionic oxides of MgO, ZrO_2, ThO_2, Al_2O_3, TiO_2, and Fe_2O_3 from CH_2O adsorption, but not on SiO_2 without a mesoporous structure [21]. The first

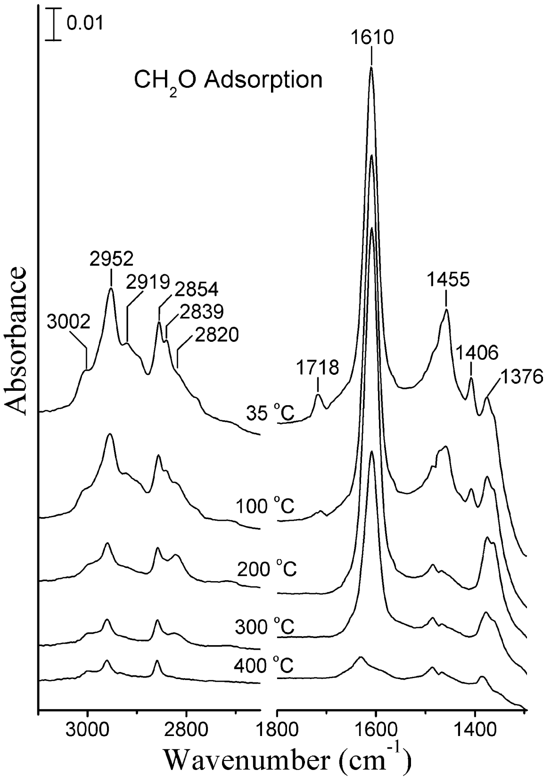


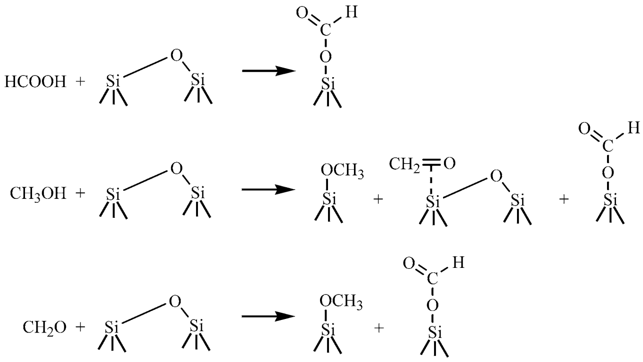
Fig. 3. Infrared spectra of a MCM-41 surface exposed to ∼ 1 Torr CH_2O and then evacuated at the indicated temperatures for 1 min. All the spectra were recorded with 50 scans at 35 °C.

three metal oxides have predominantly a basic character, in contrast to the acidic character of the last three [21]. CH_2O polymerizes on nonmesoporous SiO_2 [21], Pt/Cu/SiO_2 [26], and $H_3PMo_{12}O_{40}/SiO_2$ [27] at room temperature. In the first case, $–[CH_2–O]_n–$ was reported to absorb at 1385, 1425, 1480, 2915, and 2980 cm^{-1}. Therefore the 1406 cm^{-1} band in the 35 °C spectrum of Fig. 3 is tentatively assigned to polymerized CH_2O. The adsorbed and polymerized CH_2O on MCM-41 are no more observed in the 200 °C spectrum. $CH_3O_{(a)}$ and $HCOO_{(a)}$ are still present on the surface heated to 400 °C. Recently in a study of acetalization of cyclohexanone with methanol, it is reported that MCM-41 evacuated at 60 °C is more reactive than that evacuated at higher temperatures [28]. Therefore, we carried out an experiment of CH_2O adsorption on a low-temperature MCM-41 sample which was prepared by spraying dispersed MCM-41 on a tungsten mesh and then holding the MCM-41/W sample in a vacuum at 60 °C, instead of 500 °C, for 24 h. The infrared study showed that the low-temperature MCM-41 sample was fully hydroxylated, as indicated by strong OH infrared absorptions between ∼ 3000 and 3800 cm^{-1}. CH_2O adsorption on the MCM-41 mainly generated CH_3O at 1453 cm^{-1}, but the HCOO bands at 1376 and 1610 cm^{-1} were either not seen or very small. Apparently, reactions of CH_2O on MCM-41 are sensitive to the surface active sites.

In the present study, MCM-41, preheated to 500 °C in a vacuum, catalyzes a sequential oxidation of CH_3OH ($CH_3OH \rightarrow CH_2O \rightarrow HCOO$) and a Cannizzaro-type reaction of CH_2O ($2CH_2O \rightarrow CH_3O + HCOO$) which has not been observed on nonmesoporous siliceous materials. We now discuss the possible surface reactive sites for these reactions. Dehydroxylation of SiO_2 by thermal treatment can produce asymmetrically strained siloxane bridge sites [29]. It has been reported that this sites provide both acidic (electron-deficient Si atoms) and basic (bridging oxygen atoms) characters. For example, the bridged oxygen atoms of the strained siloxane sites can be attacked by the electron-deficient boron atom of BF_3, forming $SiOBF_2$ species [30]. In the study of methylamine synthesis catalyzed by siliceous mesoporous FSM-16, which exhibits a similar structure to MCM-41, it is postulated that the active sites are the Si atoms with enhanced strength of Lewis acidity due to a prolonged Si–O bond in strained siloxane bridge sites [15]. As a contrast, amorphous SiO_2 without a mesoporous structure can hardly catalyze the methylamine synthesis [15]. The recent study of the active sites on mesoporous siliceous materials suggests that strained siloxane bridge sites may be related to ≡Si–O· radical sites [31]. As a matter of fact, radical species has been invoked to explain the transformation of CH_3OH to CH_2O on γ-irradiated SiO_2 surface [32]. Structural characteristics of mesoporous SiO_2 can also affect their reactivities. MCM-41 and SBA-15 siliceous materials have the same p6mm hexagonal mesostructure, but they are different with respect to wall thickness, pore shape, and pore size [33]. Comparison of adsorption of the molecules, investigated in present study, on these two mesoporous SiO_2 may provide more insight into the effect of structural features.

4. Conclusions

Scheme 1 summarizes the dissociative adsorption of HCOOH, CH_3OH, and CH_2O on MCM-41 at 35 °C. In this scheme, asymmetrically strained siloxane bridge sites are assumed to be the active centers. Decomposition of HCOOH and CH_3OH can generate silanol (Si–OH) groups, but they are not shown in Scheme 1. Adsorbed HCOO on MCM-41 is assumed to adopt a unidentate configuration. A bridging configuration is also possible.



Scheme 1.

Acknowledgment

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