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Report Title

Development of Nanocrystalline Zeolite Materials for the Decontamination of Chemical Warfare Agents

ABSTRACT

The main objective of this research is to use novel nanocrystalline zeolite materials synthesized in our laboratories for the decontamination of chemical warfare agents (CWAs). A wide range of macroscopic and microscopic tools have been used to evaluate the chemistry of CWA simulants with nanocrystalline zeolite materials. In these studies, we have focused our attention on the decontamination of 2-CEES and DMMP, two simulants for mustard gas. We have used a flow cell apparatus to evaluate the adsorption capacity of 2-CEES on nanocrystalline zeolites. We have shown that the adsorption capacity is increased on these materials relative to commercial materials. Second, we have used FT-IR spectroscopy to follow the adsorption and decontamination chemistry of 2-CEES and DMMP on nanocrystalline ZSM-5 and NaY. Third, we have begun to use computational chemistry to understand better how the real agent will interact with these materials so that rational choices for which simulant to use with a given zeolite material can be made. Fourth, we have begun to evaluate new materials including cation-exchanged zeolites for decontamination chemistry.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Knagge, K.; Johnson, M.; Grassian, V. H. and Larsen, S. C. "Adsorption and Thermal Oxidation of DMMP in Nanocrystalline NaY" *Langmuir* 2006, 22, 11077-11084.

Stout, S. C.; Larsen, S. C. and Grassian, V. H. "Adsorption, Desorption and Thermal Oxidation of 2-CEES on Nanocrystalline Zeolites" *Microporous and Mesoporous Materials* 2007, 100, 77-86.

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Grassian, V. H.; Larsen, S.C. "Synthesis, Characterization and Environmental Applications of Nanocrystalline Zeolites" in *Handbook of Nanoscience and Nanotechnology*, University of Oxford Press, Oxford, UK 2008.

Grassian, V. H. and Larsen, S.C. "Applications of Nanocrystalline Zeolites to CWA Decontamination" V.H. Grassian, and S.C. Larsen book chapter in *ACS Book on Decontamination Technologies* 2008.

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(c) Presentations

Applications of nanocrystalline zeolites to CWA decontamination, National ACS meeting, Boston, MA, August 21, 2007

Applications of Nanocrystalline Zeolites and Zeolite Structures in Environmental Catalysis, Decontamination, and Drug Delivery, Department of Chemistry, University of Michigan, April 13, 2007.

Nanocatalysts for Environmental Technology, 3rd Annual Frontiers in NanoSystems" conference sponsored by the California NanoSystems Institute (CNSI), Kauai, HI, March 19-21, 2007.

Adsorption and Reaction of the CWA Simulants, 2-CEES and DMMP on Nanocrystalline Zeolites, Decon2006 Conference, Westminster, Colorado, Nov. 2, 2006

Applications of Nanocrystalline Zeolites and Zeolite Structures in Environmental Catalysis, Decontamination, and Drug Delivery, NSF Workshop on Materials Chemistry and Nanoscience, St. Louis, MO, October 12-15, 2006

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Shannon Stout	0.50
Anamika Mubayi	0.50
Pragati Galhotra	0.50
FTE Equivalent:	1.50
Total Number:	3

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Kevin Knagge	1.00
FTE Equivalent:	1.00
Total Number:	1

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<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Vicki Grassian	0.05	No
Sarah Larsen	0.05	No
FTE Equivalent:	0.10	
Total Number:	2	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Matthew Johnson	0.10
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Names of Personnel receiving masters degrees

NAME

Shannon Stout

Total Number:

1

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

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Sub Contractors (DD882)

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Applications of Nanocrystalline Zeolites to CWA Decontamination

V.H. Grassian, and S.C. Larsen

Department of Chemistry, University of Iowa, Iowa City, IA 52242

1. Statement of the Problem

Decontamination of chemical warfare agents (CWA's) is important not only for battlefield applications, but for cleanup as well. Some common CWA's are VX-(O-ethyl S-(2-isopropylamino)ethyl methylphosphonotioate), which is a nerve gas, and HD (mustard gas), which is a blistering agent. For much of the CWA decontamination research, CWA simulants which have similar chemical structures and properties as CWA's but are much less toxic, are used. In the work described here, DMMP (dimethylmethylphosphonate) and 2-CEES (2-chloroethyl sulfide) will be used as CWA simulants for VX and HD, respectively. The chemical structures of VX and DMMP and HD and 2-CEES are shown in Figure 1.

Nanocrystalline solid adsorbents and catalysts show great potential for decontamination. Recent work by Klabunde and coworkers has demonstrated that nanocrystalline metal oxides are promising destructive adsorbents for a variety of CWAs and CWA simulants(1-8). The unique properties of the nanocrystalline metal oxides as destructive adsorbents are attributed to the unusual crystal shapes, polar surfaces and high surface areas of these materials relative to conventional metal oxides. For example, nanocrystalline MgO exhibits high reactivity for the dehydrochlorination of 2-CEES while microcrystalline MgO is unreactive(3). The decontamination of CWAs and simulants on nanoporous materials, such as zeolites which are porous aluminosilicates, has also been investigated. Decontamination of VX and HD on NaY and AgY was investigated by Wagner and Bartram.(9) They found that AgY was effective for decontamination of HD, but NaY was not and that VX could be successfully decontaminated by NaY and possibly AgY depending on the acceptability of certain toxic intermediates. Bellamy also found that HD could be decontaminated by 13X zeolites.(10) These previous studies suggest that nanomaterials may have unique properties and promising reactivity for the decontamination of CWAs.

Nanocrystalline zeolites are zeolites with crystal sizes of 100 nm or less. Nanocrystalline zeolites are porous nanomaterials with internal surface porosity and a much greater external surface than conventional micron-sized zeolites. We have synthesized nanocrystalline zeolites, such as NaY, NaZSM-5 and silicalite (purely siliceous form of ZSM-5) with crystal sizes of approximately 25 nm (Table 1). The synthesis and characterization of these materials in our laboratory has been described previously.(11-14) The nanocrystalline zeolites have external

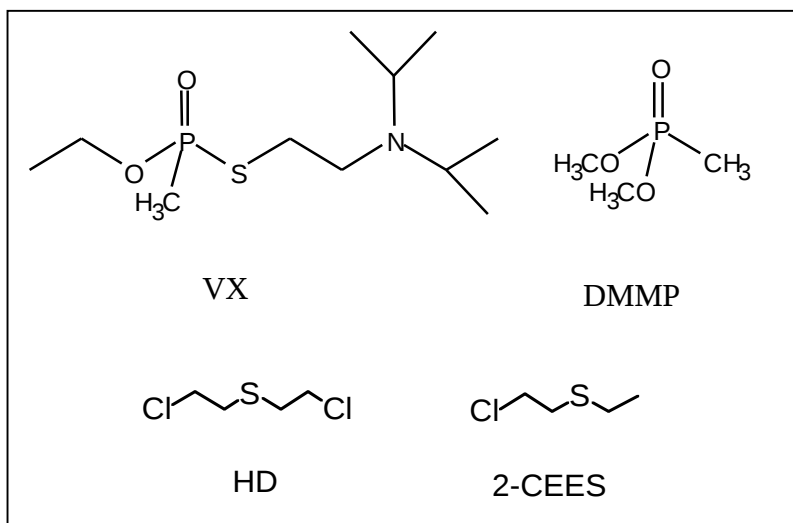


Figure 1. Two CWA's and their simulants

surface areas $>100 \text{ m}^2/\text{g}$ which accounts for about 30% of the total zeolite surface area compared to 2% of the total surface area for micron-sized zeolites as shown in Table 1. The enhanced external surface has the potential to be a new surface for adsorption and catalytic reactivity.

Nanocrystalline zeolites, NaY and NaZSM-5 and silicalite, synthesized by us, were evaluated for the decontamination of the CWA simulants, DMMP(15) and 2-CEES(16,17). The increased surface area and external surface reactivity of nanocrystalline zeolites provides potential advantages for CWA decontamination that are not found in conventional zeolite materials. The adsorption capacity and the thermal oxidation of these simulants on nanocrystalline zeolites was investigated using FTIR spectroscopy and solid state NMR spectroscopy and the reactivity on different materials was compared.

Table 1. External and Internal Surface Areas of Nanocrystalline Zeolites

Zeolite	Crystal size (nm) ^a	Total (External) Surface Area(m ² /g) ^b	Adsorbed 2-CEES ^c mmol/g
Silicalite	23	473 (138)	3.7 (1.3)
Silicalite	1000	343 (2)	--
NaZSM-5	15	556 (208)	4.5 (2.6)
NaY	22	584 (178)	--

^a determined from SEM images, ^bBET surface area measured after (before) calcination to remove the organic template. ^cThe total adsorption of 2-CEES with the adsorption of 2-CEES on the external surface given in parentheses(16).

2. Summary of the Most Important Results.

A. Adsorption and thermal oxidation of a mustard gas simulant on nanocrystalline zeolites.

The 2-CEES molecule has a chemical structure similar to mustard gas (Figure 1) without one chlorine atom but it is significantly less toxic. Zawadski and Parsons have shown that 2-CEES and mustard gas have very similar crystal structures(18), therefore it is expected that 2-CEES will closely mimic the reactivity of mustard gas. FTIR spectroscopy and flow reactor measurements were used to investigate the adsorption, desorption and thermal oxidation of the mustard gas simulant, 2-CEES, on nanocrystalline zeolites. Thermal oxidation reactivity of 2-CEES on nanocrystalline NaZSM-5 (15 nm) is compared to that on nanocrystalline silicalite-1 (23 nm) and NaY(22 nm)(16).

The adsorption of 2-CEES on nanocrystalline NaZSM-5 and silicalite was monitored using a flow reactor apparatus and the thermal conductivity detector (TCD) of a gas chromatograph. During the initial adsorption period, the total amount of 2-CEES adsorbed on silicalite (ZSM-5) at room temperature was measured and quantified as listed in Table 1. 3.7 and 4.5 mmol/g of 2-CEES were adsorbed on silicalite (25 nm) and NaZSM-5 (15nm), respectively. The desorption during a room temperature helium purge was measured and was found to be 1.3 and 2.6 mmol/g for silicalite (23 nm) and NaZSM-5 (15 nm), respectively. The amount of 2-CEES desorbed during the room temperature helium purge was interpreted to be from 2-CEES desorbed from the external zeolite surface since approximately twice as much 2-CEES desorbed from NaZSM-5 (15 nm) compared to silicalite (23 nm) which is qualitatively similar to the ratio of the external surface areas. The 2-CEES adsorbed on the external surface is only weakly bound to the surface as suggested by its room temperature desorption. Overall, approximately 20% more 2-CEES was adsorbed on NaZSM-5 (15 nm) relative to silicalite (23 nm) and this was attributed to an increase in 2-CEES adsorption on the external surface of NaZSM-5. The external surface provides an additional adsorptive surface for 2-CEES that can also provide enhanced reactivity for 2-CEES decomposition.

The thermal oxidation of 2-CEES in nanocrystalline silicalite-1 and NaZSM-5 was investigated with FTIR spectroscopy to assess the reactivity of 2-CEES. Gas-phase products were monitored as a function of time as 2-CEES was oxidized on silicalite-1 (23 nm) and NaZSM-5 (15 nm).(16) FTIR spectra were collected every two minutes with 64 scans at 4 cm^{-1} resolution after saturating the sample with adsorbed 2-CEES and heating in the presence of 10 Torr of O_2 to $T = 200\text{ }^\circ\text{C}$. Figure 2 shows representative spectra following the evolution of gas-phase products as a function of reaction time for 2-CEES oxidation on nanocrystalline NaZSM-5. The observed products detected include C_2H_4 , HCl , CO_2 , CO , SCO , CH_3CHO , CS_2 , SO_2 , and $\text{C}_2\text{H}_5\text{Cl}$.

In the presence of nanocrystalline NaZSM-5, all of the 2-CEES reacted within the first eight minutes. In the presence of nanocrystalline silicalite-1 (not shown), 2-CEES didn't completely disappear from the gas phase until longer times. CO_2 begins to form immediately in the thermal oxidation of 2-CEES on both silicalite-1 and NaZSM-5. HCl is formed and then disappears early in the 2-CEES/NaZSM-5 oxidation reaction but is not observed in the 2-CEES/silicalite-1 reaction.

The time course behavior of several of the major products is represented in the integrated absorbance versus time plots(not shown)(16). These results are presented in Table 2 in which the ratios of product formation rates and product amounts formed on nanocrystalline NaZSM-5

(15 nm) and silicalite-1 (23 nm) are listed. The reaction between 2-CEES and NaZSM-5 was found to be faster overall and produced higher concentrations of the final oxidation products than the reaction between 2-CEES and silicalite-1. The increased reactivity of NaZSM-5 to 2-CEES was attributed to the reactive aluminum sites in NaZSM-5 that are not present in silicalite-1.

Since aluminum was hypothesized to be responsible for the increased reactivity of nanocrystalline NaZSM-5 relative to silicalite, the 2-CEES reactivity on nanocrystalline NaY, which has a much lower Si/Al ratio than ZSM-5, was evaluated. The 2-CEES thermal oxidation activity of several different nanocrystalline zeolites was compared as shown in Figure 3. The amounts of selected products (CH₄, CO₂, CO and SO₂) formed on nanocrystalline NaY(22 nm), NaZSM-5(15 nm) and silicalite-1 (23 nm) is shown in Figure 3. The largest quantities of these products are formed on NaZSM-5 (15 nm), followed by silicalite (23 nm) and then NaY(22 nm). The higher aluminum content of NaY does not lead to increased reactivity suggesting that the shape selective properties of the zeolite may also play a role in the reactivity. NaZSM-5 has elliptical pores with ~5.6Å pore diameters that will provide a “better fit” for the adsorption of the linear 2-CEES relative to NaY which has super cages with 7.4Å pore windows.

Table 2. NaZSM-5: silicalite-1 ratio of initial rate and amount of product formation during the thermal oxidation of 2-CEES

<i>Gas Phase Product</i>	<i>Relative Initial Rates of Product Formation</i>	<i>Relative Amounts of Product Formation</i>
Carbon monoxide, CO	1.8	2.0
Carbon dioxide, CO ₂	1.7	1.8
Ethylene, C ₂ H ₄	7.3	4.5
Acetaldehyde, CH ₃ CHO	4.1	1.3
Carbonyl sulfide, SCO	3.6	1.3
Sulfur dioxide, SO ₂	7.5	3.1
Carbon monoxide, CO	1.8	2.0

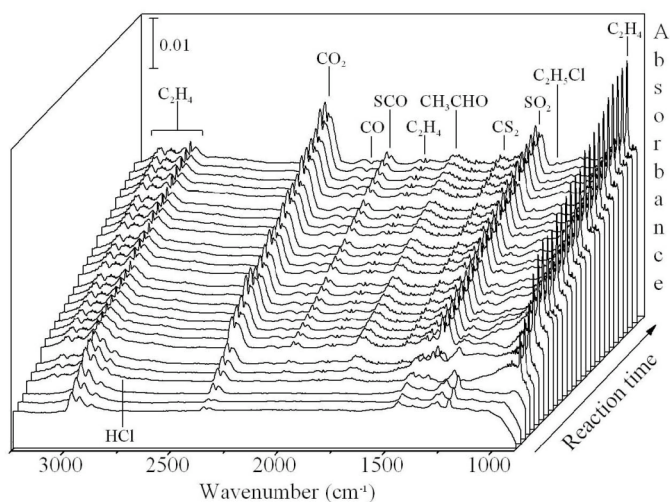


Figure 2. Gas-phase oxidation products of 2-CEES on nanocrystalline NaZSM-5 (15 nm particle size), $p(\text{O}_2)=10$ torr and $T=200^\circ\text{C}$.

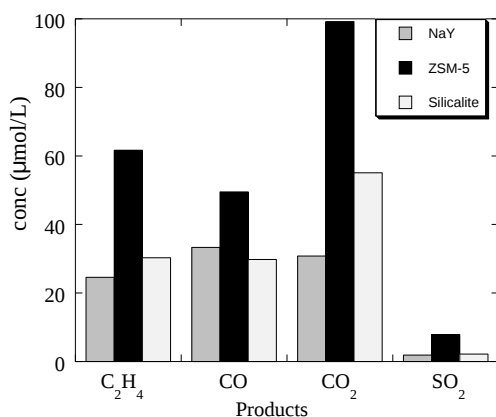


Figure 3. Comparison of gas phase products formed after reaction of 2-CEES with oxygen over NaZSM-5 (15 nm) = solid bar, silicalite (23 nm)=gray bar and NaY (22 nm)= striped bar

B. Adsorption and thermal oxidation of a nerve gas simulant, DMMP, on nanocrystalline NaY

Decontamination of chemical warfare agents, such as the nerve gas, VX, is required in a variety of situations including battlefields, laboratories, storage facilities, and destruction sites. Most research has dealt with battlefield decontamination due to the speed and ease of use of a decontaminant required in this situation. Because of the requirements of battlefield decontamination, reactive inorganic powders have been widely explored as possible catalysts for CWA decontamination. Studies have been performed examining the neutralization of VX on

nanosized MgO(3), nanosized CaO(2), AgY(9), and nanosized Al₂O₃(1) and other similar compounds on nanosized MgO.(19)

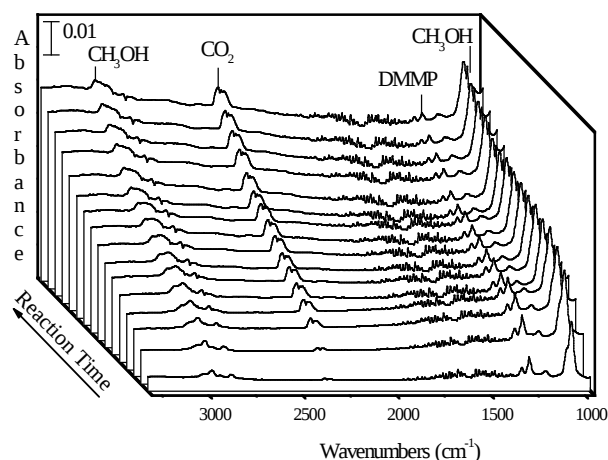
The most common simulant of phosphorus-containing CWAs, such as VX, is dimethyl methyl phosphonate (DMMP). The adsorptive and reactive properties of VX and DMMP, on aluminosilicates, such as zeolites have also been examined. For use as decontamination materials, it has been shown by solid state NMR that VX hydrolyzes on NaY and AgY at room temperature through cleavage of the P–S bond to yield ethyl methylphosphonate (EMPA).(9) The reaction proceeds more quickly on AgY relative to NaY and the reaction continues on AgY as EMPA reacts further to form the desulfurized analogue of VX, 2-(diisopropylamino) ethyl methylphosphonate, also called QB. This is important since the QB has an LD₅₀ that is 3 orders of magnitude less than the LD₅₀ of VX. Recently, another zeolite application of chemical warfare agent detection was reported in which zeolite films immobilized on a quartz crystal microbalance were used as gas sensors for DMMP. (20)

The use of nanocrystalline NaY for the thermal reaction of DMMP was evaluated thus taking advantage of the inherent reactivity of Y zeolites and the enhanced properties of the nanocrystalline form of Y zeolites. Nanocrystalline NaY with a crystal size of ~30 nm was evaluated for the adsorption and thermal reaction of the VX simulant, DMMP. FTIR and solid state ³¹P NMR spectroscopy were used to identify the gas phase and adsorbed species formed during the adsorption and reaction of DMMP in nanocrystalline NaY. DMMP adsorbs molecularly on nanocrystalline NaY at room temperature.

The thermal reaction of DMMP and H₂O in nanocrystalline NaY was investigated using infrared spectroscopy. Gas phase products of the thermal reaction of DMMP, O₂ and H₂O in nanocrystalline NaY were monitored by FTIR spectroscopy as a function of time at 200°C. Gas phase FTIR spectra were acquired every minute for 5 h. Representative infrared spectra of the reaction of DMMP, O₂, and H₂O in nanocrystalline NaY at 200°C are shown in Figure 4. The major gas phase products observed are CH₃OH and CO₂. CH₃OCH₃ is another possible product, but a large degree of spectral overlap with methanol vibrational peaks makes quantification difficult. In this reaction, major DMMP peaks are observed at 1050 cm⁻¹, 1272 cm⁻¹ and 1312 cm⁻¹ throughout the reaction indicating that DMMP does not completely react on the surface of nanocrystalline NaY and remains in the gas phase before reacting to form products, such as CO₂ and CH₃OH.

The hydroxyl region of the FTIR spectrum reveals the external surface reactivity of nanocrystalline NaY in the thermal oxidation of DMMP. The hydroxyl group region of the FTIR spectrum of nanocrystalline NaY before (solid line) and after thermal treatment (dashed line) with DMMP, O₂ and H₂O at 200°C for 5 h. is shown in Figure 5. As reported previously, several bands due to hydroxyl groups are observed in the FTIR spectrum of nanocrystalline NaY.(14,21-23). In the OH stretching region of the FT-IR spectrum of nanocrystalline NaY zeolite, three absorptions are observed between 3765 and 3630 cm⁻¹ (Fig. 5, top spectrum). The most intense and highest frequency band at 3744 cm⁻¹ is assigned to terminal silanol groups that are on the external surface of the zeolite crystals. The absorption band at 3695 cm⁻¹ is assigned to hydroxyl groups attached to Na⁺. An absorption band at 3656 cm⁻¹, associated with hydroxyl groups attached to extra framework alumina (EFAL) species which have been shown to be located on the external NaY surface.(21-23) The hydroxyl group region shows a complete loss of spectral intensity for all three absorption bands after reaction of DMMP on nanocrystalline NaY with O₂ and H₂O as shown in Figure 5, bottom spectrum. These results indicate that hydroxyl groups

located on the external zeolite surface participate in these decomposition and reaction reactions



of DMMP and thus represent active sites for the decontamination of DMMP.

^{31}P MAS NMR experiments were conducted to investigate the phosphorus surface species(9,24,25) formed during the DMMP thermal reactions in nanocrystalline NaY since this information was difficult to obtain from the FTIR experiments due to spectral overlap and broadening. The ^{31}P MAS NMR spectra

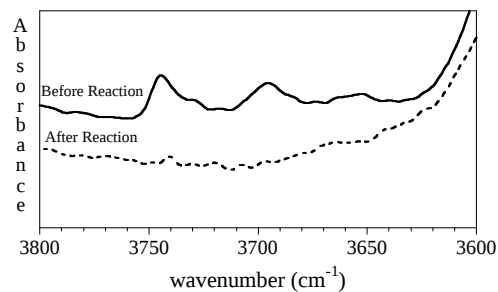


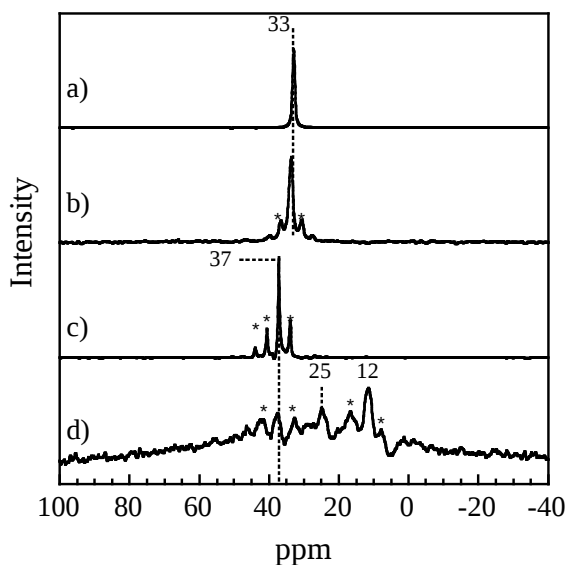
Figure 4. FTIR spectra of gas phase products of the thermal reaction of DMMP in the presence of water and oxygen on nanocrystalline NaY (30 nm) at 200°C. Representative spectra obtained every 20 minutes for four hours are shown here. Reproduced with permission from reference 15. Copyright 2006 American Chemical Society.

Figure 5. FTIR spectrum of the hydroxyl region of nanocrystalline NaY (30 nm) before (solid line) and after thermal treatment (dashed line) with DMMP, O₂, and H₂O at 200°C for 5 h. Reproduced with permission from reference 15. Copyright 2006 American Chemical Society.

obtained after thermal reaction of DMMP, O₂ and H₂O all in nanocrystalline NaY at 200°C are shown in Figure 6. The NMR samples were contained in sealed sample tubes that were heated to 200°C ex-situ. All NMR spectra were recorded at room temperature under conditions of thermal equilibrium.

The ³¹P chemical shift for neat DMMP (Fig. 6a) is 33 ppm. When DMMP is adsorbed in nanocrystalline NaY, the peak shifts slightly downfield to 34 ppm and spinning sidebands (marked with asterisks) appear in the NMR spectrum (Fig. 6b). The spinning sidebands indicate appreciable chemical shift anisotropy and a decrease in mobility suggesting that DMMP strongly adsorbs on the nanocrystalline NaY surface. When water is coadsorbed with DMMP, the peak shifts further downfield to 37 ppm and is narrower although spinning sidebands are still observed in the NMR spectrum (Fig. 6c).

DMMP was reacted with H₂O and O₂ at 200°C for 5 hours. The resulting ³¹P MAS NMR spectrum is shown in Figure 6d and several different peaks are observed in the range 10 to 50 ppm. The peak at 37 ppm corresponds to unreacted DMMP adsorbed on nanocrystalline NaY in the presence of water. A peak at 25 ppm is observed in the ³¹P MAS NMR spectrum which is close to the chemical shift of hydroxy methyl phosphonic acid (OHCH₂PO(OH)₂) or HMPA. Another peak appears at 12 ppm and this peak is close to the chemical shift for an authentic



sample of dimethyl phosphite (CH₃O)₂P(O)H or DMP. There is

Figure 6. ^{31}P MAS NMR spectra of a) DMMP neat, b) DMMP adsorbed on nanocrystalline NaY (30 nm), c) DMMP adsorbed with H_2O on nanocrystalline NaY (30 nm), and d) after reaction of DMMP, O_2 , H_2O and nanocrystalline NaY (30 nm) at 200°C for 5 h. Adapted from reference 15.
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also a broad peak present in the ^{31}P NMR spectrum due to a strongly adsorbed immobile surface species. This peak is difficult to assign due to the width of the peak.

Thermal reaction of DMMP in the presence of water in nanocrystalline NaY at 200°C resulted in the formation of methanol, carbon dioxide and phosphorus decomposition products such as hydroxy methylphosphonic acid and dimethylphosphite. The external surface hydroxyl sites (silanol and EFAL) which are uniquely present in nanocrystalline NaY are important in the reaction and decomposition of DMMP. Future improvements in reactivity may be achieved by incorporating a reactive transition metal ion or oxide into the nanocrystalline NaY to provide additional reactive sites.

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