In Situ ¹³C Solid-State NMR Studies of the Catalytic Conversion of Methanol on Expanded Montmorillonites and Saponites

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Received: October 14, 1994; In Final Form: February 14, 1995[®]

In situ ¹³C NMR was used to monitor the catalytic behavior of supercritically dried (SCD) and air dried (AD) expanded montmorillonites and saponites in the conversion of methanol. The motion of MeOH molecules in expanded montmorillonites is highly restricted. No carbon monoxide is produced below 350 °C on either catalyst. Various aliphatic and aromatic hydrocarbons are found after heating at 350 °C, of which *n*-pentane, *n*-hexane, and *n*-heptane are dominant. AD and SCD expanded montmorillonites have similar catalytic activity. Saponites give a wider variety of hydrocarbons and are more active than montmorillonites. In turn, AD saponite is more active than SCD saponite. With clay catalysts, acidic strength is less important than the size and distribution of the pores, so that different drying conditions lead to very different catalytic results. Because of the lower acidic strength and acid site density of montmorillonites and saponites in comparison with zeolites, the temperature at which a given hydrocarbon appears in the conversion of methanol is higher for clay catalysts than for zeolite ZSM-5.

Introduction

The interlamellar space in smectite minerals such as montmorillonite and saponite can be easily expanded by intercalating water or other polar compounds. In a process known as pillaring, small charge-balancing cations such as Na⁺, K⁺, Ca²⁺, or Mg²⁺ in the clay can be ion exchanged for polyoxocations of Al and Zr or for positively charged colloidal particles from sol solutions of Al₂O₃, Al₂O₃·SiO₂, TiO₂, or SiO₂·TiO₂.¹⁻⁶ Thermal dehydroxylation of the intercalating species results in heat-stable metal oxide clusters which permanently separate the silicate layers, thus making the interlayer space available to sorption and catalysis.

Properties of a clay expanded with a given compound depend on the method of drying. After pillaring with colloidal SiO₂·TiO₂ particles and supercritical drying (SCD) with CO₂, montmorillonite and saponite acquire a high surface area (450– 600 m²/g), macroporosity (350–400 m²/g), and pore volume (ca. 1.5 cm³/g). The products are thermally stable up to 800 °C, while after air drying (AD) the same clays lose their macroporosity and have lower Brønsted acidity.^{6,7}

Expanded montmorillonites and saponites are of interest to the petroleum industry, particularly for catalytic cracking. The declining world oil reserves have stimulated considerable efforts toward the exploration of alternative sources of energy and organic chemicals. One solution is to use the abundant supply of coal as a source of synthesis gas (CO + H₂), which is readily converted to methanol (MeOH).⁸ MeOH can be then transformed into higher molecular weight hydrocarbons over acidic catalysts, of which ZSM-5 has already been used on an industrial scale.⁹ We have used in situ NMR^{10,11} to monitor the behavior of SCD and AD montmorillonites and saponites in the catalytic conversion of MeOH.

0022-3654/95/2099-6980\$09.00/0

Experimental Section

Natural Na-montmorillonite (KUNIPIA F) and synthetic saponite (SUMECTON SA) were obtained from Kunimine Industries, Japan. The samples were expanded using a SiO₂'TiO₂ sol solution as described by Yamanaka et al.⁴ Tetraethylorthosilicate was hydrolyzed with an excess of a mixture of HCl (1 M) and ethanol and then reacted with titanium tetraisopropoxide (hydrolyzed with 1 M HCl) to form a sol with the composition TiO₂·10SiO₂. The sol was then added to a slurry containing 1% clay, and the mixture was stirred for 1.5 h at 60 °C. After it was filtered and washed, part of the sample was dried in air at 60 °C. The remaining part was washed with ethanol (in order to displace interlamellar water) and then dried with supercritical CO₂ at 120 atm and 40 °C.⁷

MeOH 99% enriched in ¹³C was diluted to 50 wt % with ordinary MeOH and purified by the freeze-pump-thaw method. Catalyst samples for ¹³C MAS NMR experiments were placed in specially designed Pyrex microreactors^{10,11} and dehydrated by evacuation followed by heating at 400 °C for 10 h. The final gas pressure above the samples was less than 10^{-5} Torr. The samples were cooled to room temperature prior to adsorption of 50 Torr of ¹³C-enriched MeOH and allowed to equilibrate for 1 h before being isolated from the bulk of gaseous MeOH. The neck of the microreactor was finally sealed with a microtorch flame, while the sample itself was maintained at -196 °C. Sealed sample capsules were placed in a furnace and maintained at precisely controlled temperatures in the 20-370 °C range for various lengths of time and then quenched in liquid nitrogen in order to arrest the progress of the catalytic reaction. Subsequent to NMR examination samples were treated at higher temperatures and reused in further measurements.

¹³C MAS NMR spectra with high-power proton decoupling were recorded at 100.5 MHz on a Chemagnetics CMX-400 spectrometer with 45° pulse lengths and 5 s recycle delays.

[®] Abstract published in Advance ACS Abstracts, April 15, 1995.

TABLE 1: Assignment of ¹³C MAS NMR Spectra with Proton Decoupling of AD and SCD Montmorillonites after Adsorption of 50 Torr of MeOH and Various Thermal Treatments⁴

compound	peak no. ^b	20 °C	150 °C 10 min	270 °C 5 min	320 °C 10 min	350 °C 20 min	380 °C 1 h	450 °C 1 h
МеОН	1	VS VS	VS VS	S S	m m	m m		
DME	2			s m	VS VS	s m		
acetone		vw vw	vw vw	vw vw				
methane	3					vw vw	m w	m m
ethane	4					vw	w vw	m w
ethene						vw w	vw	
isobutane	5						vw	vw
<i>n</i> -pentane <i>n</i> -hexane <i>n</i> -heptane	6					m m	S S	S S
isopentane 3-methylpentane }	7					vw	vw w	vw w
aromatics I ^c	8					vw vw	m m	m m
aromatics II ^d	9					vw vw	w m	w m

^{*a*} Relative intensities: vs (80-100%), s (40-80%), m (10-40%), w (5-10%), and vw (<5%). The first and second entry in each group refer to results for AD and SCD montmorillonites, respectively. ^{*b*} Peak numbers refer to Figure 1. ^{*c*} Aromatics I include 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and/or pentamethylbenzene, ^{*d*} Aromatics II include toluene, m-xylene, p-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene.

These conditions ensure complete spin-lattice relaxation.^{10,11} All spectra were recorded at room temperature. Chemical shifts are given in ppm from external tetramethylsilane (TMS).

Results

Montmorillonite. Figure 1 and Table 1 give the ${}^{13}C$ MAS NMR results for AD and SCD montmorillonites heated at different temperatures for various lengths of time. After adsorption of MeOH and no thermal treatment, a very strong line at 50 ppm from the methyl group of MeOH is found in both samples. The large line width indicates that in AD and SCD montmorillonites the motion of MeOH molecules is highly restricted. A very low intensity peak at 212 ppm comes from a trace impurity of acetone. Similar spectra were measured after heating the samples at 150 °C for 10 min.

After heating at 270 °C for 5 min a line from dimethyl ether (DME) appears at 60 ppm. Although, as a result of the nuclear Overhauser effect, the intensity of proton-decoupled spectra is not strictly proportional to the carbon population, the intensity ratio may still be used to estimate the organic content of different samples subjected to similar treatments, particularly since intensities of the same functional groups are being compared. Thus after heating at 270 °C for 5 min, the DME/MeOH intensity ratios of the AD and SCD samples are 1.26 and 0.53, respectively. After heating at 320 °C for 10 min, both samples contain the same compounds as the samples at 270 °C, but the intensity ratios change to 6.94 and 8.26, respectively.

A variety of hydrocarbons are found in both samples after heating at 350 °C for 20 min. Assignment of NMR resonances is based on earlier work^{10,11} and the literature.¹² The aliphatic lines used for the calculation of the intensity ratio are methane (-10 ppm), ethane (4 ppm), ethene (121 ppm), isobutane (25 ppm), *n*-pentane (23 ppm), *n*-hexane (23 ppm), *n*-heptane (23 ppm), isopentane (10.6 ppm), and 3-methylpentane (10.6 ppm) (Figure 1 and Table 1). Resonances from aromatic carbons are weak and broad and thus impossible to assign to individual compounds. However, aromatic hydrocarbons can be divided into two groups on the basis of the ¹³C chemical shift of their aliphatic fragments. Thus the aliphatic resonances of aromatics I are at ca. 15.2 ppm, corresponding to 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and/or pentamethylbenzene. The aliphatic resonances of aromatics II are at ca. 20.8 ppm, corresponding to toluene *m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and/or pentamethylbenzene. Most resonances are shifted in comparison with the liquid due to the substantial contribution of the van der Waals term to the chemical shift and changed magnetic susceptibility.

After heating at 350 °C for 20 min the contents of all hydrocarbons, particularly ethene, in the SCD sample are higher than in the AD sample. A trace of ethane is found only in the AD sample, and a small amount of isoalkanes is found only in the SCD sample. The absolute amount of MeOH in both samples does not change much between 320 and 350 °C. The amounts of reaction products are consistent with the lower DME/ MeOH ratio in the SCD sample (1.50) than in the AD sample (2.86), indicating that the former material is more active in this reaction. The SCD sample also tends to produce more isoal-kanes.

Upon heating at 380 °C for 1 h MeOH and DME in both samples are completely converted. The products are similar to those found at 350 °C, and the spectra are dominated by lines from *n*-pentane, *n*-hexane, and *n*-heptane. The SCD sample contains a larger amount of aromatic hydrocarbons, isopentane, and 3-methylpentane than the AD sample. Ethene and isobutane are only found in the SCD sample.



Figure 1. The aliphatic region of ¹³C MAS NMR spectra with proton decoupling of AD (left) and SCD (right) montmorillonites after adsorption of 50 Torr of MeOH and various thermal treatments. Asterisks denote spinning sidebands.

After heating at 450 °C for 1 h, the content of *n*-alkanes in both samples decreases and is accompanied by the increased content of methane and ethane. However, aromatic hydrocar-

bons, isopentane, and 3-methylpentane are still much more abundant in the SCD sample, and isobutane is only found in this sample.



Figure 2. The aliphatic region of ¹³C MAS NMR spectra with proton decoupling of AD (left) and SCD (right) saponites after adsorption of 50 Torr of MeOH and various thermal treatments. Asterisks denote spinning sidebands.

Saponite. Figure 2 and Table 2 give the ¹³C MAS NMR results for the AD and SCD saponite heated at different temperatures for various lengths of time. After adsorption of

MeOH and no thermal treatment, a strong line at 50 ppm from the methyl group of MeOH appears in the spectra of both samples. Several very weak lines, including that from DME

compound	peak no. ^b	20 °C	150 °C 13 min	270 °C 20 min	320 °C 10 min	350 °C 20 min	380 °C 20 min	380 °C 1 h
MeOH	1	vs	vs	m	m	m	vw	
		VS	vs	m	m	m	w	
DME	2	vw	vw	s	vs	S		
		vw	vw	vs	VS	S	m	
acetone		vw	vw	vw	vw			
		vw	vw	vw	vw			
methane	3					vw	w	w
		vw	vw	vw	vw	vw	vw	m
ethane	4						vw	vw
						vw	vw	VW
ethene						vw	vw	
						vw	vw	vw
isobutane]	5					vw	vw	vw
<i>n</i> -butane }							vw	vw
neopentane	6						w	w
neopennane	-						vw	vw
isopentane	7					vw	vw	vw
isopeniune							vw	vw
3-methylpentane	8					vw	w	w
, - F	-						vw	w
isohexane	9						vw	vw
							vw	vw
isoheptane	10						vw	vw
isonopulio	10						vw	vw
n-pentane 1	11					w	s	\$
<i>n</i> -hexane	••					w	m	s
n-heptane								
aromatics I ^c	12					vw	w	m
						vw	vw	
aromatics II ^d	13					vw	m	m
						vw	w	m
hexamethylbenzene	14							vw
,								
со								vw
						vw	vw	vw

TABLE 2: Assignment of ¹³C MAS NMR Spectra with Proton Decoupling of AD and SCD Saponites after Adsorption of 50 Torr of MeOH and Various Thermal Treatments^a

^{*a*} Relative intensities: vs (80–100%), s (40–80%), m (10–40%), w (5–10%), and vw (<5%). The first and second entry in each group refer to results for AD and SCD saponites, respectively. ^{*b*} Peak numbers refer to Figure 2. ^{*c*} Aromatics I include 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, and/or pentamethylbenzene. ^{*d*} Aromatics II include toluene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and/or pentamethylbenzene.

(at 60 ppm), are also found, which indicates that a very small amount of MeOH has reacted during the sealing of the microreactors. Similar spectra are found after heating at 150 $^{\circ}$ C for 13 min.

After heating at 270 °C for 20 min the amount of DME increases significantly. The intensity ratios of DME/MeOH of the AD and SCD samples are 3.63 and 5.62, respectively. After heating the AD sample for 10 min and the SCD sample for and 20 min at 320 °C, both give results similar to those at 270 °C. The DME/MeOH intensity ratios for the AD and SCD samples change to 5.76 and 5.74, respectively, which indicates that up to this stage the two samples are virtually identical.

Various hydrocarbons are found in both samples after heating at 350 °C for 20 min. The lines from aliphatic and aromatic hydrocarbons taken for calculating the intensity ratio are the same as those in montmorillonites, except for the compounds which are only found in saponites: butane (ca. 25 ppm), isohexane (42.5 ppm), isoheptane (40.5 ppm), and neopentane (29 ppm) (see Figure 2 and Table 2). As with montmorillonites, the resonances from aromatic carbons are weak and broad and thus difficult to assign. Aromatic hydrocarbons have therefore been divided on the basis of resonances from their aliphatic carbons into two groups, aromatics I and II, as described above.

After heating at 350 °C for 20 min the absolute contents of methanol in both samples do not change very much, and ca. 25% of DME is further converted in both the AD and SCD samples. However, upon heating at 380 °C for 20 min, the two samples give significantly different results. DME in the AD sample is converted completely and MeOH is nearly completely converted, whereas in the SCD sample only 50% more DME has reacted than at 350 °C. The content of all hydrocarbons in the AD sample is higher than in the SCD sample. The products are similar to those for montmorillonites. In addition, *n*-butane, neopentane, isohexane, and isoheptane are found in both samples.

After heating at 380 °C for 1 h, MeOH and DME are completely converted. Lines from *n*-pentane, *n*-hexane, and *n*-heptane dominate the spectra of both samples. Both give fairly strong lines from aromatics, methane, and 3-methylpentane. The SCD sample contains twice as much methane as the AD sample but much less neopentane. Unlike in montmoril-

 TABLE 3: Surface Properties of AD and SCD

 Montmorillonites and Saponites Calcined in Air at 400 °C⁶

sample	BET surface area (m ² /g)	Hg surface area (m²/g)	Hg pore volume (cm ³ /g)
AD montmorillonite	125	14	0.03
SCD montmorillonite	467	365	1.50
AD saponite	567	43	0.07
SCD saponite	651	390	1.47

lonites, carbon monoxide is found in the SCD sample after heating at 350 °C and in the AD sample after heating at 380 °C. Unlike in montmorillonites, there are two kinds of methane molecules in AD and SCD saponites corresponding to two separate resonances. We assign the narrow peak to mobile methane molecules and the broad peak to strongly adsorbed methane.

Surface Properties. Results in Table 3 indicate that the occlusion of colloidal particles of $TiO_2 \cdot 10SiO_2$ between the silicate layers in natural montmorillonite and synthetic saponite⁶ yields expanded structures with porosities which greatly depend on the drying method used. When the solids are dried using a supercritical CO₂ fluid at 120 atm, house-of-cards structures are obtained with surface areas and pore structures resembling those found in alumina and aluminosilica supports used in hydrotreating catalysts preparation.^{6,13} When SCD is replaced by AD, the expanded clays lose most of their macroporosity and, in the case of this natural montmorillonite, most of their BET surface area. Surface losses during AD are not as pronounced when the catalyst preparation is performed using a Wyoming bentonite.¹³

Discussion

In all samples of montmorillonite and saponite MeOH is converted to DME at 270 °C and to hydrocarbons at 350 °C. These temperatures are higher than those required for the same conversion over zeolite ZSM-5 (150 and 300 °C, respectively)^{10,11} because of (1) the lower acidic strength of montmorillonite and saponite in comparison with ZSM-5 and (2) the low concentration ratio (< 1) of Brønsted to Lewis acid sites in these clays in comparison with ZSM-5 (> 1).

No carbon monoxide is produced below 350 °C. MeOH is first dehydrated to DME which is then converted to alkanes and aromatics. This difference between ZSM-5 and clays must involve different reaction mechanisms under significantly different conditions of porosity and acidity distribution. Also, the dominant products with montmorillonite and saponite are *n*-pentane, *n*-hexane, and *n*-heptane, while with ZSM-5 higher hydrocarbons dominate. This indicates that the active sites in clay samples are less reactive for secondary conversion reactions. The reason could be that the active centers are further apart from one another due to the much larger pore size and/or that MeOH is not able to cluster around these active centers because of steric reasons.

Saponite gives a wider variety of hydrocarbon products and is more reactive than montmorillonite, which could in part be attributed to the larger surface area in saponites. In turn, AD saponite is more active than SCD saponite. The former converts DME completely after heating at 380 °C for 20 min. At this temperature more neopentane is found in AD saponite and more methane in SCD saponite. There is more isoalkane in SCD montmorillonite than in its AD counterpart. Formation of isoalkanes in SCD montmorillonite could be facilitated by the macroporosity which is not found in AD montmorillonite.

It is known that montmorillonite and saponite contain both Brønsted and Lewis acid sites when expanded with SiO₂·TiO₂ clusters and that the SCD treatment enhances Brønsted acidity.^{6,14,15} In zeolites, the regular microporous structure and the Si/Al ratio (directly related to the number of Brønsted acid sites) are important to the kind and distribution of products. The stronger the acidity, the higher the conversion. However, with clay samples this is not the case. Thus AD montmorillonite is much less acidic than SCD montmorillonite, but their activities are very similar. Similarly, AD saponite is less acidic but more active than SCD saponite. It follows that in the conversion of MeOH over clay catalysts acidity is less important than structure. The AD and SCD samples have different pore structures, but neither is as regular as that in zeolites. In this case acidity may not play a key role, and the size and distribution of the pores could be more important. Different drying conditions may therefore lead to very different catalytic results. This is the most likely reason why our results are so unusual.

A range of bifunctional acid—base catalysts, such as WO_3/γ -Al₂O₃, can also convert MeOH to lower alkanes. However, ZSM-5 produces significant levels of methane at high conversions,¹⁶ and it is thought that the mechanism of formation of the first carbon—carbon bond is different with bifunctional catalysts and zeolite ZSM-5. It has been suggested that a radical type reaction proceeds over bifunctional catalysts, and there is a consensus that in the case of ZSM-5 the methyloxonium cation is the first important surface intermediate.¹⁷ Although the physical and chemical properties of clays are close to those of zeolites, our results show that reaction mechanisms of methanol conversion in ZSM-5 on the one hand and montmorillonites and saponites on the other are not the same. At this stage we do not have sufficient information to consider detailed reaction mechanisms.

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JP942822M