and acetylenes, should itself be unreactive toward further insertion of acetylene. Such behavior is not uncommon; most studies with dihydrides have similarly reported insertion into only one M–H bond, for example, the work of Otsuka et al.[1,2,53] with the dihydrides $Cp_2MH_2$, M = Mo or W.

More recently, however, it has been pointed out[54] that insertion into both M–H bonds of these hydrides can be observed with alkynes of low steric hindrance. Clearly, with the Pt(II) dihydrides used in our investigations, steric effects must be particularly important. The stereochemistry of tricyclohexylphosphine Pt(II) complexes will be discussed in detail elsewhere, and it is sufficient here to point out that the tricyclohexylphosphine behaves like a bulky conic cog, with cone angle[55] values determined from crystal structure studies in the range 163–181°.[56] It is also likely that in the monoalkenyl product, the P–Pt–P angle containing the second hydride ligand will be less than 180°; in the hydridoalkenyl product described here and containing the P-*t*-$Bu_2$-*n*-Bu ligand of comparable size, this angle is 163.5 (1)°. The second hydride ligand is, therefore, essentially "lined" and protected by the two cis tricyclohexyl phosphines; its lack of reactivity toward alkyne insertion is then attributed entirely to steric effects.

**Acknowledgment.** The continued financial support (to H.C.C., GF., and to E.G.J.) of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged, as is the loan of platinum compounds by Johnson and Matthey Ltd.

**Registry No.** DMA, 762-42-5; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)($PCy_3$)$_2$, 104215-64-7; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)($PCy_3$)$_2$, 104215-65-8; *trans*-PtH(*trans*-$CH_3OOC{=}CHCH_3$)($PCy_3$)$_2$, 104215-66-9; *trans*-PtH(*trans*-$CH_3OOC{=}CHPh$)($PCy_3$)$_2$, 104215-67-0; *trans*-PtH(*trans*-$NCC{=}CHCH_3$)($PCy_3$)$_2$, 104215-68-1; *trans*-PtH(*trans*-$NCC{=}CHPh$)($PCy_3$)$_2$, 104215-69-2; *trans*-PtH(*trans*-$CF_3C{=}CHPh$)($PCy_3$)$_2$, 104215-70-5; *trans*-PtH($CH_3OOCC{=}CH_2$)($PCy_3$)$_2$, 104215-71-6; *trans*-PtH($NCC{=}CH_2$)($PCy_3$)$_2$, 104215-72-7; *trans*-PtH($CF_3C{=}CH_2$)($PCy_3$)$_2$, 104215-73-8; *trans*-PtH($CH_2{=}CHCH_2OOCC{=}CH_2$)($PCy_3$)$_2$, 104215-74-9; *trans*-PtH($CH{\equiv}CCH_2OOCC{=}CH_2$)($PCy_3$)$_2$, 104215-75-0; *trans*-PtH(*trans*-(4-$O_2NC_6H_4$)$C{=}CHPh$)($PCy_3$)$_2$, 104240-24-6; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*i*-$Pr_3$)$_2$, 104215-76-1; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*i*-$Pr_3$)$_2$, 104215-77-2; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*t*-$Bu_2$-*n*-Bu), 104215-58-9; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*t*-$Bu_2$-*n*-Bu)$_2$, 104215-59-0; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*t*-$Bu_2Me$)$_2$, 104215-60-3; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*t*-$Bu_2Me$)$_2$, 104215-61-4; *trans*-$PtD_2$($PCy_3$)$_2$, 104215-62-5; *trans*-$PtCl_2$($PCy_3$)$_2$, 60158-99-8; *cis*-Pt($PEt_3$)$_2$Cl(*trans*-$CH_3OOCC{=}CHCOOCH_3$), 65059-02-1; *trans*-Pt($PEt_3$)$_2$Cl(*cis*-$CH_3OOCC{=}CHCOOCH_3$), 65059-01-0; *trans*-Pt($PEt_3$)$_2$Cl(*trans*-$CH_3OOCC{=}CHCOOCH_3$), 65059-03-2; *cis*-Pt($PEt_3$)$_2$Cl(*cis*-$CH_3OOCC{=}CHCOOCH_3$), 57127-81-8; *trans*-PtH($PCy_3$)$_2$(DMA), 104240-19-9; *trans*-PtH($PCy_3$)$_2$($HC{\equiv}CCOOCH_3$), 104240-20-2; *trans*-PtH($PCy_3$)$_2$($DC{\equiv}CCOOCH_3$), 104240-21-3; *trans*-PtH($PCy_3$)$_2$($C_6H_5C{\equiv}CCOOCH_3$), 104240-22-4; *trans*-PtH($PCy_3$)$_2$($C_6H_5C{\equiv}CCF_3$), 104240-23-5; *trans*-PtH(P-*t*-$Bu_2Me$)$_2$($CH_3OOCC{\equiv}CCOOCH_3$), 104215-63-6; $PCy_3$, 2622-14-2; P-*i*-$Pr_3$, 6476-36-4; *p*-*t*-$Bu_2$-*n*-Bu, 29949-72-2; P-*t*-$Bu_2Me$, 6002-40-0; $CF_3C{\equiv}CCF_3$, 692-50-2; $CH_3C{\equiv}CCOOCH_3$, 23326-27-4; $C_6H_5C{\equiv}CCOOCH_3$, 4891-38-7; $CH_3C{\equiv}CCN$, 13752-78-8; $C_6H_5$-$C{\equiv}CCN$, 935-02-4; $C_6H_5C{\equiv}CCF_3$, 772-62-3; $HC{\equiv}CCOOCH_3$, 922-67-8; $HC{\equiv}CCN$, 1070-71-9; $HC{\equiv}CCF_3$, 661-54-1; $HC{\equiv}CCOOCH_2CH{=}CH_2$, 14447-00-8; $C_6H_5C{\equiv}C$(*p*-$C_6H_4NO_2$), 1942-30-9; $HC{\equiv}CCOOCH_2C{\equiv}CH$, 4383-39-5; $D_2$, 7782-39-0.

**Supplementary Material Available:** A listing of calculated hydrogen coordinates, thermal parameters, and bond angles (6 pages); tables of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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# Comparison of the Photochemical and Photophysical Properties of Clays, Pillared Clays, and Zeolites[†]

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**Abstract:** Uranyl-containing pillared clays, uranyl-exchanged clays, and zeolites have been used to photooxidize solutions of ethanol and diethyl ether. Product analysis indicates that uranyl ions in the clay pillars produce a more selective catalyst than materials obtained by inserting uranyl ion in the interlamellar spacings of the clay. Mechanisms are proposed to distinguish reactivity and selectivity differences of these photocatalysts. Incorporation of uranyl ions does not significantly affect the cracking properties of pillared clay catalysts.

## I. Introduction

Photochemical methods,[1-11] such as luminescence excitation, emission, and lifetime experiments on organic[1-4] and inorganic dopants,[3,5-10] have been proven useful in understanding processes that occur during electron transfer,[8] energy transfer[9,10] and photoassisted catalysis on solid surfaces.[2,3,7] Luminescence can provide information concerning excited-state species that occur on aluminosilicate surfaces and changes that these species undergo

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**Table I.** Bentonite Oxide Composition (wt %) Before and After Pillaring[a]

| | bentonite- | | | |
|---|---|---|---|---|
| | Ca | $UO_2$ | ACH-($UO_2^{2+}$) | ($UO_2^{2+}$,ACH) |
| $SiO_2$ | 62.88 | 58.81 | 57.70 | 50.08 |
| $Al_2O_3$ | 20.00 | 20.77 | 28.29 | 28.15 |
| $Na_2O$ | 0.53 | 0.35 | 0.41 | 0.36 |
| $K_2O$ | 2.32 | 0.39 | 0.49 | 0.53 |
| CaO | 2.58 | 0.55 | 0.35 | 0.58 |
| MgO | 2.16 | 2.18 | 1.80 | 2.31 |
| $Fe_2O_3$ | 4.38 | 4.01 | 3.68 | 3.83 |
| $UO_2^{2+}$ | - | 9.91 | 0.33 | 2.96 |
| | 94.85 | 96.97 | 93.05 | 88.80 |

[a] Chemically bonded water is not included.

during chemical and physical treatments.[4-6] Photoassisted catalytic reactions[2,3,7] on high surface area solids with well-ordered microporosity (like zeolites and heat-stable pillared clays[12,13]) could yield the selectivity effects observed in catalytic cracking and hydrocarbon conversion reactions.[14]

Pillared clays are catalysts obtained by replacing charge compensating cations between the clay silicate layers with large polyvalent cations.[15-17] When heated, these polyoxocations form inorganic clusters (pillars) that prop the clay silicate layers open, exposing its interlamellar space to sorption and catalysis.[16,18] The most commonly used pillars (or propants) are those derived from the dehydroxylation of polyoxocations of zirconium[15] and aluminum,[16,17] as well as from colloidal alumina and alumina-coated silica particles.[19,20] Pillared clays have been reviewed recently by Pinnavaia.[21]

The purpose of this paper is to compare the photochemical and photophysical properties of uranyl-exchanged clays,[7] pillared clays, and zeolites.[3] Luminescence excitation, emission, and lifetime behavior of these catalysts have been studied; the $UO_2^{2+}$ ion is known to luminesce and in the excited state is an excellent oxidant. Ethanol conversion to acetaldehyde, and acetal and diethyl ether oxidation to acetaldehyde and ethanol will be reported. Product selectivities and conversions are given, and mechanisms are proposed which can account for the observed product selectivities.

## II. Experimental Section

**$UO_2^{2+}$-Bentonites.** A clay slurry (pH ~9.7) was formed by vigorously stirring 100 g of Ca-Bentonite (obtained from the American Colloid Co.) in 10 L distilled water at 40 °C for 24 h. The ion-exchange solution was prepared by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ in distilled water and aging the 0.1 M solution at 60 °C for 24 h at pH ~1.95. The uranyl nitrate solution was then added (dropwise) to the bentonite slurry at 40 °C; stirring was continued for 1 h at pH ~3.28. After filtration (under vacuo) the uranyl-exchanged clay ($UO_2^{2+}$-bentonite) was washed with 10 L of distilled water at 60 °C. Approximately one-third of the cake was formed into $^1/_{16}$-in. extrudates which were then dried in air at 120 °C for 10 h, sized to 100 × 325 mesh granules, and tested for catalytic properties.

**ACH-($UO_2^{2+}$-Bentonite).** The remaining two-thirds of the $UO_2^{2+}$-bentonite was reslurried in 6 L of distilled water and heated to 50 °C, and the $UO_2^{2+}$ ions were back-exchanged with a solution prepared by diluting 100 g of aluminum chlorohydroxide (ACH) solution (Chlorhydrol from the Reheis Chemical Co.) with 2 L of water. The pH dropped to 4.2 from 6.0 and the slurry assumed (at the end of titration) a yellowish coloration characteristic of $UO_2^{2+}$-containing solutions. The slurry was then filtered and the ACH-($UO_2^{2+}$-bentonite) was washed with hot (50 °C) water until $Cl^-$ could no longer be detected; its chemical composition is presented in Table I. The preparation of reference materials containing only $Al_2O_3$ pillars (ACH-bentonite) has been described elsewhere.[18]

**($UO_2^{2+}$,ACH)-Bentonite.** The catalyst was prepared by reacting Ca-bentonite with a mixture prepared by adding 0.1 M $UO_2(NO_3)_2{\cdot}6H_2O$ to diluted Chlorhydrol; the exchange solution was then aged for 24 h at 60 °C prior to use. The finished catalyst preparation is similar to that of ACH-bentonite; the chemical composition is shown in Table I.

**Other Samples.** Conditions for the preparation of other uranyl-containing clays and zeolites have been reported elsewhere.[3,7] Catalyst preparation involves the ion exchange of uranyl ($UO_2^{2+}$) ions into the solid support at room temperature; microanalyses can be found in the corresponding articles.[3,7] Cheto clay (an acid-washed bentonite) was obtained from the Filtrol Corp. Two other Na-bentonite samples were obtained from the American Colloid Co.; 90% of the clays have particles smaller than 200 and 325 mesh, respectively. Typical analysis gave 63% $SiO_2$ and 21% $Al_2O_3$ with 3.0-4.0% iron (as $Fe_2O_3$) impurities. The hectorite sample was obtained from the Industrial Chemical Division of National Lead Industry.

**Luminescence Studies.** Luminescence excitation and emission spectra were collected on a Spex Fluorolog in the right angle mode. Variations in the emission intensity of the Xe lamp source were corrected with a quantum counter. Samples were loaded into cuvettes for room-temperature studies.

Luminescence lifetime experiments were done with a PRA Model 3000 system which was modified in several ways as described below. A PRA Nitromite nitrogen laser was used as an excitation source and a Bausch & Lomb UV-vis grating monochromator (Model 33-86-79) was inserted between the sample compartment and the photomultiplier tube. Deconvolution was done with a program capable of separating three lifetime components.

**Bulk Photolyses.** A continuous output Xe lamp (Kratos Corp., Model LH-51) irradiated the catalyst suspended in organic solutions. The light was filtered through a bottle (40-mm path length) of distilled water and then through a 400-nm cutoff filter (No. GG.400) from Schott Optical Glass, Duryea, PA. After photolyses, samples were syringed into a gas chromatograph. Retention times and columns used have been described elsewhere.[3,7]

Solutions (~0.1 M) of isopropyl alcohol, diethyl ether, ethyl alcohol, and methyl alcohol were prepared by dissolution in acetonitrile as solvent. Approximately 0.3 g of catalyst and 5 mL of organic solution were used in all photolysis experiments.

**Gas Chromatography Mass Spectrometry Analyses.** Products of the bulk photolysis experiments were analyzed by using a Hewlett-Packard Model 5985 GC/MS. Carbowax 20M columns employed in gas chromatography experiments were also utilized for GC/MS analyses. NBS and EPA libraries permitted identification of unknown compounds.

**Gas Oil Cracking Experiments.** Cracking activity was evaluated by a microactivity test similar to that described by Ciapetta and Anderson.[22] Prior to testing, catalysts were heated (in dry air) at 300 °C for 10 h. Percent conversion is defined as $(V_f - V_p)100/V_f$ where $V_f$ is the volume of the fresh feed (FF) cracked and $V_p$ is the volume of product boiling above 204 °C.

## III. Results

Luminescence lifetime experiments were performed to determine the number of emitting excited-state species present. Previous luminescence lifetime results for uranyl-exchanged zeolites[3] have shown double-exponential decays, indicating the presence of at least two excited-state species attributed to two different crystallographic sites of the $UO_2^{2+}$ ion. An alternative explanation

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**Table II.** Diethyl Ether Photolysis[a]

| sample[b] | % $UO_2$ | mol of acetaldehyde | mol of ethanol | ratio[c] |
|---|---|---|---|---|
| $UO_2^{2+}$–bentonite[e] | 6.7 | $1.7 \times 10^{-4}$ | $1.3 \times 10^{-4}$ | 1.3 |
| $UO_2^{2+}$–bentonite[f] | 5.9 | $1.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | 1.5 |
| $UO_2^{2+}$–hectorite | 5.9 | $5.5 \times 10^{-4}$ | $2.1 \times 10^{-4}$ | 2.6 |
| $UO_2^{2-}$cheto clay | 4.9 | $1.9 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | 1.1 |
| ($UO_2^{2+}$,ACH)–bentonite | 9.9 | $9.0 \times 10^{-5}$ | $6.5 \times 10^{-5}$ | 1.4 |
| ACH–($UO_2^{2+}$–bentonite) | 0.3 | $7.0 \times 10^{-6}$ | $7.5 \times 10^{-6}$ | 0.9 |
| $UO_2^{2+}$–X zeolite | 7.0 | $1.5 \times 10^{-4}$ | $1.0 \times 10^{-5}$ | 1.5 |
| ACH–bentonite | | *d* | *d* | *d* |

[a] Photolysis for 4 h, 750–W Xe lamp power. [b] See Experimental Section for synthesis details. [c] Ratio of moles of acetaldehyde to ethanol. [d] No products observed. [e] 200 mesh. [f] 325 mesh.

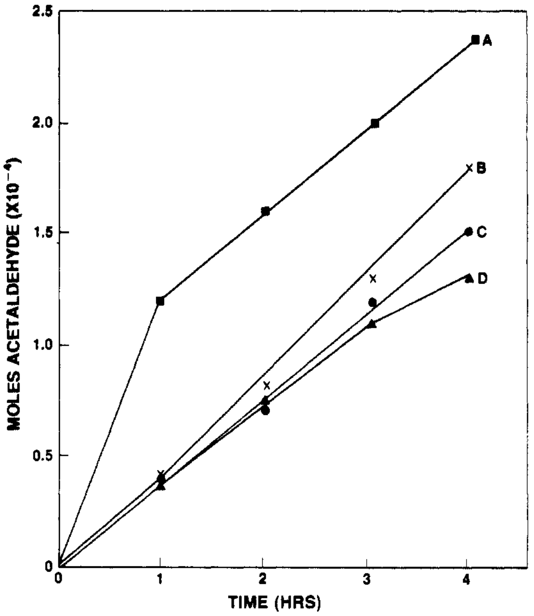

**Figure 1.** Acetaldehyde production from photolysis of diethyl ether solutions with uranyl-exchanged clay catalysts. (A) $UO_2^{2+}$–hectorite. (B) $UO_2^{2+}$–cheto clay. (C) $UO_2^{2+}$–bentonite (200 mesh). (D) $UO_2^{2+}$–bentonite (325 mesh).

may be that the uranyl coordination environment is different for the two different species. Lifetime data for clays[9] show either double- or triple-exponential behavior. All these lifetimes range from 6 to 180 μs.[3,9]

($UO_2^{2+}$,ACH)–bentonite (prepared by adding uranyl ions to the ACH solution prior to pillaring) has single-exponential character. The fit to a double exponential (even over a larger channel number) for this material is much worse with respect to the $\chi^2$ value and the randomness of the sum of the squares of residuals. The single-exponential lifetime for this material is 48.7 ± 0.3 μs. Luminescence lifetime measurements of bentonites exchanged with ACH solutions were not possible since these materials did not emit in the wavelength range (~520 nm) assigned to the $UO_2^{2+}$ moiety.[4,7,9,25,26]

**Photoassisted Catalytic Experiments.** Results from the photolyses of diethyl ether with $UO_2^{2+}$-containing zeolites, clays, and pillared clay are given in Table II. Acetaldehyde and ethanol production (in ether solution) as a function of time are shown in Figures 1 and 2, respectively. Results from ethanol photolyses are in Table III; Figures 3 and 4 show the corresponding plots of acetaldehyde and acetal formation over a 4-h time period.

The results in Figures 1–4 show that the rates of production of acetaldehyde, ethanol, and acetal are greatest for $UO_2^{2+}$-ex-

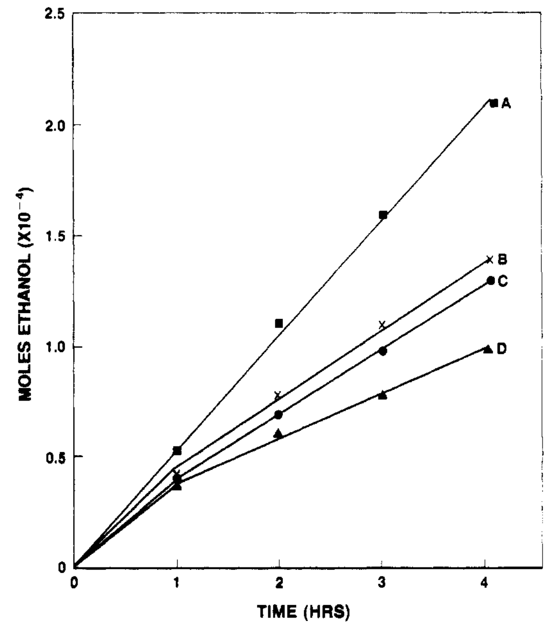

**Figure 2.** Ethanol production from photolysis of diethyl ether solutions with uranyl-exchanged clay catalysts. (A) $UO_2^{2+}$–hectorite. (B) $UO_2^{2+}$–cheto clay. (C) $UO_2^{2+}$–bentonite (200 mesh). (D) $UO_2^{2+}$–bentonite (325 mesh).

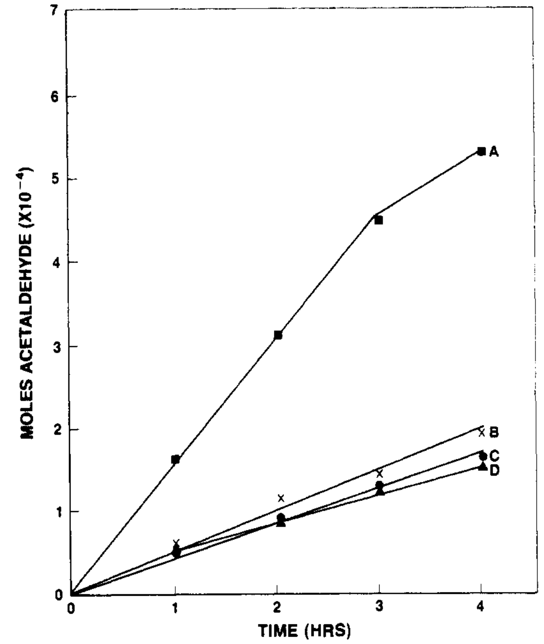

**Figure 3.** Acetaldehyde production from photolysis of ethanol solutions with uranyl-exchanged clay catalysts. (A) $UO_2^{2+}$–hectorite. (B) $UO_2^{2+}$–bentonite (325 mesh). (C) $UO_2^{2+}$–cheto clay. (D) $UO_2^{2+}$–bentonite (200 mesh).

**Table III.** Ethanol Photolysis[a]

| sample[b] | mol of acetaldehyde | mol of acetal | ratio[c] |
|---|---|---|---|
| $UO_2^{2+}$–bentonite[f] | $1.3 \times 10^{-4}$ | $1.4 \times 10^{-5}$ | 9.6 |
| $UO_2^{2+}$–bentonite[g] | $1.9 \times 10^{-4}$ | $4.1 \times 10^{-5}$ | 4.6 |
| $UO_2^{2+}$–hectorite | $2.4 \times 10^{-4}$ | $1.1 \times 10^{-5}$ | 2.2 |
| $UO_2^{2+}$–chetoclay | $1.5 \times 10^{-4}$ | $2.0 \times 10^{-5}$ | 7.7 |
| ($UO_2^{2+}$,ACH)–bentonite | $1.1 \times 10^{-4}$ | *d* | *d* |
| ACH–($UO_2^{2+}$–bentonite) | $1.4 \times 10^{-5}$ | $3.7 \times 10^{-6}$ | 3.6 |
| $UO_2^{+2}$–X zeolite | $2.6 \times 10^{-4}$ | *d* | *d* |
| ACH–bentonite | *e* | *e* | *e* |

[a] Photolysis time = 4 h, 750-watt Xe lamp power. [b] See Experimental Section for synthesis details. [c] Moles of acetaldehyde to acetal. [d] No acetal detected. [e] No products detected. [f] 200 mesh. [g] 325 mesh.

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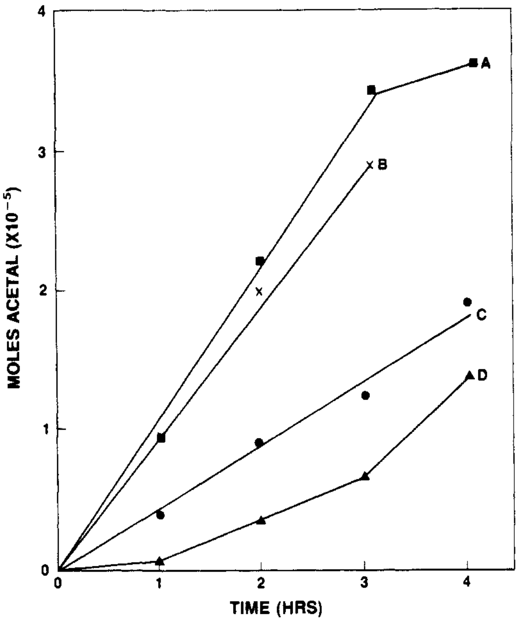

**Figure 4.** Acetal production from photolysis of ethanol solutions with uranyl-exchanged clay catalysts. (A) $UO_2^{2+}$-hectorite. (B) $UO_2^{2+}$-bentonite (325 mesh). (C) $UO_2^{2+}$-cheto clay. (D) $UO_2^{2+}$-bentonite (200 mesh).

changed hectorites. This is particularly evident in the production of acetaldehyde from photolysis of diethyl ether solutions. The other $UO_2^{2+}$-containing catalysts are less active; however, the order of activity appears to depend on the specific organic substrate that is being oxidized. For example, the order of decreasing activity is cheto > bentonite > 200-bentonite > 325-bentonite for diethyl ether photolysis. For ethanol photolysis, the order changes, 325-bentonite > cheto > 200-bentonite. This relative ordering is the same irrespective of the specific photochemical reaction product.

When photolyzed in the presence of isopropyl alcohol, uranyl-exchanged zeolites produced only acetone,[3] whereas uranyl-exchanged clays produced acetone, acetaldehyde, and isopropyl formate.[7] Selective formation of acetone was also observed when ($UO_2^{2+}$,ACH)-bentonite was photolyzed in an isopropyl alcohol/acetonitrile mixture. The ($UO_2^{2+}$,ACH)-bentonite selectivity for the photooxidation of organic substrates resembles that of zeolites, whereas that of ACH-($UO_2^{2+}$-bentonite) resembles that of $UO_2^{2+}$-bentonite and other clays. In addition to acetone, uranyl-exchanged clays and ACH-($UO_2^{2+}$-bentonite) produced acetaldehyde and isopropyl formate. The latter product was identified by GC/MS.

**Cracking Experiments.** By exchange of $Ca^{2+}$ and $K^+$ with $UO_2^{2+}$ cations, a $UO_2^{2+}$-bentonite containing 9.9% $UO_2^{2+}$ and with *d*(001) spacing of 13.6 Å is obtained; see Figure 5B. Back-exchanging $UO_2^{2+}$ ions with polyoxocations of aluminum increases the basal spacing to 17.7 Å (Figure 5C), the BET surface area increased to 392 m$^2$/g (from 110 m$^2$/g), and the ACH-($UO_2^{2+}$-bentonite) acquired a cracking activity for gas oil similar to that of zeolite-containing fluid cracking catalysts (FCC). The clay's *d*(001) spacing did not change in the presence of intercalating solvents, indicating that these materials are indeed pillared and not swelled due to solvent incorporation.

The clay's oxide composition before and after pillaring and before and after uranyl incorporation are given in Table I. Product selectivities from gas oil cracking over pillared clays are shown in Table IV. The presence of $UO_2^{2+}$ ions in the pillared structure, as in ($UO_2^{2+}$,ACH)-bentonite, has little effect on the catalyst cracking properties.

After heating at 700 °C/4 h in air, the clay retained 70% of its internal surface area and 94% of its original cracking activity. Heating in the presence of steam reduces the catalyst stability significantly; at 730 °C there is a total collapse of the microporous structure and loss of catalytic activity. In contrast, zeolite-containing cracking catalysts are stable at these hydrothermal conditions.

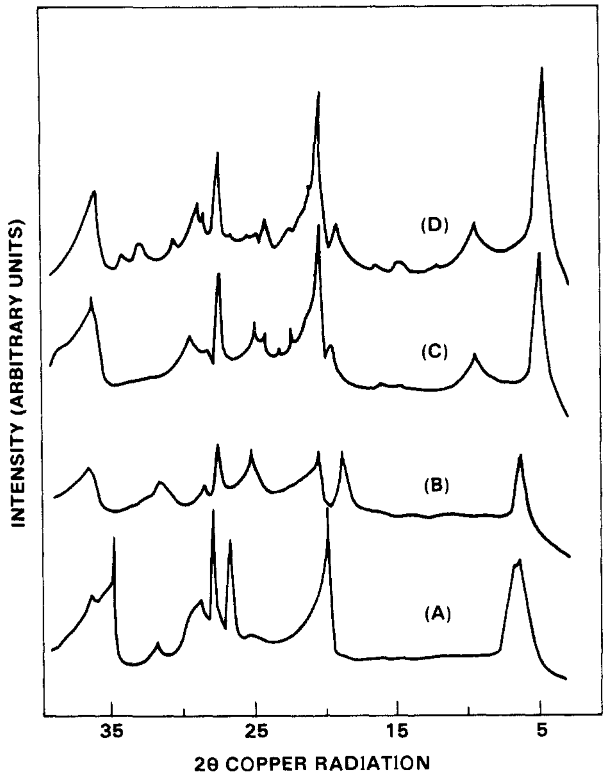

**Figure 5.** X-ray diffractograms of (A) Calcium bentonite, (B) $UO_2^{2+}$-bentonite, (C) ACH-($UO_2^{2+}$-bentonite), and (D) ACH-bentonite.

**Table IV.** Cracking Properties of $UO_2^{2+}$-Containing Pillared Bentonite Catalysts

| | bentonite- | | |
|---|---|---|---|
| | $UO_2^{2+}$ | ($UO_2^{2+}$,ACH) | ACH |
| conversion, vol % FF | 12.2 | 87.9 | 89.3 |
| gasoline, vol % FF | 11.5 | 60.1 | 62.4 |
| LCGO, vol % FF | 27.4 | 10.4 | 9.0 |
| SO, vol % FF | 60.4 | 2.1 | 1.7 |
| $H_2$, wt % FF | 0.09 | 0.36 | 0.41 |
| C, wt % FF | 2.24 | 13.3 | 18.1 |
| BET SA, m$^2$/g | 110.0 | 392.3 | 391.4 |

[a] (1) 100 × 325 mesh granules, dried at 300°C/4 hours in air.

## IV. Discussion

**Luminescence Experiments.** The purpose of luminescence excitation, emission, and lifetime studies of uranyl-containing clays, zeolites, and pillared clays is to determine the location and number of uranyl species in an effort to understand the role that the structural properties of the support have on photochemical and chemical reactions. Uranyl-exchanged clays[7] and zeolites[3] all give at least two components. Stern-Volmer plots of isopropyl alcohol quenching of the $UO_2^{2+}$ moiety[28] also are indicative of at least two types of $UO_2^{2+}$ crystallographic sites. The single exponential behavior of the ($UO_2^{2+}$,ACH)-bentonite is unusual. Its value (48.7 μs) falls in the range of uranyl salts[3] and aluminosilicate compounds[3,7,9] and suggests that uranyl ions are trapped into the pillars. The pillaring solution was prepared by refluxing a $UO_2(NO_3)_2$/Chlorhydrol mixture; therefore, the formation of pillars containing both $Al_2O_3$ and $UO_2$ clusters seem to be a reasonable possibility.

Single-exponential decays are not observed in the present clay or in uranyl-exchanged clays that have subsequently been pillared.

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[28] Suib, S. L.; Bordeianu, O. G.; McMahon, K. C.; Psaras, D. In *Inorganic Reactions in Organized Media*; ACS Symposium Series 177; American Chemical Society: Washington, DC, 1982; pp 225–238.

Since the amount of uranyl ion in this clay is substantial (Table I), self-quenching could be responsible for the observed single-exponential behavior of ($UO_2^{2+}$,ACH)-bentonite. Studies of the hydrolyzed $AlCl_3$ solutions have been performed by using $^{27}Al$ NMR and pH titration measurements by Bottero and co-workers.[29] ACH-($UO_2^{2+}$–bentonite) did not luminesce; its low (0.32%) $UO_2$ content may be outside the instrument's limit of detection.

**Photocatalysis Experiments.** Photolyses with diethyl ether yield two products with all catalysts tested and indicate that $UO_2^{2+}$ ions are indeed necessary for conversion; $UO_2^{2+}$–bentonite was the only catalyst capable of producing more acetaldehyde than ethanol (see Table II). The ranking, with respect to the total amount of products generated (as well as selectivity with respect to acetaldehyde and ethanol production), depends on the clay mineral surface area (see Table II) as well as on the location of the $UO_2^{2+}$ ions. Hectorites (80–90 $m^2/g$) are more active (and selective) than bentonites which have only 40–50 $m^2/g$ of BET surface area.

Photooxidation of diethyl ether could proceed by the following reaction sequence:

$$CH_3CH_2OCH_2CH_3 \rightarrow CH_3\dot{C}HOH + CH_3CH_2^{\cdot} \qquad (1)$$

$$2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH \qquad (2)$$

In these reactions, carbon–oxygen bond breaking[25] as well as hydrogen abstraction occurs; the radical species ($^{\cdot}CH_3CHOH$) has been detected by EPR measurements of frozen glasses of uranyl ions in organic alcohol mixtures.[26] Pulse radiolysis and radiation chemical studies[27] of uranyl salt solutions in the presence of alcohols and ethers support the disproportionation reactions shown in eq 1 and 2.

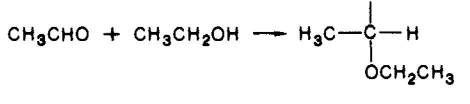
Photolyses with ethanol in the presence of ($UO_2^{2+}$,ACH)–bentonite and $UO_2^{2+}$–X zeolite produced only acetaldehyde, while uranyl-exchanged clays and ACH–($UO_2^{2+}$–bentonite) produced acetaldehyde and significant amounts of acetal; see Table III. Relative rates of acetaldehyde (Figure 3) and acetal production (Figure 4) for the $UO_2^{+}$-exchanged clays resemble those for diethyl ether photolyses. However $UO_2^{2+}$–bentonite is much more active in ethanol oxidation than in diethyl ether oxidation reactions, especially with respect to acetal production.

In addition to selectivity and total conversion trends, it is observed that ethanol photolysis with the smaller particle size bentonite (325 mesh) generates more than twice the acetal produced with the larger (particle size) $UO_2^{2+}$–bentonite, suggesting that acetal formation is a surface reaction. The absence of acetal with high surface area materials such as $UO_2^{2+}$–X zeolites and ($UO_2^{2+}$–ACH)–bentonite is attributed to pore size (opening) limitations. A uranyl-impregnated ACH–bentonite (prepared by the incipient wetness method) is 10 times less active than an ion-enchanged uranyl–bentonite. Since both materials have the same weight percent of $UO_2$, it is believed that internal sites are responsible for a major portion of the photoassisted catalytic activity.

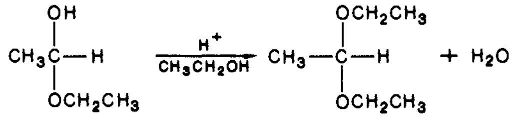
We propose the following reaction sequence for ethanol photooxidation:

$$UO_2^{2+*} + CH_3CH_2OH \xrightarrow{h\nu} UO_2^{1+} + H^+ + CH_3\dot{C}HOH \qquad (3)$$

$$CH_3\dot{C}HOH + UO_2^{2+} \longrightarrow CH_3CHO + UO_2^{1+} + H^+ \qquad (4)$$



$$CH_3CHO + CH_3CH_2OH \longrightarrow H_3C-C(OH)(H)-OCH_2CH_3 \qquad (5)$$



$$CH_3C(OH)(H)OCH_2CH_3 \xrightarrow[CH_3CH_2OH]{H^+} CH_3-C(H)(OCH_2CH_3)_2 + H_2O \qquad (6)$$

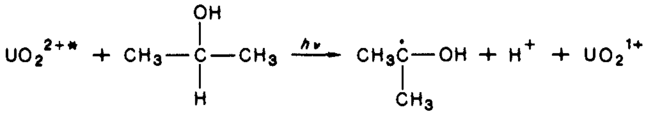
In this case, acetal is produced in a dark step provided that acid sites are available.

Reactions 5 and 6 are usually suppressed when $UO_2^{2+}$–X zeolite or ($UO_2^{2+}$,ACH)–bentonite are used, probably because acetaldehyde and ethanol cannot form in pores like those found in zeolites and pillared clays. These steps represent reactions occurring on the catalyst external surface. In fact, lifetime data usually indicate at least two different $UO_2^{2+}$ sites. The catalytic data given here suggest that these sites may be associated with locations inside and outside the pores. These latter (external sites) are not as selective as internal sites.

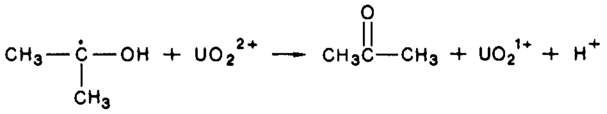
Only natural clays were able to produce large oxidative coupling products such as isopropyl formate and acetal, suggesting again that these photochemical reactions are occurring on the clay's external surface. Pillared clays and zeolites' restrict pore dimensions control product selectivity. Dimerized products are seldom formed in solution; the clay medium must allow the precursor radicals to exist until they can react.

($UO_2^{2+}$,ACH)–bentonite and $UO_2^{2+}$–X zeolite produced only acetone from isopropyl alcohol photooxidation. On the other hand, photolyses of uranyl-containing clays with isopropyl alcohol produced acetone, acetaldehyde, and isopropyl formate; all of the products reported here have been confirmed by GC/MS studies. Photolyses with zeolites[3,28] and pillared clays gave higher selectivity than photolyses with natural clays; their restricted pore sizes prevent oxidative coupling reactions from occurring, providing, in this way, greater selectivity.

Isopropyl alcohol oxidation (with uranyl-exchange zeolites and clays) is proposed by us to occur by the following reaction sequence:



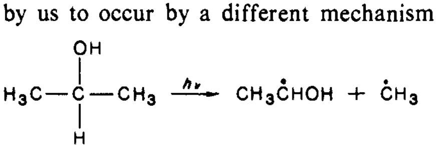
$$UO_2^{2+*} + CH_3-C(OH)(H)-CH_3 \xrightarrow{h\nu} CH_3\dot{C}(CH_3)-OH + H^+ + UO_2^{1+} \qquad (7)$$



$$CH_3-\dot{C}(CH_3)-OH + UO_2^{2+} \longrightarrow CH_3C(=O)-CH_3 + UO_2^{1+} + H^+ \qquad (8)$$

The $UO_2^{1+}$ species is then reoxidized to $UO_2^{2+}$ by dissolved oxygen as proposed elsewhere.[3] These reactions are catalytic with respect to a mass balance. Therefore, disproportionation of $UO_2^{1+}$ does not occur, and the presence of oxygen is necessary to regenerate $UO_2^{2+}$ ions.

Isopropyl alcohol photooxidation by uranyl-exchanged clays is thought by us to occur by a different mechanism, such as



$$H_3C-C(OH)(H)-CH_3 \xrightarrow{h\nu} CH_3\dot{C}HOH + \dot{C}H_3 \qquad (9)$$

$$2CH_3\dot{C}HOH \longrightarrow CH_3CHO + CH_3CH_2OH \qquad (10)$$

The reaction shown in eq 9 suggests that carbon–carbon bond cleavage competes with hydrogen abstraction (eq 7 and 8) as in the case when acetone is produced. Equation 10 can be used to explain the formation of acetaldehyde, but ethanol was not detected in these studies. For this reason, hydrogen abstraction from ethanol[25] (see eq 3) may also occur. Production of isopropyl formate is attributed to radical coupling. Reaction results shown in eq 9 and 10 are discussed elsewhere.[7]

The excited state of the uranyl ion is a powerful oxidant that can break C–O bonds as well as O–H bonds. Although the selectivity of photoassisted oxidation reactions may be controlled by the geometrical environmental of the $UO_2^{2+}$ ion, it appears that the structure of the solid support plays an important role on products selectivity. The support must be crystalline and of a fairly large effective pore opening (> 5 Å) for substantial photoassisted catalysis to occur. These results are consistent with early studies of uranyl-exchanged zeolites[28] where the order of decreasing activity was $UO_2^{2+}$–ZSM-5 > $UO_2^{2+}$–Y > $UO_2^{2+}$–X >>> $UO_2^{2+}$–mordenite ~ $UO_2^{2+}$–A. The support also diminishes the propensity for disporportionation reactions of reduced $UO_2^{1+}$

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(29) Bottero, J. Y.; Cases, J. M.; Fiessinger, F.; Poirier, J. E. *J. Phys. Chem.* **1980**, *84*, 2933–2939.

species. Well-ordered supports are more selective than less ordered supports, and their structures influence reaction pathways.

**Cracking Experiments.** Pore sizes, surface area, and acidity also control the activity and cracked product selectivities of these catalysts when used in upgrading gas oil to transportation and heating fuels. Because of their lack of surface acidity, low (40–90 m$^2$/g) surface area, and small pore opening, natural clays are not active cracking catalysts. Similarly, UO$_2^{2+}$-exchanged bentonite (with 9.91% UO$_2^{2+}$), because of its small ($\sim$4.6 Å) pore height, cannot sorb or crack the high molecular weight hydrocarbons present in gas oil; therefore (like zeolites with 4–6-Å pore openings), it is inactive, Table IV. Introduction of oxycations of aluminum and dehydroxylation (in air at 300 °C/4 h) generates a microporous structure with 392 m$^2$/g of BET surface area and a pore height of $\sim$8.2 Å capable of sorbing C$_6$–C$_{10}$ normal paraffins and branched aromatics;[23,24] the ACH–(UO$_2^{2+}$–bentonite) contains 0.33% UO$_2$.

The presence of 2.96% UO$_2$ as in (UO$_2^{2+}$,ACH)–bentonite does not significantly affect activity nor product selectivity; these properties depend mainly on the area generated by pillaring and on the nature of the silicate layer.[20]

Pillared clays (after a mild thermal aging) are as active as commercially available fluid cracking catalysts containing a zeolite (of the faujasite type) with an effective pore opening of 8.2 Å;[16] see Table IV. However, commercial FCC are more carbon selective and hydrothermally stable to temperatures at which pillared clays collapse with loss of surface and catalytic properties.

## Conclusion

Pillared clays can bridge the gap between small pore zeolites and larger pore amorphous aluminosilicates and mixed oxide catalysts. Photochemical selectivity can be controlled by choosing a support with different pore sizes. In general, the order of increased selectivity for the photooxidation reactions reported here is clay < pillared clay ≤ zeolite. Photochemical selectivity (as well as product selectivity for gas oil cracking) is controlled by the catalysts' pore sizes and surface area.

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**Registry No.** UO$_2^{2+}$, 16637-16-4; H$_3$CCH$_2$OCH$_2$CH$_3$, 60-29-7; H$_3$CCHO, 75-07-0; H$_3$CCH$_2$OH, 64-17-5; H$_3$CCH(OCH$_2$CH$_3$)$_2$, 105-57-7; ACH, 1327-41-9; hectorite, 12173-47-6.

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# Mechanisms of Arene Exchange in (Arene)tricarbonylchromium Compounds: Intermolecular and Intramolecular Exchanges in Complexes of Propenylbenzene, Stilbenes, and 1,1-Diphenylethylene

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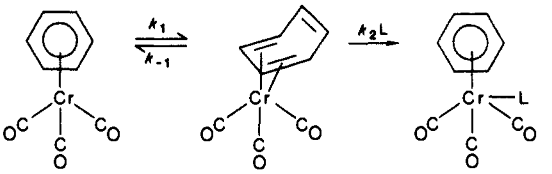
**Abstract:** Kinetic studies of arene exchange of (*trans*-propenylbenzene)tricarbonylchromium with benzene reveal intramolecular and intermolecular participation by the propenyl substituent. Intramolecular participation via direct bonding of Cr(CO)$_3$ to the alkene portion of the ligand is supported by the observed "internal" exchange in Cr(CO)$_3$ complexes of the three isomers of diphenylethene. The magnitudes of the internal exchange rate constants and the effect of added donor catalysts on internal exchange indicate that the geometry of the unsaturated hydrocarbon influences the movement of Cr(CO)$_3$ along $\pi$ systems.

Our first report on arene exchange reactions of (arene)tricarbonylchromium complexes[1] confirmed and expanded upon the earlier results[2-4] and clarified the mechanisms of arene exchange of benzene with alkyl-substituted benzene complexes. The significant elementary step of the proposed mechanism for arene complex reaction, with any of the ligands investigated, is a reduction in coordination of the arene ligand, eq 1. The first-order dependence upon ligand concentration is ascribed to unsuccessful competition for the vacant coordination site by attacking ligand compared to the "uncoordinated" ene of the arene ligand ($k_{-1} \gg k_2[\mathrm{L}]$). Studies of arene exchange in polycyclic aromatic complexes by Strohmeier,[5] Cais,[6] and others[7,8] have indicated an increase in rate of exchange compared to benzene derivatives. Coordinated naphthalene is more labile than coordinated benzene, exchanging [$^{14}$C]naphthalene primarily via a unimolecular process.[5] This could result from a stabilization of the tetrahapto intermediate as shown in eq 2. Tricarbonylchromium also moves from ring-to-ring in naphthalene and substituted naphthalene Cr(CO)$_3$ complexes.[7] These migrations occur readily only in coordinating solvents, implying intermolecular dissociative exchange via (solvent)$_3$Cr(CO)$_3$ intermediates. A theoretical



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