

Figure 11. Adsorption spectrum measured at the end of the CO_2^{-1} reaction (50 μ s) with lumichrome (2 $\times 10^{-5}$ M) at pH 6.0 in nitrous oxide saturated solutions containing 0.1 M sodium formate (37 rd) (\oplus). Adsorption spectrum measured at the end of the CO_2^{-1} reaction (40 μ s) with lumichrome (3.7 $\times 10^{-5}$ M) at pH 10.0 in nitrous oxide saturated solutions containing 0.1 M sodium formate (37 rd) (O). The insert shows the effect of pH on the optical density at 450 nm measured at the end of the CO_2^{-1} reaction with lumichrome (3.7 $\times 10^{-5}$ M, 37 rd).

pHs. It appears likely though that the pK_a lies between 10.0 and 12.5.

(d) Lumichrome. At pH 6, CO_2^{-} reacts with lumichrome to produce a species whose absorption spectrum is shown in Figure 11. As expected from similar experiments with

the 1- and 3-methyl derivatives, the spectrum resembles those already assigned to the neutral free radical (ϵ_{450nm} = 3900 M^{-1} cm⁻¹ in Figure 11). At pH 10, it can be calculated that approximately 42% of the total lumichrome concentration is in the form of the 1-methyl monoanion while 55% exists as the 3-methyl monoanion with 3% in the neutral form.⁵ On this basis and taking the extinction coefficient of the 3- and 1-methyl anion radicals at 450 nm to be 6800 and 4000 M^{-1} cm⁻¹, respectively, we can calculate that the apparent extinction coefficient measured at this wavelength for species formed after reaction of CO_2^{-} . with lumichrome at pH 10 should be 5000 M^{-1} cm⁻¹. The value determined from Figure 11 is 5050 M⁻¹ cm⁻¹. Further detail of this effect of pH can be seen in Figure 11 in addition to other effects between pH 10 and 12, presumably further deprotonation of the species present at pH 10. Taken in total, these results with lumichrome indicate that the spectral and acid-base properties of the neutral and anionic free radicals formed in the reaction of CO_2^{-} . with lumichrome and its monoanions are those expected from a similar reaction with a mixture of lumichrome and the monoanions derived from the 1- and 3-methyl derivatives.

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Selective Photoactivation of Carbon–Hydrogen Bonds in Paraffinic Hydrocarbons. Dimerization of Alkanes

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When contacted with a silver-loaded zeolite Y, containing both isolated silver atoms and very low nuclearity cationic silver clusters, under broad-band irradiation (220-300 nm) and at room temperature and atmospheric pressure, low molecular weight paraffinic hydrocarbons undergo a selective dimerization, namely, methane leads to ethane, ethane to *n*-butane, and propane to hexanes. The species thought to be responsible for the activation of the C-H bond of the paraffinic hydrocarbons is suggested to be a lattice V-center obtained in the zeolite under UV irradiation, the formation of which is enhanced by the presence of small charged silver clusters (bifunctional reduction of electron-hole recombination processes). The V-centers are both accessible to and highly reactive toward alkanes C_nH_{2n+2} , thereby abstracting a hydrogen atom from the alkane to form a lattice hydroxy species and the respective gaseous alkyl radical C_nH_{2n+1} . The reaction conditions lead neither to a breakage of the C-C bond of the alkane to an appreciable extent nor to its dehydrogenation to the alkene. The alkane photodimerization reaction on silver loaded zeolite Y, namely, $2C_nH_{2n+2} + h\nu \rightarrow C_{2n}H_{4n+2} + 2H_{ads}$ is intriguing in that it bears a number of similarities to the water photosplitting reaction, namely, $2H_2O + h\nu \rightarrow O_2 + 4 H_{ads}$ on the same substrate. In both cases, lattice reaction with the alkane or water reagents predominates, making the major product generating channel stoichiometric rather than catalytic.

Introduction

The activation of C–C and C–H bonds in paraffinic hydrocarbons is a challenging problem in the field of catalysis.¹ In particular, selective activation of C–H or C–C bonds is very difficult to devise and known processes of hydrocarbon cracking and re-forming, using heterogeneous catalysts and requiring severe conditions of temperature and pressure, are usually nonselective in their action.²

It is the object of this paper to describe our observations concerning the reactivity of alkanes with certain silverloaded zeolites under UV-visible irradiation, which consists

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⁽²⁾ M. L. Poutsma in "Zeolite Chemistry and Catalysis" J. A. Rabo, Ed., ACS Monograph No. 171, American Chemical Society, Washington, DC, 1976, p 437; S. M. Csicsery, *ibid.*, p 680; A. P. Bolton, *ibid.*, p 714.

TABLE I:

sample notation	wt % Ag	% exchange	no. of Ag per unit cell
Ag ₆ Na-Y	5	11	6
Ag ₁₃ Na-Y	10	23	13
Ag ₂₈ Na-Y	20	50	28

of a selective dimerization of the starting alkane, for example, methane is converted to ethane with a selectivity in excess of 90%. Moreover, the reaction is conducted at room temperature and atmospheric pressure.

Experimental Section

The starting material was a Na-Y zeolite supplied by the Linde Division of Union Carbide Corp. The Na⁺ ions were exchanged by conventional ion-exchange techniques with silver nitrate aqueous solution. The material was handled and stored in the dark. The silver content of the zeolite samples was obtained by a neutron activation analysis at the University of Toronto Slowpoke reactor facility. The level of exchange of sodium by silver ranged between 11% and 50%. Table I gives the exact composition of the AgNa-Y samples.

After preparation, the zeolite sample (denoted Ag, Na-Y) was dehydrated by heating it under vacuum $(10^{-5}-10^{-6})$ torr), stepwise by 100 °C increments, each for 2 h, up to 500 °C. These pretreatments were performed in the dark to avoid a possible photoreduction of the silver. A sample pretreated under vacuum up to 500 °C is denoted with the subscript 500, e.g., Ag₆Na-Y₅₀₀. In some cases samples previously treated under vacuum at 500 °C were then oxidized by treatment in oxygen (1 atm) at 500 °C. These samples are denoted with the subscript ox500, e.g., Ag_6Na-Y_{ox500} . So that the reaction of the alkanes under irradiation could be studied, the zeolite sample (weight 0.75 g, particle size $\sim 100 \ \mu m$) was introduced into a cylindrical quartz cell (length 10 cm, diameter 4 cm, total volume 200 mL) which was placed horizontally and allowed to spin in the proximity (distance of cell from lamp, approximately 10 cm) of a Hanovia 450-W mercury lamp (emitting photons in the range 220-700 nm). This procedure allowed a relatively large surface area of the zeolite powder to be irradiated. The lamp was surrounded by a water cell to filter out infrared radiation. The cell was equipped with a valve for vacuum treatment and introduction of the gases, and with a septum for gas sampling. The temperature of the sample during irradiation in most cases was close to room temperature and never exceeded 35 °C. After the pretreatment of the zeolite sample in situ in the quartz cell, the alkane hydrocarbon (methane, ethane, propane, research grade from Matheson of Canada) was introduced into the cell at atmospheric pressure. The gas phase above the zeolite was analyzed during the irradiation by gas chromatography with two types of column: Porapak S for the analysis of hydrocarbons from C_1 to C_3 , saturated and unsaturated; *n*-octane/Porasil C for the analysis of hydrocarbons from C_3 to C_6 , saturated and unsaturated. The detector was of the flame ionization type. Two other columns were used in some cases: 5 Å molecular sieve for the analysis of hydrogen and carbon monoxide with a thermal conductivity detector; Chromosorb 101 for the analysis of methanol, formaldehyde, ethanol, and acetaldehyde with a flame ionization detector. Blank experiments were performed with a zeolite sample containing no silver, which had been treated under vacuum up to 500 °C by the same procedure as described above for the silver-loaded samples. Separate experiments were also performed where the silver loaded sample was placed in

TABLE II: Initial Activity of Different ZeoliteCompositions in the Dimerization of Methane a

expt no.	substrate compn and pretreatment	$\begin{array}{c} 10^{3} (\text{mole} \\ \text{of } C_{2}H_{6} / \\ \text{mole of} \\ Ag \cdot h) \end{array}$	10^{7} (mole of C ₂ H ₆ /g subs·h)
1	Na-Y 500		0.67
2a	Ag, Na-Y	0.43	2.00
2b	Ag, Na-Y	0.13	0.63
2c	Ag Na-Y m b	0.07	0.31
3	Ag, Na-Y 500	0.30	2.80
4	Ag ₂₈ Na-Y ₅₀₀	0.01	0.24
5	Ag Na-Y ox soo	0.08	0.43

^a Activity measured during the first 3 h of irradiation when the amount of ethane produced increases linearly with time. ^b Samples obtained after heating the sample Ag₆Na-Y₅₀₀ (2a), which had been subjected to 41 h of irradiation in the presence of methane, under vacuum at 250 °C for 6 h (2b) and at 500 °C for 1 h (2c).

a glass tube and heated to 300 °C in the presence of methane and ethane to check the reactivity of the alkane hydrocarbon in the presence of the same substrate at high temperature. This was found to be useful, since at the end of a photochemical reaction the silver zeolite sample was heated to 150–200 °C in order to desorb the hydrocarbons formed and adsorbed onto the zeolite at room temperature, thereby permitting one to know the total amount of hydrocarbon formed by the photochemical process.

Results

Experiments Performed in the Absence of Light. When methane is heated to 300 °C in the presence of Na- Y_{500} or Ag₆Na- Y_{500} , no C₂ or C₃ hydrocarbons are detected in the gas phase. When ethane or propane are submitted to the same reaction conditions, the hydrocarbons appearing in the gas phase are ethylene and propylene, respectively, in relatively small amounts, produced by dehydrogenation of the starting alkane. This dehydrogenation reaction was found to take place only at temperatures higher than 150 °C. No hydrocarbons of lower or higher carbon number than the starting alkane were detected.

These results indicate that dimerization or cracking of paraffinic hydrocarbons do not occur by thermal treatment up to 300 °C in the presence of our zeolite samples. However, dehydrogenation of the ethane and propane occurs to a minor extent under the same conditions and this should be taken into account when the catalyst is submitted to heat treatment after a photochemical reaction to desorb the adsorbed hydrocarbons for analysis purposes.

Experiments Performed in the Presence of UV Light. (a) Methane. When methane is contacted with our zeolite samples, Na- Y_{500} , Ag_xNa- Y_{500} , or Ag₆Na- Y_{0x500} , under UV irradiation (range 220–300 nm, the range with $\lambda > 300$ nm being inefficient), a small amount of ethane appears in the gas phase, the concentration of which increases linearly with irradiation time during the first hours of the photoreaction. Table II gives the initial activity for ethane formation for zeolite samples with different compositions, having been subjected to different pretreatment conditions. Figure 1 illustrates the variation of the ethane concentration in the gas phase with time during the irradiation of a silver zeolite Ag_6Na-Y_{500} (experiment 2a) in the presence of 760 torr of methane (the same curve shape is obtained with the other samples of Na-Y and Ag_xNa-Y). After desorption of the hydrocarbon products by heating at 150 °C for 2 h without light, following 41 h of irradiation, it appears that methane has been converted at a low level (approximately 0.25%) mainly to ethane (93%) and propane (7%). Traces of butanes (*n*-butane/isobutane $\simeq 4$)



Figure 1. Variation of the amount of ethane produced with irradiation time in the reaction of CH₄ with Ag₆Na-Y₅₀₀ under 220-300-nm irradiation.

were also detected in the gas phase. No hydrogen was detected during the irradiation or after the desorption at 150 °C (although the detection limit of the thermal conductivity detector is below the amount of hydrogen expected from the stoichiometry $2CH_4 \rightarrow C_2H_6 + H_2$). Moreover, neither unsaturated hydrocarbons (e.g., ethylene, propylene, butenes) nor oxygenated products were detected in the dimerization of methane.

In a separate experiment, with a Ag_6Na-Y_{500} sample, molecular oxygen was added to the methane feed $(O_2/CH_4 \simeq 1/40 \text{ and } O_2/Ag \simeq 1)$. No activity was observed in the methane dimerization reaction and no other products (e.g., hydrocarbons other than ethane or oxygenated products) were detected. However, after pumping off the CH_4/O_2 mixture at room temperature for 0.5 h, and replenishing with pure CH_4 , the methane photodimerization activity was reinstated.

In two other experiments, CO and H_2 were added to the methane separately (CO/CH₄ $\simeq 1/40$ and $H_2/CH_4 \simeq 1/15$). In both cases no quenching of the methane photodimerization activity was observed. Furthermore, in the case of CO, no other products, in particular oxygenated products, were detected.

The same type of selectivity for ethane formation is obtained either with the zeolite alone Na- Y_{500} or with the Ag_xNa- Y_{500} samples although the percentage conversion is less for the former.

(b) Ethane. After contacting ethane (1 atm) under irradiation (22.5 h) with the zeolite Ag_6Na-Y_{500} under the same conditions as those employed for the methane reaction, and after heating the catalyst to 250 °C to desorb all the hydrocarbon products formed, it appears that the ethane has been selectively converted (0.33%) mainly to *n*-butane (>95%) with a low amount of methane, propane, and hexanes (total corresponding to <5%).

(c) Propane. When propane is subjected to the same irradiation in the presence of Ag_6Na-Y_{500} for 15 h and the zeolite subsequently heated to 200 °C, it appears that propane has been converted (0.30%) mainly to hexanes (approximately 90%) with a low amount of C_1 , C_2 , C_4 , and C_5 saturated hydrocarbons, the total amount representing

about 10%. The composition of the hexane fraction was as follows: n-hexane, 35%; methylpentane, 55%; dimethyl-2,3-butane, 10%.

Discussion

Our results indicate that a zeolite Na-Y containing no silver, as well as containing different amounts of silver, from 6 to 28 silver ions per unit cell, activated at 500 °C, are able to selectively convert an alkane hydrocarbon C_nH_{2n+2} to the corresponding alkane dimer $C_{2n}H_{4n+2}$, under UV irradiation, thereby achieving the overall reaction

$$2C_nH_{2n+2} \rightarrow C_{2n}H_{4n+2} + H_2 \tag{I}$$

Moreover, the activity of the zeolite samples depend largely on the silver content and on the mode of activation, as is apparent from the results of Table II, in the case of methane dimerization. Indeed, if one looks at the activity of different samples, all treated at 500 °C under vacuum $(Na-Y_{500}, Ag_6Na-Y_{500}, Ag_{13}Na-Y_{500}, and Ag_{28}Na-Y_{500})$, one can see that the sample containing 6 Ag per unit cell (Ag_6Na-Y_{500}) exhibits an activity three times larger than the zeolite without silver $(Na-Y_{500})$ but that when the silver content is increased above 6 Ag per unit cell $(Ag_{13}Na-Y_{500})$ and $Ag_{28}Na-Y_{500}$) this activity, expressed in moles of ethane obtained per mole of silver present, decreases to attain a value below that of $Na-Y_{500}$ for $Ag_{28}Na-Y_{500}$. If one examines the activity of, for example, the zeolite composition Ag_6Na-Y , as a function of pretreatment, it appears that the sample oxidized at 500 °C (Ag₆Na- Y_{0x500}) has an activity comparable to that of Na-Y₅₀₀; it is also interesting to note that vacuum treatment at 250 or 500 °C of Ag₆Na-Y₅₀₀ following an irradiation does not regenerate this initial activity.

The absence of any hydrogen in the gas phase suggests that the hydrogen necessarily formed by reaction I is strongly adsorbed on the solid substrate. From the results of Table II and Figure 1 it is obvious that the dimerization activity is low and decreases fairly rapidly with time, indicating a fast deactivation of the substrate.

All of these observations argue in favor of a stoichiometric reaction between the alkane hydrocarbon and some surface species, common to Na-Y and AgNa-Y.

A physicochemical study of the silver zeolite samples Ag_rNa-Y, which used fluorescence emission and excitation, diffuse reflectance, and electron spin resonance spectroscopies, has been performed and details of the results³ that are pertinent to the present study will be given here. In brief, the spectroscopic data collectively indicate the formation of both isolated silver atoms and small, charged silver clusters, during the dehydration process to 500 °C. After oxygen treatment at 500 °C, of Ag_xNa-Y₅₀₀, the samples Ag_xNa-Y_{0x500} obtained have been shown to contain the isolated silver atoms but not the silver clusters. The spectroscopic properties and chemical reactivity toward oxygen of these two types of species have provided evidence that the silver atoms are stabilized in the center of the hexagonal prism^{3,4} (site I) and are therefore inaccessible to hydrocarbon molecules, whereas the charged silver clusters are residing in the large cavities (α cage) of the zeolite lattice^{3,4} and are fully accessible to hydrocarbon molecules. Furthermore, the optical data suggest the presence of a single silver cluster cation Ag_n^{q+} (where n lies in the range 5-13) in the samples Ag_6Na-Y_{500} and Ag₁₃Na-Y₅₀₀, but for Ag₂₈Na-Y₅₀₀, the presence of larger silver clusters is indicated.

⁽³⁾ G. A. Ozin, F. Hugues, S. Mattar, and D. McIntosh, J. Phys. Chem., in press and submitted manuscripts.
(4) R. Kellerman and J. Texter, J. Chem. Phys., 70, 1562 (1979).

In this context, it has been shown recently that charged silver clusters can be obtained readily in zeolites, by a thermal autoreduction process or by hydrogen reduction. For example, dehydration of silver-exchange zeolite A to 400 °C has been shown to produce the cluster Ag_3^{2+} in the sodalite cages of the zeolite, characterized by X-ray diffraction.⁵ Dehydration of silver-exchange zeolite X and Y, followed by oxygen treatment, leads to the clusters Ag_2^{p+} and Ag_3^{q+} , arising from the occupancy of one site I and one (or two) site I', respectively.⁶ Hydrogen reduction at low temperature of silver-exchange zeolite Y is likely to produce charged silver clusters, as indicated by the stability of these clusters toward sintering at high temperature in absence of reducing agents.⁷ In the same way, hydrogen reduction at temperatures less than 20 °C of silver-exchanged zeolite A has been shown to produce the charged cluster Ag_6^{p+} characterized by ESR spectroscopy.⁸ All these positively charged clusters would be stabilized by a strong Coulombic interaction with the negatively charged zeolite lattice. Therefore, it seems very likely that our small Ag_n^{q+} has a quite large positive charge q which would account for its high thermal stability toward sintering.

Irradiation of zeolites by different means, γ rays, X rays, and UV photons, has been shown to produce F- and Vcenters.⁹ In particular, irradiation of H-Y and Na-Y zeolites by γ rays leads to the formation and the stabilization, even at room temperature, of a hole center localized on a lattice oxygen according to the scheme¹⁰

$$T = Al \text{ or } Si \qquad V \text{-center}$$
(II)

Also it has been shown recently¹¹ that a zeolite Na-Y exhibits an absorption band centered at 240 nm which has been attributed to an $Al^{3+}-O^{2-} \rightarrow Al^{2+}-O^{-}$ charge transfer excitation and could be responsible for the UV generation of an electron hole associated with a lattice oxygen adjacent to a lattice aluminum.

We would therefore propose that such a V-center is formed under UV irradiation.

A V-center of this type has some similarity to the O⁻ species produced by γ or UV irradiation of various inorganic oxides.¹² It has also been shown^{12,13} that such a $O^$ species is very reactive toward C-H bonds of saturated hydrocarbons, causing the abstraction of the hydrogen atom and leading to a hydroxyl species OH⁻ and to an alkyl radical.

Therefore we would propose that the species most likely responsible for the dimerization of the alkane is the Vcenter produced by UV irradiation. Thus the mechanism of dimerization could be written

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Moreover, when the samples Ag₆Na-Y₅₀₀ and Ag₁₃Na- Y_{500} are submitted to UV irradiation, there is a monotonic decrease of the optical absorptions attributed to the cluster cation Ag_n^{q+} with irradiation time and their gradual replacement by a new set of absorptions. The latter bands have been interpreted as arising from the cluster cation Ag_n^{p+} (with p < q), a photoreduced version of Ag_n^{q+} , which is also located in the α cage of the zeolite lattice and is indefinitely stable under irradiation.³ Support for this proposal stems from the observation that the Ag_n^{q+}/Ag_n^{p+} clusters are found to be photochemically (200-300 nm) and thermally (500 °C) interconvertible, which argues that the integrity of the cluster is maintained during the photochemical reaction. The occurrence of such an electron transfer to the silver cluster cation

$$Ag_n^{q+} + xe^- \rightarrow Ag_n^{p+}$$
 with $q = p + x$

can explain why certain zeolite samples $Ag_x Na-Y_{500}$ (x = 6 and 13) exhibit a higher activity in methane dimerization, compared to the samples $Na-Y_{500}$ or Ag_6Na-Y_{ox500} containing no such Ag_n^{q+} species.

Indeed the electron produced along with the hole center (V-center) has to be trapped somewhere in the lattice to stabilize the V-center and prevent the reverse electron-hole recombination process from occurring:¹⁶

$$T \xrightarrow{\circ}_{Si} + e^{-} \xrightarrow{}_{T} \xrightarrow{\circ}_{Si}$$
 (IV)

It has been pointed out that the zeolite lattice and isolated cations are not very good electron scavengers, which implies that the above equilibrium is not particularly in favor of V-center formation, in the case of Na-Y and Ag₆Na-Y_{ox500}.

Thus one can consider that the presence of a charged cluster cation like Ag_n^{q+} which is likely to be a better electron acceptor than a single ion Na⁺ or Ag⁺ is likely to enhance the production of electron holes and thereby drive the alkane dimerization reaction. The Ag_n^{q+} , T-O-Si/ Ag_n^{p+} , T-O-Si pairs can therefore be considered to exhibit a bifunctional mode of operation.

An explanation of the drop in activity of the silver zeolite samples when the silver loading increases from 5% to 20% can be traced to the presence of silver clusters larger than Ag_n^{q+} in the higher loaded sample, as discussed earlier, but the exact role that such large clusters play is presently unclear.

With this model of the photoejected electron during the formation of the V-center being trapped by Ag_n^{q+} , it is now possible to write a plausible mechanism of C-H activation in saturated alkanes as follows:



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⁽⁶⁾ L. R. Gellens, W. J. Mortier, and J. B. Uytterhoeven, Zeolites, 1, 11 (1981).

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This mechanism adequately explains why the activity drops with irradiation time: first, the active photogenerated V-center is continuously converted by alkane into a lattice hydroxyl group, from which the production of a V-center by the preceding scheme (II) is less favored than from a T–O–Si group, as shown by Vedrine et al.;¹⁰ second, the cluster cation Ag_n^{p+} seems not able to accept and more electrons as shown by its indefinite stability under UV irradiation. Therefore, the major product-forming channel is not catalytic, rather at best stoichiometric.

An approximate calculation of the ratio of ethane molecules formed after 41 h of irradiation of Ag_6Na-Y_{500} in the presence of methane (experiment 2a) to the number of available silver cluster cations can be conducted if we make the following hypotheses: (a) n = 9 (taking the average n = 5-13 and x = 1; (b) one Ag_9^{q+} and two Ag^0 are formed for every two unit cells in the zeolite Ag_6Na-Y_{500} ; (c) the penetration depth of the UV light is 2 μ m¹⁴ and the average particle size of the zeolite powder is ~100 μ m. The following result is obtained

$$C_2 H_{\beta}(\text{produced}) / 2Ag_n^{q+}(\text{accessible}) \simeq 1$$

If one uses the stoichiometry of (V) and the above assumptions, this ratio is equivalent to the number of CH_4 molecules reacting with a V-center. Although this number should be treated with caution because of the large number of uncertainties involved in the calculation it is nevertheless consistent with the stoichiometry expected based on the proposed mechanism.

This mechanism can account for the fact that a vacuum treatment at 250 or 500 °C of an irradiated Ag_6Na-Y_{500} sample does not regenerate the initial alkane dimerization activity because lattice hydroxyl groups are not removed quantitatively at 500 °C. Removal of OH groups in H–Y zeolite usually requires temperatures up to 600 °C. This mechanism can also explain the reversible poisoning effect of oxygen if one assumes, as shown by Vedrine and Naccache, ¹⁵ that molecular oxygen reacts reversibly with the V-center, according to the scheme

$$T \xrightarrow{\circ}_{S_1} + \circ_2 \xrightarrow{\circ}_{vacuum, 25 \circ C} T \xrightarrow{\circ}_{S_1} (VI)$$

It is interesting to note that molecular oxygen does not irreversibly influence the ability of Ag_n^{q+} to trap photogenerated electrons, which can be rationalized in terms of a reversible O₂ adsorption at 25 °C.

The fact that carbon monoxide and hydrogen do not quench the activity of the substrate, as found for oxygen, is not fully explained, and this point needs further investigation. Our results, however, suggest that in the case of a H_2/CH_4 mixture, CH_4 reacts preferentially with the V-center and that deactivation originates from H abstraction from CH_4 by the V-center to produce hydroxyl groups rather than from an H_2 molecule generated from CH_4 by the dimerization reaction $2CH_4 \rightarrow C_2H_6 + H_2$. In the case of $CH_4 + CO$, our results rule out the possibility of a preferential reaction of CO with the V-center to form a



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(15) J. C. Vedrine and C. Naccache, J. Phys. Chem. 77, 1606 (1973).

species analogous to the CO_2^- surface species obtained from CO and O⁻ on MgO,¹⁶ as well as adsorption on Ag_n^{q+}, which would tend to decrease its capacity to trap electrons.

In the case of the ethane and the propane reaction, it is interesting to compare our results with those recently obtained by Lunsford and co-workers¹³ who have shown that surface O⁻ ions formed by reacting MgO powder with N₂O gas react with ethane and propane to give the corresponding *alkene* in a stoichiometric reaction and *not* the corresponding alkane dimer as in our case, through the following series of proposed steps for ethane:

$$C_{2}H_{6} + (O^{-})_{s} \longrightarrow C_{2}H_{5} + (OH^{-})_{s}$$

$$I_{-}I + C_{2}H_{5} + (O^{2-})_{s} \longrightarrow (OC_{2}H_{5}^{-})_{s} + I_{-}I$$
hole
$$alkoxide$$

$$(OC_{2}H_{5}^{-})_{s} \longrightarrow C_{2}H_{4} + (OH^{-})_{s}$$

It is also worth comparing our alkane dimerization reaction with the results obtained by Kasansky and coworkers¹² concerning the reaction of CH₄ and C₂H₆ with hole centers (O⁻, V-centers) produced on P⁵⁺/SiO₂, V⁵⁺/ SiO₂, and TiO₂ by γ rays or UV irradiation. As in our system, some dimer (ethane) was found in the case of the methane reaction, but only in minute quantities. However, no alkane dimer was observed in the case of the ethane reaction. Moreover, some oxidation products such as HCHO, CO, and CO₂ were detected even in the absence of molecular oxygen which were not formed in our Ag_xNa-Y experiments. The Kasansky results¹² were explained as in the case of the Lunsford results¹³ in terms of an alkoxy surface species formed from the alkyl radical and a O⁻ anion:

$$(O^{-})_{s} + CH_{4} \rightarrow (OH)_{s}^{-} + CH_{3}$$
$$CH_{3} + (O^{-})_{s} \rightarrow (CH_{3}O^{-})$$
$$(CH_{3}O^{-})_{s} \rightarrow CO + H_{2} + H + e^{-}$$
$$(C_{2}H_{5}O^{-})_{s} \rightarrow CH_{4} + CO + H + e^{-}$$

In our case the absence of alkene hydrocarbons in the ethane and propane reactions and the absence of oxygenated products in all the alkane reactions studied suggest that the alkyl radical formed in the first step does not react with a V-center, a reaction which would lead either to the corresponding alkene by another hydrogen abstraction, analogous to the Lunsford scheme, or to an oxidation product in a step analogous to the decomposition of the alkoxy surface species in the Kasansky scheme. However, the incorporation of a lattice oxygen in the product is a highly improbable event under our reaction conditions.

Therefore, if we assume the reaction steps of (V), the high selectivity for the dimer R-R is not surprising, since the product formation is governed by the concentration of R, which is governed by the partial pressure of R-H; so with CH₄ alone, the relatively high concentration of CH₃ leads to C_2H_6 as the main product and only minor amounts of C_3H_8 are formed from C_2H_5 and CH₃, due to the low concentration of C_2H_5 .

An important point is that the reaction conditions lead neither to a breakage of the C–C bond of C_2H_6 (or C_3H_8) to an appreciable extent nor to the dehydrogenation of the alkane. This result should be compared with the insertion of ²P Cu atoms into the C–H bond of CH₄ and C_2H_6 in 12 K matrices, to form almost exclusively CH₃CuH and C_2H_5 CuH,¹⁸ and contrasted with the gas-phase decomposition of ethane at 25 °C in the presence of Hg(6³P₁) as

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a photosensitizer.¹⁷ In the latter at low conversion and low light intensity, the major products of the decomposition are H₂ and butane and the following stoichiometry could be deduced from the amounts of $\mathrm{C}_2\mathrm{H}_6$ reacted and H_2 and butane produced:

$$2C_2H_6 \rightarrow H_2 + C_4H_{10}$$

The formation of low amounts of ethylene was explained by the gas-phase disproportionation of the C_2H_5 radical:

$$2C_2H_5 \rightarrow C_2H_6 + C_2H_4$$

On a final note it is instructive to compare and contrast our alkane photodimerization reaction on $Ag_{x}Z-Y_{500}$ with the water photosplitting reaction on similar substrates recently reported by Schumacher¹⁹ and Jacobs.²⁰ In their work, it was discovered that silver ion exchange zeolites are sensitive to visible light, releasing oxygen from adsorbed water. The activity of the system was also found to decrease with irradiation time, but was regenerated by treatment under vacuum at 600 °C, releasing hydrogen from the zeolite. Photochemical/thermal splitting of water can therefore be achieved with silver zeolites. Although the mechanistic details of the process are not fully understood it is speculated that, during exposure to light, Ag⁺ ions are reduced to some form of Ag⁰, with concomitant production of lattice hydroxyl groups and evolution of oxygen according to

$$2Ag^{+} + 2ZO^{-} + H_2O \xrightarrow{n\nu} 2Ag^0 + 2ZOH + \frac{1}{2}O_2$$

It is proposed that Ag⁰ so formed is either trapped in the zeolite pores or migrates and agglomerates to form Ag_n clusters (or cluster cations), the location of which is unknown. The reoxidation step can be achieved from the reduced $Ag^{0}(Ag_{n})$ /zeolite by thermal treatment at 600 °C giving H_2 evolution according to

$$2Ag_n^0 + 2nZOH \rightarrow 2nAg^+ + 2nZO^- + nH_2$$

The overall reaction can therefore be viewed as a photochemical/thermal cleavage of water to H_2 and O_2 driven by visible light. If the latter step could be achieved photochemically the splitting reaction might be arranged to be truely photocatalytic.²¹ Intimate details of the oxidation and reduction steps of the water splitting reaction on silver zeolites are not presently understood. Future comparisons with the alkane photodimerization reaction will be most intriguing.

The deactivation with irradiation time in both systems although likely to be different in detail may be comprehended in terms of a lattice reaction with alkane or water, making the major product generating channel to C_2H_6 or O_2 , respectively, stoichiometric rather than catalytic. Clearly a difficult and common problem will have to be overcome before an alkane dimerization or water splitting reaction on silver zeolite Y can be made photocatalytic in a practical sense, namely, how does one simply remove the proton of a lattice hydroxyl group and convert it to gaseous hydrogen?

Conclusion

We have obtained some evidence that, under UV irradiation (220–300 nm), a zeolite $Ag_x Na-Y_{500}$ can partially convert methane to ethane, ethane to *n*-butane, and propane to hexanes with a very high selectivity. A mechanism is proposed for the alkane dimerization reaction which is based on the abstraction of a H atom of the alkane by a photogenerated V-center giving an alkyl radical which leads to the corresponding dimer by a very efficient coupling reaction. The formation of a V-center on the zeolite appears to be significantly enhanced by the presence of a low nuclearity, charged silver cluster cation which acts as an electron trap, thereby reducing electron-hole recombination processes. This appears therefore to constitute a genuine example of a bifunctional heterogeneous photoassisted conversion of an alkane to its respective dimer. Although not catalytic, this reaction offers interesting insight into the problem of selectively activating C-H bonds in saturated hydrocarbons. Work is in progress to further explore the mechanism of the transformation, to probe its generality, and to search for ways of making the system photocatalytic.

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