Inorg. Chem. **1985**, *24*, 858-863

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Photoassisted Catalysis in Organized Media: Olefin Isomerization via Photolysis of Metal Carbonyls in Zeolites

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Received April 18, 1984

Interactions of $Fe(CO)_5$ with several hydrated and dehydrated zeolites have been studied. Photochemical activation of $Fe(CO)_5$ in the presence of the zeolite and 1-pentene leads to isomerization of the olefin. If hydrated zeolites and the solvent benzene are used, then leaching of the iron into solution results. When a solvent such as isooctane is substituted for benzene, heterogeneous photoassisted catalytic isomerization takes place with an increase in selectivity for the *cis*-2-pentene species. Mössbauer, atomic absorption, and infrared characterization studies support these conclusions.

Introduction

Transition metals have been introduced into zeolite molecular sieves in a variety of ways, including ion exchange, adsorption, and sublimation.[1] During the past 5 years there has been much activity in the area concerning preparation of new zeolite catalysts that have been treated with transition-metal ions and complexes. There are several reasons why these studies are now being carried out. First of all, it has been realized that zeolites have a wide range of chemical properties that are important in the petroleum and detergent industry.[1] Secondly, new sophisticated instrumental methods such as Fourier transform infrared spectroscopy[3] and magic angle spinning nuclear magnetic resonance spectroscopy[4] have become available in several laboratories and have provided great insight as regards catalytic intermediates and the nature of active sites in these materials.

Several synthetic and characterization studies of metal carbonyls in zeolite environments have been made.[6-18,20] Our purpose is not to review such work but to mention studies that are particularly relevant to the research reported here. Ballivet-Tkatchenko and co-workers[15] have studied the interactions of $Fe(CO)_5$ with several zeolites. Thermal decomposition and infrared studies were carried out. Bein and Jacobs[10] have studied $Fe(CO)_5$ with dehydrated and dealuminated zeolites and suggest that the interaction of $Fe(CO)_5$ varies depending on the cation and the type of zeolite. Electrostatic fields create restricted mobility of the intact $Fe(CO)_5$.

In contrast to these synthetic and characterization studies there are relatively few examples of heterogeneous catalytic reactions involving zeolite-supported transition-metal carbonyls. A rhodium carbonyl cluster on zeolite Y has been reported to be an active hydroformylation catalyst.[12] In the past 5 years several groups have used adsorbed transition-metal carbonyls on zeolites as Fischer-Tropsch catalysts.[9,26,41] $Ni(CO)_4$ on alkali-metal- and alkaline-earth-X zeolites have been reported to be good benzene hydrogenation catalyst.[21]

Photochemical activation of trnsition-metal carbonyl complexes in zeolites has been reported by Derouane and co-workers.[22] No catalytic reactions were studied although it was proposed that highly dispersed pyrophoric iron(0) particles could be obtained by irradiation of $Fe(CO)_5$ in H-Y zeolite.

The purpose of the present study was to investigate the photochemical activation of various transition-metal carbonyl complexes both supported on the surface of small-pore zeolites and adsorbed in the supercages of large-pore zeolites. The reaction of interest is the photoassisted catalytic isomerization of 1-pentene to *cis-* and *trans*-2-pentene. This paper describes the preparation of the samples, the isomerization of 1-pentene, and spectroscopic methods that were used to characterize the zeolite before and after reaction.

Experimental Section

A. Materials. Iron pentacarbonyl was purchased from Alfa Products and used without further purification. Aldrich Chemical Co. was the source of 1-pentene. Reagent grade benzene was acquired from MCB Reagents. Zeolites A, X, and Y were obtained from Alfa Products. Zeolite ZSM-5 was synthesized according to procedures found elsewhere.[23] Glass band-pass filters, UG-1 and UG-11, were supplied by Schott Optical Glass, Inc. α-Alumina was supplied by Strem Chemicals, Inc. Amorphous silica was obtained from the Illinois Mineral Co.

B. Sample Preparation. Iron pentacarbonyl was placed on the zeolites by both vapor deposition and incipient wetness methods. Systems were also studied in which the zeolite was added to a solution of iron pentacarbonyl in pentene solution.

In the vapor deposition method of iron pentacarbonyl was placed in one side of an inverted U-tube with a syringe. The iron pentacarbonyl was immediately frozen with liquid nitrogen, and the zeolite was placed in the other side of the tube. The inverted U-tube was attached to a vacuum line, and with the iron pentacarbonyl still frozen, the tube was evacuated for 15 min to a pressure of less than 1×10^{-3} atm. Preparation of samples containing 5% iron by weight involved the deposition of 0.05 mL of iron pentacarbonyl on 0.39 g of zeolite.

The incipient wetness method of preparation involved using a syringe to place iron pentacarbonyl onto the zeolite. The third method of prep-

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aration involved the addition of iron pentacarbonyl to the pentene solution and then mixing of this solution with the solid zeolite.

Regardless of the preparation method, samples for photolysis were made of approximately 0.05 mL of iron pentacarbonyl supported on 0.39 g of zeolite and 2.0 mL of 1-pentene in benzene. The concentration of the 1-pentene ranged from 0.11 to 0.18 M. A 0.39-g zeolite sample that contains 5% iron by weight contains 1.8×10^{-4} mol of iron.

All samples of irradiation were placed in Pyrex tubes with constrictions. The tubes were equipped with small Teflon-coated magnetic stirring bars. The sample tubes were freeze–pump–thaw degassed three times and then were sealed off under vacuum. Other photolyses involved the use of isooctane, methylcyclohexane, and triisopropylbenzene.

C. Photolysis Apparatus. Photolyses were carried out with use of a 1000-W xenon arc lamp operated at a power of 500 W. The light was first passed through a copper sulfate solution filter transmitting light of wavelength 365.0–366.3 nm.[24] The light then passed through a Schott U-G-1 glass filter, which has a maximum transmittance between 355 and 360 nm.

D. Deactivation of the Solid. A series of experiments was carried out with iron pentacarbonyl supported on zeolite A, Y, and ZSM-5 to study the deactivation of the catalyst. The supported carbonyls were prepared by the vapor deposition method. After each sample had been photolyzed, the liquid and solid fractions were separated. The liquid fraction was analyzed by gas chromatography and atomic absorption. The solid fraction was sealed off in another tube with 2.0 mL of fresh pentene solution and photolyzed again. After photolysis, the liquid and solid fractions were separated and the solid was reused.

E. Dehydrated Zeolites. Na–Y was heated for 3.5 h under vacuum at 400 °C in order to dehydrate the zeolite. After dehydration, Na–Y was placed in a glovebox under a nitrogen atmosphere. Na–Y was then transferred to an inverted U-tube containing frozen iron pentacarbonyl. Iron pentacarbonyl was vaporized onto the zeolite in the manner previously described. The solid was used for photolysis and for Mössbauer analysis.

F. Ion-Exchanged Zeolites. Cs–A and Li–A zeolties were prepared by ion exchange. Salt solutions were 0.1 M. Similar procedures[26] have been previously described.

G. Gas Chromatography. Analysis of photolysis products was carried out on a Hewlett-Packard Model 5880A gas chromatograph. Flame ionization detection was used for all analyses. Silver nitrate columns, 20 ft × 0.125 in. (i.d. = 0.08 in.), were used. Column preparation involved mixing 29.6 g of silver nitrate with 20 mL of ethylene glycol. This mixture was added to 39 g of 30–60 mesh Chromosorb P and then rotated for homogeneous coverage.[25]

H. Atomic Absorption. Atomic absorption spectroscopy experiments were done with a Varian Techtron atomic absorption spectrophotometer using a multielement lamp at the iron wavelength of 248.1 nm. The solid (0.39 g) being analyzed was digested in 10–20 mL of concentrated nitric acid. The digested solutions were diluted to either 1 L or 500 mL with distilled water. Analyses of liquid samples were carried out in the same manner except that concentrated nitric acid was not added to these.

I. Fourier Transform Infrared Spectra. A Nicolet 60SX Fourier transform infrared spectrophotometer was used to characterize liquid and solid phases of samples before and after photolysis. Liquid samples were analyzed without dilution. Sodium chloride infrared cells were used for liquid analyses. Either a photoacoustic detector or a diffuse-reflectance detector was utilized to analyze the powdered solids. Carbon black was used as a background reference. In both types of detection, 32 scans were made on each sample. All samples were stored under N_2 after catalytic reactions and during the FTIR work.

Table I. Photolysis Data

zeolite	wt % iron	photolysis time, h	% conversion	trans:cis	sample no.
Na–Y	5	1.5	92.7	2.88	1
	5	18	98.3	4.37	2
	10	1.5	93.1	4.17	3
	10	18	97.2	3.76	4
Na–A	5	1.5	93.6	3.10	5
	5	18	98.6	3.74	6
	7.5	6.5	96.5	3.35	7
	7.5	15	97.8	3.96	8
Na–ZSM-5	5	1.5	83.7	2.81	9
	5	18	98.0	3.36	10
	10	1.5	85.4	2.74	11
	10	18	97.9	3.49	12
H–ZSM-5	5	1.5	97.4	3.26	13
Na–X	5	1.5	97.1	2.88	14
Li–A	5	1.5	95.5	3.70	15
	5	18	98.2	3.38	16
Cs–A	5	1.5	97.9	3.94	17

J. Mössbauer Spectra. Mössbauer transmission spectra were recorded with use of instrumentation described by Suib and co-workers.[26] All samples were referenced to iron foil.

K. X-ray Powder Diffraction. X-ray diffraction data were collected on a Diano-XRD 8000 X-ray powder diffraction apparatus. Scans were taken from 10° 2θ to 50° 2θ. Further details concerning experimental work can be found elsewhere.[42]

Results

Iron pentacarbonyl on zeolites Na–A, Na–X, and Na–Y produced samples that were yellow immediately after preparation. Zeolite ZSM-5 with iron pentacarbonyl was a pale green color after preparation. If the catalysts were exposed to air, further color changes occurred. Zeolites ZSM-5 and Na–A on exposure to air very quickly grew darker, turning to a deep rust color and generating heat. Na–Y and Na–X underwent the same reaction, but it took much longer for the color change to begin. Such oxidized materials were avoided for photolysis. Solutions that were photolyzed with newly synthesized catalysts underwent a change in color usually from clear or pale yellow to a darker yellow.

Photolyses. The variables that were investigated included tube lengths, photolysis time, stirring during photolysis, lamp power, wavelength of light transmitted, and exposure of the iron pentacarbonyl or zeolite to air before preparing samples. The results show that a 122-mm tube length, a UG-1 filter, a lamp power of 500 W, 1.5-h photolysis time, and stirring generated the highest percent conversion with all of the zeolite materials.

Representative photolysis data for zeolites Na–Y, Na–X, Na–A, Na–ZSM-5, H–ZSM-5, the ion-exchanged A zeolites, Li–A, and Cs–A, and dehyrated Na–Y are indicated in Table I. These types of experiments are reproducible to within 5%. The results of Table I clearly show that the type of zeolite influences the percent conversion and the trans to cis ratio. Zeolite A gave isomerized pentenes that are significantly different than the thermodynamic ratio (vide infra). Cation exchange of the A zeolite alters the trans to cis ratio especially in the case of Cs–A zeolite.

Control experiments were carried out in order to better understand the role of the zeolite in photolysis. These experiments included the photolysis of a liquid sample of iron pentacarbonyl with 1-pentene solution (no zeolite), samples prepared by three different methods, vapor deposition (5% iron by weight), incipient wetness (5% iron by weight), and addition of zeolite to the liquid system (5% iron by weight), samples of zeolite with 1-pentene solution (no iron pentacarbonyl), and samples of alumina and silica. The results are recorded in Table II.

Control experiment data of Table II show that there is a long induction time for an active iron species to form in homogeneous solution. When $Fe(CO)_5$ is absent, no isomerization occurs either in solution or in the presence of a zeolite. In general the percent conversion and the trans to cis ratio increase when the preparation method is varied from incipient wetness to addition of solid to liquid to the vapor deposition method. Finally, nonporous silica

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Table II. Control Experiment Data

syst investigated	prepn method	photolysis time, h	% conversion	trans:cis	sample no.
$Fe(CO)_5$ with 1-pentene	simple addition	1.5	*b*	*b*	20
		18	83.5	3.00	21
$Fe(CO)_5$ on Na-Y	(1) incipient wetness	1.5	78.5	1.67	22
	(2) addition of solid to liquid	1.5	67.3	2.50	23
	(3) vapor deposition	1.5	92.7	2.88	24
$Fe(CO)_5$ on Na-A	(1) incipient wetness	1.5	28.2	0.40	25
	(2) addition of solid to liquid	1.5	53.1	0.80	26
	(3) vapor deposition	1.5	93.6	3.10	27
1-pentene with Na-A	simple addition	1.5	0.00	*a*	28
$Fe(CO)_5$ on alumina	vapor deposition	1.5	68.3	3.01	29
		3.5	77.4	2.85	30
$Fe(CO)_5$ on silica	vapor deposition	1.5	60.1	2.54	31
		20	97.3	4.02	32

[a] No isomerization observed. [b] No *cis*-2-pentene observed.

Table III. Deactivation Studies

zeolite	total time of photolysis, h	% conversion	trans:cis	amt of iron in soln, mg[a]
Na-Y	1.5	92.7	2.88	6.3
	3.0	97.1	3.19	9.5
	4.5	97.8	3.52	9.65
	6.0	93.4	3.76	9.77
	7.5	31.7	2.81	9.85
	9.0	5.7	*b*	9.90
Na-A	1.5	93.6	3.10	3.8
	3.0	98.9	4.95	9.3
	4.5	96.1	3.88	9.57
	6.0	21.1	3.39	9.64
	7.5	1.6	*b*	9.71
ZSM-5	1.5	83.7	2.81	7.8
	3.0	89.7	3.27	12.5
	4.5	89.9	3.73	12.71
	6.0	60.0	3.50	12.82
	7.5	12.1	*b*	12.90

[a] Measured by atomic absorption spectroscopy. [b] Amount of *cis*-2-pentene too small to be observed by gas chromatography.

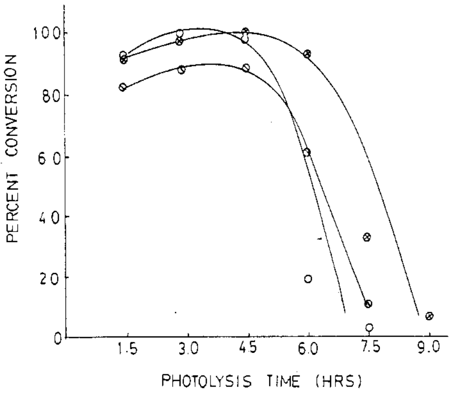

Figure 1. Percent conversion vs. time of photolysis: (○) Na-A; (⊗) Na-Y; (⊖) Na-ZSM-5. The pentene solution was replaced every 1.5 h.

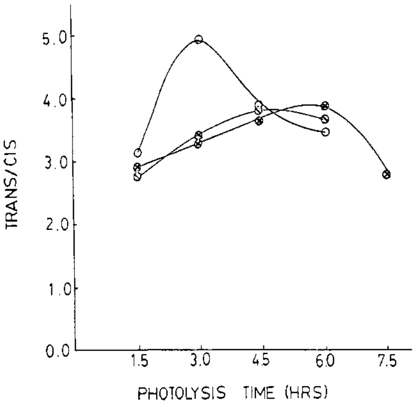

Figure 2. Product ratio of *trans*-2-pentene to *cis*-2-pentene vs. time of photolysis. The pentene solution was replaced every 1.5 h. Legend is the same as in Figure 1.

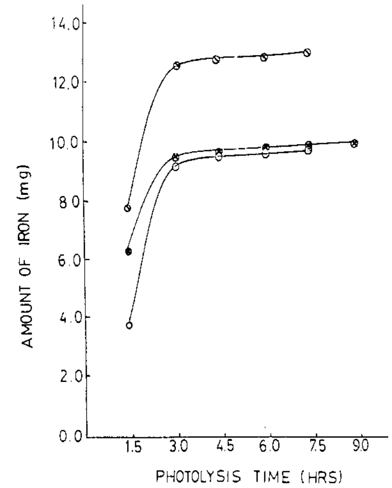

Figure 3. Amount of iron in solution vs. time of photolysis. The pentene solution was replaced every 1.5 h. Legend is the same as in Figure 1.

Table IV. Fourier Transform Infrared Data

compd	IR band freq, cm^{-1}	assignts/ref
$Fe(CO)_5$/Na-Y[a]	2034, 2006	$Fe(CO)_4$
$Fe(CO)_5$/Na-A[a]	2041, 2009	$Fe(CO)_4$
$Fe(CO)_5$/ZSM-5[a]	2043, 2013	$Fe(CO)_4$
	2170, 2161, 2023, 2014, 2088, 1760	$Fe_3(CO)_{12}$
$Fe(CO)_5$/Na-Y[b]	2110, 2056, 2037, 2010, 1990, 1956	$Fe(CO)_5$, $Fe(CO)_4$, $Fe_3(CO)_{12}$
$Fe(CO)_5$/Na-A[b]	2075, 2019, 1994, 1956	$Fe(CO)_4$ (1-pentene)
$Fe(CO)_5$/Na-Y dehydrated[a]	2059, 2044, 2013, 1985	$Fe(CO)_5$
$Fe(CO)_5$	2023, 2001	*c*
$Fe(CO)_4$	2040, 1970, 1940	*e*
$Fe(CO)_4$-(1-pentene)	2083, 2024, 2002, 1981	*c*
$Fe(CO)_3$-(1-pentene)$_2$	1925	*c*
$HFe(CO)_3(\eta^3\text{-}C_5H_9)$	2059, 1989, 1945	*c*
$Fe(CO)_5$/H-Y	2112, 2040, 2030, 2010, 1985, 1950	*d*
$Fe_3(CO)_{12}$/H-Y	2112, 2056, 2030, 1985, 1950, 1760	*d*

[a] Solid samples, unphotolyzed, photoacoustic detection. [b] Solution infrared of samples photolyzed with the solids mentioned. [c] Reference 35. [d] Reference 15. [e] Reference 10.

and alumina materials have lower percent conversions than zeolite systems.

Spectroscopy. Analyses of iron in the liquid and solid fractions of photolyzed samples were carried out by atomic absorption. The results assembled in Table III indicate that significant amounts of iron leach into solution from all zeolites. In all cases after 3 h most of the iron left the zeolite and went into solution. Figure 1 is a plot of the percent conversion vs. photolysis time. Figure 2 includes kinetic information concerning the ratio of *trans*- to *cis*-2-pentene vs. photolysis time. A plot of the total amount of iron in solution vs. photolysis time is given in Figure 3. These

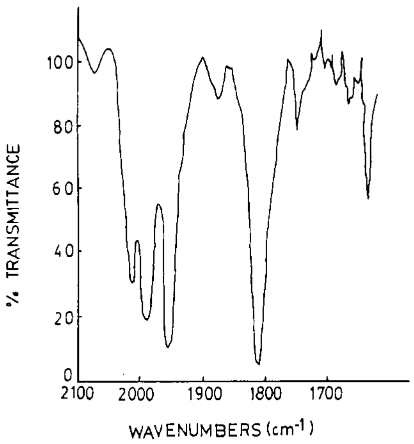

Figure 4. FTIR spectrum of photolyzed $Fe(CO)_5$ on Na–Y with 1-pentene in benzene.

Table V. Mössbauer Studies

sample	isomer shift, mm/s[a]	quadrupole splitting ΔE_Q, mm/s	assignt[b]
unphotolyzed $Fe(CO)_5$ on ZSM-5	+0.22 +0.15	1.11 0	$Fe_3(CO)_{12}$
unphotolyzed $Fe(CO)_5$ on Na–Y	+0.40	0.90	$Fe(CO)_4O/Z$
dehydrated $Fe(CO)_5$ on Na–Y	+0.04	2.57	$Fe(CO)_5$

[a] Relative to iron foil. [b] See ref 37.

figures clearly provide evidence that a majority of the iron carbonyl species leaves the solid phase.

The data for Fourier transform infrared analyses of solutions filtered from the photolyzed solid zeolite/slurries and of the photolyzed solid zeolites are given in Table IV. Infrared assignments with literature references are also incorporated here. A detailed discussion of the infrared assignments for our samples will be given later. A few points are clear from these data. Different iron carbonyl species exist on the solid zeolites even before photolysis. Secondly, solutions of the photolyzed zeolite olefin slurries indicate the presence of several iron carbonyl species. Figure 4 is an infrared spectrum of the photolyzed $Fe(CO)_5$ on Na–Y with 1-pentene in benzene. The 2100–1700-cm^{-1} region is indicative of carbonyl bands. FTIR spectra were also obtained at lower frequency, between 1000 and 950 cm^{-1}. Photolyzed samples clearly show the presence of *trans*-2-pentene at 966 cm^{-1}.

Mössbauer data for unphotolyzed zeolite samples are presented in Table V. A simple glance at the isomer shifts and quadrupole splittings of these unphotolyzed samples indicates that all three samples give different Mössbauer spectra. The listed assignments are based on the study of Herber and co-workers.[37]

We emphasize here that the data for $Fe(CO)_5$ on dehydrated Na–Y are extremely difficult to obtain. The $Fe(CO)_5$ species on dehydrated Na–Y is extremely unstable and readily oxidizes even in normal drybox environments. We are not aware of other literature reports concerning the observation of $Fe(CO)_5$ on any surface by room-temperature Mössbauer spectroscopic techniques.

Variable-Solvent Studies. Various organic solvents besides benzene were chosen in an attempt to discourage the $Fe(CO)_5$ species from migrating into solution from the zeolites. The 5 and 10 wt % samples described above are relatively high loadings. These above-reported studies also involved very high percent conversion.

Table VI. Isooctane/Na-Y Dehydrated Photolyses[a]

photolysis time, min	% conversion	trans:cis	photolysis time, min	% conversion	trans:cis
5	20	1.4	30	40	3.3
10	26	1.9	60	60	3.6
15	33	2.9	90	40	4.1
20	35	2.2			

[a] Conditions: 1 wt % $Fe(CO)_5$, Na-Y dehydrated at 400 °C, 1-pentene in isooctane.

For these reasons 1 % $Fe(CO)_5$/dehydrated zeolite samples were investigated. Vapor deposition of $Fe(CO)_5$ into a dehydrated (400 °C) Na–X zeolite was used. Solvents such as isooctane, triisopropylbenzene, and methylcyclohexane were used in subsequent photolysis experiments. Isooctane was the only solvent that did not cause some leaching, and further studies centered around this solvent. Photolysis data for low percent conversions with trans/cis ratios are given in Table VI. Fresh pentene/isooctane solutions were used after each photolysis period, but the same original zeolite was used in all of these experiments.

The data of Table VI indicate that the percent conversion steadily increases as does the trans to cis ratio of 2-pentenes with time. This behavior is markedly different from that in the studies with benzene as a solvent. The leaching experiments of this catalyst indicate that there is no loss of iron into solution and that heterogeneous catalysis is taking place.

Discussion

Photoassisted Catalytic Isomerization of Alkenes. The photochemical isomerization and hydrogenation of olefins by iron pentacarbonyl has been of much interest recently. A mechanism for photochemical isomerization proposed by Wrighton[29] has been outlined in eq 1–8. This reaction involves the formation of various

$$Fe(CO)_5 \rightarrow Fe(CO)_4 + CO \tag{1}$$

$$Fe(CO)_4 + \text{alkene} \rightarrow Fe(CO)_4(\text{alkene}) \tag{2}$$

$$Fe(CO)_4(\text{alkene}) + \text{alkene} \rightarrow Fe(CO)_3(\text{alkene})_2 + CO \tag{3}$$

$$Fe(CO)_3(\text{alkene})_2 \rightarrow Fe(CO)_3(\text{alkene}) + \text{2-alkene} \tag{4}$$

$$Fe(CO)_3(\text{alkene}) \rightarrow HFe(CO)_3(\eta^3\text{-}C_nH_{2-n}) \tag{5}$$

$$HFe(CO)_3(\eta^3\text{-}C_nH_{2-n}) \rightarrow Fe(CO)_3(\text{2-alkene}) \tag{6}$$

$$Fe(CO)_3(\text{2-alkene}) + \text{alkene} \rightarrow Fe(CO)_3(\text{alkene})(\text{2-alkene}) \tag{7}$$

$$Fe(CO)_3(\text{alkene})(\text{2-alkene}) + CO \rightarrow Fe(CO)_4(\text{alkene}) + \text{2-alkene} \tag{8}$$

16- and 18-electron species. The mechanism also includes the formation of a π-allyl hydride complex (step 5).

Schroeder and Wrighton reported the iron pentacarbonyl catalyzed isomerization of 1-pentene with near-ultraviolet irradiation.[30] When a solution of 1-pentene and iron pentacarbonyl in benzene was photolyzed, the thermodynamic ratio of 3.3% 1-pentene, 20.7% *cis*-2-pentene, and 76.0% *trans*-2-pentene was reached in approximately 95 min. Wrighton and co-workers have also bound iron pentacarbonyl to phosphinated polymers.[35] After 12 h of photolysis in a benzene solution, 29.6% conversion to the 2-pentenes was observed.

Photoassisted Zeolite Isomerizations. The photolysis data for the $Fe(CO)_5$/zeolite benzene slurries recorded in Tables I and II show that there is at least a secondary influence of the type of zeolite used. Cation effects are also evident. The preparation method very likely controls the degree of dispersion of the iron carbonyl species. For instance, the incipient wetness data suggest that the dispersion of the iron species is lower than for the vapor deposition method.

The presence of these zeolites clearly alters the percent conversion and the trans to cis ratio as compared to those for homogeneous reactions or reactions on other supports like silica or alumina. The trans to cis ratio is found to vary from about 2.7

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to 4.4. Zeolites Na–Y and Na–X, which have a similar structure but different Si/Al ratios, behave very similarly in terms of overall activity and in product selectivity. Longer photolysis time usually leads to increased percent conversion as well as an increase in the trans to cis ratio. Compare, for instance, samples 1 and 2, 5 and 6, 7 and 8, 9 and 10, 11 and 12, and 15 and 16.

The last two entries of Table I are included to show that ion exchange of other cations besides sodium does indeed affect the percent conversion and the product isomer ratio. Both the lithium and cesium ion-exchanged materials yielded greater percent conversion and a higher *trans*-2-pentene to *cis*-2-pentene ratio than the sodium form of zeolite A. Tempere and Imelik have investigated the thermal isomerization of 1-butene on various metal-exchanged A zeolites.[31] Their data clearly indicate that *trans*-2-butene can be obtained in higher yields than *cis*-2-butene depending on the cation size. For example, on Li–A a trans to cis ratio of 10:1 was obtained. Isomerization on Na–A gave products with a ratio of 1:2.

These cation affects are perhaps understandable with respect to the proposed electrostatic field effects[10,22] that the iron carbonyl species encounter on the zeolite surfaces.[10] Nagy, Van Eenoo, and Derouane[22] have proposed that the low *cis*-2-butene yields in thermal experiments occur due to a coulombic field effect between the pore mouth and the reactant molecules. They suggest that the dipole moment of *cis*-2-butene does not allow it to enter the zeolite pores. Such electrostatic effects may be operative in the systems described here.

The data of Table II indicate that other solid supports such as alumina and silica can provide sites or an activation pathway for the iron carbonyl species. The lower percent conversions suggest that the pore systems of the zeolites are important in providing a mechanism for the photoisomerization to take place.

Catalyst Preparation. The interaction of $Fe(CO)_5$ with zeolites has been described by several researchers.[10,15,22,26,27] Dehydrated zeolites allow the $Fe(CO)_5$ to remain intact. The infrared and Mössbauer results of Tables IV and V indicate that hydrated zeolites do indeed cause decomposition of the $Fe(CO)_5$ to an oxidized form, to another cluster ($Fe_3(CO)_{12}$), or to combinations of the above. After photolysis both these oxidized species and the trinuclear cluster migrate into the solution if benzene is used as a solvent.

Such studies suggest that benzene is a poor choice of solvent when $Fe(CO)_5$ is present. Indeed it is well-known that iron–benzene complexes do form. X-ray structural studies show that no gross degradation of the zeolites occurs before or during photolysis. Stable $Fe(CO)_5$ species can be prepared by using dehydrated zeolites. Stable $Fe(CO)_5$/zeolite slurries can be prepared with isooctane as solvent.

Catalyst Stability. It is clear from the data of Table III and Figures 1–3 that one role of the zeolite is to catalyze the formation of the active iron species *in solution* in order to obtain higher conversions. Such an induction period is also apparent for $Fe(CO)_5$ in solution. In these hydrated systems the $Fe(CO)_5$ has been oxidized to a $Fe(CO)_4$ (zeolite) species according to Mössbauer experiments (see below).

For the catalysts prepared with benzene as a solvent, the percent conversion for the large-pore zeolites X and Y is retained at a higher value for a longer period of time (Figure 1) than for ZSM-5 or zeolite A. This is likely explained by the retention of some of the $Fe(CO)_x$ species in the interior cavities of the zeolite. The amount of iron in solution (Figure 3) and the trans to cis ratio (Figure 2) peak at a longer photolysis time (6 h) for zeolite Y than for the ZSM-5 and A systems (4 h). This could again be due to retention of $Fe(CO)_x$ species in the pores of zeolite Y for a longer period of time.

The fact that Na–Y yielded a greater conversion than either Na–A or Na–ZSM-5 can perhaps be explained by the pore sizes of the zeolites and the size of $Fe(CO)_5$. The Na–Y zeolite has a pore size of 7.4 Å while Na–A has a smaller pore size (4.2 Å).[32] The size of the $Fe(CO)_5$ molecule is 5.90 Å.[33] The smaller pore A zeolite would therefore not allow the iron pentacarbonyl to enter the inner channels. This is not the case with zeolite Y. Several others have suggested that $Fe(CO)_5$ does indeed enter the internal cavities of Na–Y and H–Y.[10,22,26]

The dehyrated Na–Y zeolite with $Fe(CO)_5$ has been studied at low percent conversions as reported in Table VI. Leaching experiments indicate that iron species do not leave the solid zeolite when isooctane/olefin mixtures are used in the photolysis experiments. The data concerning the heterogeneous photoassisted isomerization of 1-pentene with the isooctane solvent indicate that at short photolysis times *cis*-2-pentene is the favored product. At longer photolysis times it is possible that the product distribution changes due to an equilibrium shift toward the thermodynamically favored *trans*-2-pentene.

On the basis of mass balances of the amount of isomerization vs. the total moles of iron present in these systems, these reactions are catalytic. For instance, the number of moles of isomerization products is greater than 10 times the number of moles of iron carbonyl present on the zeolite for the isooctane mixture described above.

Supporting Characterization Work. Chase and Weigert[34] and Wrighton and co-workers[35] have used infrared methods to determine the mechanism of olefin isomerization.[40] The infrared data of Table IV have already been referred to for the unphotolyzed samples. The photolyzed materials, however, lead to information concerning the change of the $Fe(CO)_5$ species near the surface of the photocatalyst. Peaks between 3200 and 3000 cm^{-1} can be attributed to the carbon–hydrogen bonds of the olefin and benzene. The peaks between 3000 and 2800 cm^{-1} are due to the carbon–carbon single bonds of the pentene. A band at 966 cm^{-1} is due to *trans*-2-pentene.[34] The data indicate that several species exist on the photolyzed surface.

The carbonyl bands between 2450 and 1800 cm^{-1} are of most interest in the present work. Although carbonyl peaks are generally found in the range of 2200–1800 cm^{-1}, shifts to higher wavelengths in the presence of the zeolite have been attributed to weaker carbonyl bonds due to lattice interactions.[5] The data of Figure 4 show the change that occurs in the FTIR spectra after photolysis.

Infrared and leaching experiments support the mechanism outlined in eq 1–8. Since the starting zeolite species prepared with benzene is a subcarbonyl species or a trinuclear cluster (see Mössbauer results also), it is likely that only three carbonyl groups or less are needed during the photoisomerization. Table IV contains information that suggests that loss of CO is facile in the benzene solvent systems.

The Mössbauer data of Table V indicate that $Fe_3(CO)_{12}$ has formed on the unphotolyzed ZSM-5 surface. The unphotolyzed zeolite Na–Y sample, on the other hand, is consistent with a $Fe(CO)_4O/Z$ complex. Similar isomer shifts (+0.50 mm/s) and quadrupole splittings (0.85 mm/s) have been obtained for the $Fe(CO)_4I_2$ complex.[37]

After considerable effort we have finally observed a Mössbauer spectrum for $Fe(CO)_5$ vacuum sublimed onto dehydrated Na–Y. Even in a good drybox this compound is extremely unstable. The considerably large quadrupole splitting of 2.57 mm/s and the isomer shift of +0.04 mm/s are consistent with earlier low-temperature matrix studies.[37]

Conclusions

We have shown that iron pentacarbonyl can be introduced into various zeolites and can selectively isomerize 1-pentene to various ratios of *cis*- and *trans*-2-pentene via photochemical activation. The zeolite either can act to decrease the induction period to prepare active homogeneous catalytic species or can trap the

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$Fe(CO)_5$ and be a heterogeneous catalyst if the solvent does not attact the $Fe(CO)_5$. The surface interactions between the metal carbonyl and the zeolite are quite complex, although analogies have been observed with similar systems that are thermally activated. Even when additional steps such as surface derivatization of hydroxyl groups[39] of silica or alumina are taken, leaching of metal carbonyls into solution eventually occurs. We have shown that the proper choice of solvent can prevent such leaching.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the University of Connecticut Research Foundation for partial support for this work.

Registry No. $Fe(CO)_5$, 13463-40-6; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; benzene, 71-43-2; isooctane, 540-84-1.

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Uranyl Clay Photocatalysts

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Received April 18, 1984

Uranyl-exchanged clay photocatalysts have been used to photooxidize alcohols to ketones. Luminescence excitation, emission, and lifetime studies have been used to characterize these materials before, during, and after reaction. The absorption maxima for most of the uranyl-exchanged clays shift to higher wavelengths with respect to those for other aluminosilicate catalysts. Lifetime results indicate that several sites exist on these catalysts. Saturation of alcohol/clay slurries with oxygen leads to increasing rates of ketone formation. These uranyl-sensitized photoautoxidation reactions also produce coupled products as well as aldehydes, such as acetaldehyde, as identified by gas chromatography/mass spectrometry techniques. Different clays yield different amounts of product and rates of product formation. Hectorite exchanged with uranyl ions is the most active catalyst of all aluminosilicate materials we have studied over short photolysis times.

Introduction

We have recently reported[1,2] that uranyl-exchanged zeolites are good photooxidation catalysts for isopropyl alcohol conversion to acetone. The pore size and the state of dehydration of the zeolite are important factors in this reaction. The rate of formation of acetone remained essentially the same even after 300 h of photolysis. There are two major problems, however, with these zeolite photocatalysts. One problem concerns the low yield of the products. The other problem involves the wavelength for absorption. The zeolite photooxidation catalysts absorb at 425 nm, which is an attractive wavelength for solar irradiation, but it would be useful to have systems that absorb at higher wavelengths.

Clays, like zeolites, are aluminosilicates. Clays, however, have layered structures.[3] Relatively few photochemical studies of clays have been reported. Europium- and terbium-exchanged clays have been studied with lifetime methods[4] to understand the environment of rare-earth ions in these clays. Water splitting with $Ru(bpy)_3^{2+}$ ions exchanged into clays has also been studied.[5] Fluorescent organic probes have also been used to study surface interactions.[6]

The present study involves the incorporation of uranyl ions into hectorite, montmorillonite, bentonite, and vermiculite. The luminescence excitation and emission characteristics of these materials have been studied in order to understand the behavior of uranyl ions in clays under various thermal treatments. Lifetime experiments were carried out to obtain information regarding the number of uranyl sites in these clay materials. Each of the uranyl clays was tested in photooxidation reactions of alcohols. Various products were obtained, and the reactions were shown to be catalytic. The results obtained with the clay catalysts are compared to those with zeolite catalysts.

Experimental Section

Materials. Hectorite was obtained as a white, centrifuged powder from Baroid Sales, Houston, TX. The composition of dehydrated hectorite is $Ex_xMg_{6-x}Li_xSi_8O_{20}(OH,F)_4$. Cheto clay, a natural montmorillonite, was obtained from Filtrol Corp., Chambers, AZ. Samples were ground in a mortar and pestle. The approxmate formula of cheto was $Ca_{0.24}Na_{0.07}K_{0.07}Mg_{0.32}Fe_{0.07}Al_{1.38}Si_4O_{10}(OH)_2$. The samples of vermiculite used were similar to normal packing material. The composition of dehydrated vermiculite is $Ex_xMg_3Al_xSi_{4-x}O_{10}(OH)_2$. The samples were ground in a mortar and pestle.

Bentonite, a sodium montmorillonite, was obtained in two different mesh sizes from the American Colloid Co., Skokie, IL. The samples were SPV 200 (74 μm) Microfine, HPM-20, and SPV 325 (44 μm) Volclay, Asphalt Emulsion grade powder. The composition of bentonite was $NaCa_{0.33}(Al_{1.0}Fe_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$.

Uranyl acetate dihydrate was purchased from Fisher Scientific Co., Eimer and Amend, New York, NY, lot no. 47660. Spectral grade isopropyl alcohol and acetonitrile were purchased from J. T. Baker Chemical Co., Phillipsburg, NJ.

For more details of the clay samples please refer to Table VI. Chemical analyses before and after UO_2^{2+} exchange, surface areas, and cation-exchange capacities are reported.

Synthesis of Uranyl-Exchanged Clays. Solutions of 0.10 M UO_2^{2+} were made by dissolving 4.26 g of $UO_2(CH_3CO)_2{\cdot}2H_2O$ in 100 mL of distilled and deionized water (DDW). This was added to 1.00 g of clay in a round-bottom flask and magnetically stirred for 24 h. The exchanged clays were then filtered through ground-glass funnels of fine porosity, washed with 5–10 mL of DDW, and allowed to dry in air. Most clays were ground in a mortar and pestle after drying.

Bulk Photolysis Conditions. The quartz barrel photolysis cell used in this study was 20 mm in diameter and 50 mm in length. The entry port (5-mm diameter) was stoppered during photolyses. In all cases 0.30 g of uranyl-exchanged clay was placed in the cell with 5.00 mL of a 0.65 M isopropyl alcohol in acetonitrile solution. Independent volume measurements of the solutions before and after irradiation indicated no evaporation loss in this cell. The large dimension of the cell was designed

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