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Vanadium-Catalyzed Destruction of USY Zeolites

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Both vanadium and nickel are present in the high boiling fractions of crude oils. When these fractions are used as feed for catalytic cracking units these metals deposit on the catalyst and promote the undesirable side reactions of coke and dry gas formation. Vanadium has the additional effect of reducing catalyst activity and selectivity by destroying zeolite crystallinity. A kinetic study has been made of the interaction of vanadium and steam with several zeolites that are important in catalytic cracking catalysts. Measurements were made for the vanadium–USY system at 1 atm of steam with temperatures ranging from 740 to 800°C, and at vanadium concentrations ranging from 0 to 4000 ppm. The effect of ion exchange with sodium, lithium, potassium, and rare earths on the rate of reaction was also investigated. From the experimental results it was concluded that the reaction taking place is the well-known destruction of zeolite by steam. The role of both vanadium and sodium are that of catalysts. Both catalysts are nearly equal in activity and their effects synergistic. To the best of our knowledge, this is the first kinetic proof of a catalyzed solid-state phase transformation. Potassium is essentially equivalent to sodium as a catalyst while lithium is somewhat less active. Rare earths do not change vanadium tolerance. Their effect is an indirect one of changing the base steam stability of the zeolite. It was also found that vanadium easily attacks silicalite. Since this zeolite is essentially alumina free, the experiment shows that the attack by steam can be on a Si–O bond. A mechanism is proposed involving the attack of either vanadium or sodium on surface hydroxyl groups as the step affecting the rate of nucleation, which in turn is the overall rate limiting step of the reaction.

INTRODUCTION

The effects of vanadium and nickel feed contaminants on the performance of cracking catalysts are generally well known (*1–3*). These contaminants deposit on the catalyst from the feed and promote dehydrogenation reactions that increase the yields of coke and dry gas. Vanadium has an additional effect of reducing catalyst activity and selectivity by destroying zeolite crystallinity. Antimony passivation is widely practiced to control the effects of nickel (*4*). The effects of vanadium are being controlled by the use of vanadium scavengers that usually function by binding the vanadium into some stable high melting compound (*5, 6*). However, to be effective, these scavengers must be added in large concentrations in order to successfully compete with the zeolite for the vanadium. Better understanding of the interaction of vanadium with the catalyst is an important step in the development of better technology for the passivation of vanadium.

It is generally agreed that the vanadium first deposits on the outside of the catalyst particles. When the catalyst is carried into the regenerator of the fluid catalytic cracker, the vanadium is oxidized to V_2O_5. As it is carried back and forth between the reactor and regenerator the vanadium undergoes valence changes between +4 and +5 (*7*). Researchers at Ashland Petroleum showed that an oxidative atmosphere was necessary for zeolite destruction so most of the damage to the zeolite occurs in the regenerator of commercial units (*29*). If the vanadium remained on the surface of the catalyst particles it would not be much of a problem. However, in the presence of steam, it becomes mobile and is carried into the interior

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of the particle where it can react with the zeolite crystals. Vanadium does react to some extent with the matrix components but it seems to migrate more selectively to the zeolite particles (*1, 8*). X-Ray absorbtion studies have shown that after exposure to steam the vanadium is still in the +5 oxidation state but that it is structurally different from bulk V_2O_5 (*7*).

Although the means by which the vanadium reaches the zeolite particle and that its active form is in the +5 oxidation state is generally agreed on, there is still considerable controversy about the details of the reaction between vanadium and zeolite. A number of mechanisms have been proposed for the attack on the zeolite crystal. Some of these are flawed as they are based on experimental results that do not duplicate conditions in a commercial unit. The most prevalent deviations are either the use of very high concentrations of vanadium or working with unsteamed zeolites that are representative of fresh rather than equilibrium catalysts (*9–11*). A typical catalyst make-up rate for a commercial cracking unit operating with a low metals feed is roughly 1% per day. This addition rate is to make up for catalyst lost as fines due to attrition. When operating with a high metals feed, it is common practice to withdraw catalyst in order to moderate the effects of the nickel and vanadium deposited from the feed. The cost of catalyst is such that it is not usually economical for the maximum amount of catalyst withdrawn per day to exceed 3% of the unit inventory. Therefore, the average time that a catalyst particle spends in a commercial unit is somewhere between 16 and 50 days, depending on the level of metals in the feed. The contaminate metals are being deposited continuously during this period.

In the laboratory some form of steaming of fresh or calcined catalysts is used to simulate the conversion to the equilibrium catalyst found in commercial units. These steaming conditions have not been standardized by the industry, but typically range from 700 to 800°C with times from 4 to 16 h. The steam pressure is usually near 1 atm. These laboratory steamings accomplish most of the physical changes in surface area and unit cell size that occur during equilibration in the unit. Since the laboratory steaming temperatures and pressures are close to those in the commercial unit regenerator, it is reasonable to expect that at the end of the first day in a commercial unit, a catalyst particle will closely resemble a particle steamed in the laboratory and that this is the type of particle that will be accumulating nickel and vanadium over the next 16 to 50 days. In 1980 Mitchell published a method for synthetically adding nickel and vanadium to fresh cracking catalysts that gave a good simulation of the activity and selectivity that an equilibrium sample of same catalyst would have at the same metals loading (*15*). The key factors in the method were nonaqueous impregnation of the metals precursors as organometallic compounds and some form of post-steaming to deactivate the metals. This was an important and timely contribution as it allowed one to quickly evaluate the metals tolerance of different catalyst formulations in the laboratory. However, while the Mitchell procedure is a good laboratory method for preparing a metals-contaminated catalyst from its fresh precursor that mimics an equilibrium catalyst, it is not a good method for studying the pathway from fresh to metal-contaminated equilibrium catalyst.

The earliest proposed mechanisms usually involved the formation of some low-melting vanadium-containing eutectic that attacked the zeolite via sintering. Sodium, alumina, and rare earths have all been mentioned as possible components for these eutectics (*10, 11*). The eutectic proposals can be discarded in view of the evidence that Wormsbecher and co-workers have provided showing that steam is necessary for catalyst deactivation (*13*). If sintering were the operative mechanism, destruction should take place in dry air. Two similar proposals involving rare earths postulate that the reaction with vanadium effectively removes them from the role of increasing the steam stability of the zeolite. However both of these studies used unsteamed zeolites as starting materials so the conclusions are suspect (*9, 11*). Based on thermodynamic data obtained by Yannopoulos (*14*), Wormsbecher identified the poison precursor as volatile vanadic acid, H_3VO_4, which is formed by the reaction of V_2O_5 with steam. Vanadic acid would be a strong acid analogous to phosphoric which could attack the tetrahedral alumina sites in the zeolite framework.

In this paper, the mechanism for vanadium poisoning was investigated using a kinetic approach. It is interesting to note that, although a number of reaction mechanisms have been proposed, no one has provided evidence to identify the reaction that is actually taking place. Although kinetic studies cannot be used to prove a reaction mechanism, any mechanism proposed must at least be consistent with the kinetic data. It must also be remembered that solid-state kinetic data generally give less information on the chemistry of the reaction than is typically obtained from solution kinetic data. One is really studying the physical parameters that control the reaction rather than the chemistry. The limitations on conclusions that can be drawn from solid-state kinetic data are discussed in more detail later in this paper.

EXPERIMENTAL

Most of the experiments were carried out using Union Carbide's low sodium USY zeolite, LZ-Y82, as the starting material. The zeolite, as received, contained 0.20 wt% Na_2O. Prior to adding either vanadium or sodium, the powder was steamed in shallow dishes for 16 h at 760°C. This treatment was designed to simulate the state of the zeolite in an equilibrium catalyst. During steaming the unit cell size decreased from about 24.51 to 24.23 Å. The latter value is typical of that measured on USY containing equilibrium catalyst samples from commercial units. Vanadium was added using a variation of the procedure published by Mitchell (*15*). The steamed zeolite was impregnated using a solution of vanadium acetonylacetate in methanol. The methanol was removed by evaporation and the impregnated samples were then calcined 4 h at 538°C in air. All of the time–temperature data were taken in small fixed-bed tube units under 1 atm of steam. The volume of the tubes is 90 cc and the volume of water pumped was 40 cc per h. The changes in the zeolite were followed by both X-ray crystallinity and surface area measurements using the ASTM methods. When additional sodium was needed, it was added to the steamed zeolite by ion exchange with Na_2CO_3 solutions. The sodium-exchanged zeolite was calcined 4 h at 538°C before being impregnated with vanadium.

Lithium USY was prepared by exchanging the steamed LZ-Y82 with Li_2CO_3. After calcining, the exchanged sample analyzed 0.325 wt% Li_2O. There was no significant change in the soda level. With the 0.20 wt% Na_2O already present this calculated to the molar equivalent of 0.88 wt% Na_2O on zeolite. The rare-earth-exchanged USY was prepared by exchanging the as-received LZ-Y82 with a solution of mixed rare earth chlorides until it contained 5.4 wt% RE_2O_3. The sample was then steamed for 16 h at 760°C and impregnated with vanadium using the standard procedure. The steamed zeolite had a unit cell size of 24.30 Å. Low soda CREY (Calcined Rare Earth Y) was prepared by ion exchanging a sample of CREY zeolite with ammoniumnitrate solution until it contained 0.90 wt% Na_2O. The exchanged sample, which contained 15.8 wt% mixed rare earth oxides, was then steamed and impregnated with 2000-ppm vanadium. The steamed sample had a unit cell size of 24.38 Å.

The sample of silicalite was donated by Union Carbide. Since this material has essentially no ion exchange sites, sodium was added by impregnation to incipient wetness using sodium acetate solutions.

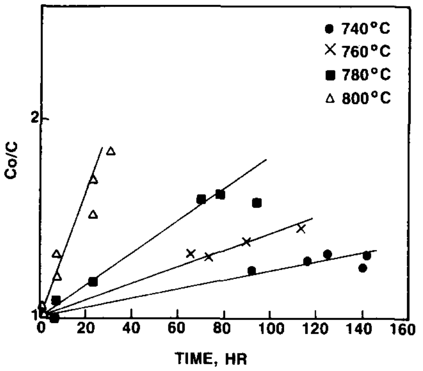

FIG. 1. First-order kinetic data at 0.20 wt% Na_2O and no added vanadium.

RESULTS AND DISCUSSION

A. Destruction of Vanadium Containing Steamed USY

Figure 1 shows typical results obtained with presteamed LZ-Y82 and no added vanadium. Figure 2 shows results with presteamed LZ-Y82 at the same sodium level as in Fig. 1 plus 1000 ppm added vanadium. The data are plotted as the logarithm of the relative zeolite crystallinity versus time. The reaction is clearly first order with no induction period. Figure 3 gives the first-order rate constants that were measured for the destruction of LZ-Y82, presteamed 16 h at 760°C, as a function of both temperature and vanadium concentration. The rate constants are directly proportional to the vanadium concentration. This would be true whether the role of vanadium was that of a reactant or of a catalyst. The fact that very small amounts of vanadium have a large effect on the reaction rate and that it is not consumed is more consistent with vanadium being a catalyst. The catalytic role is also consistent with Wormsbecker's finding that the vanadium can be added to the catalyst as V_2O_5, which is the form in which it is usually found after zeolite destruction. The fact that the data taken with added vanadium can be extrapolated to the rate constants taken without vanadium is consistent with the conclusion that the reaction under study is the well-known steam destruction of zeolite. To the best of our knowledge, this is the first proof of two items: First, the identification of the reaction taking place and, second, the first kinetic proof of a catalyzed solid-state phase transformation. There was some concern about using zeolite that had been presteamed at 760°C to make kinetic measurements at higher temperatures. In Fig. 4, data from samples presteamed at 780 and 800°C are compared with the 780 and 800°C lines from Fig. 3 that were measured using LZ-Y82 presteamed at 760°C. It can be seen that there is good agreement between the rate constants measured on the different starting materials. Figure 5 is an Arrhenius plot of the data from Fig. 3. From the slope of the lines, an average activation energy of 79.0 kcal/mole is calculated.

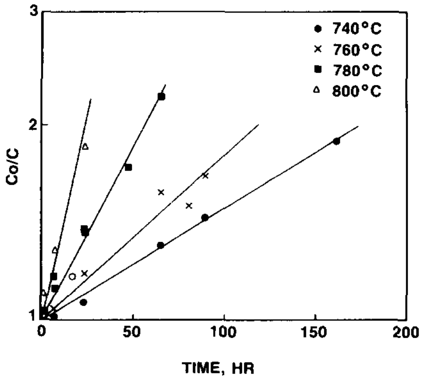

FIG. 2. First-order kinetic data at 1000 ppm vanadium and 0.20 wt% Na_2O.

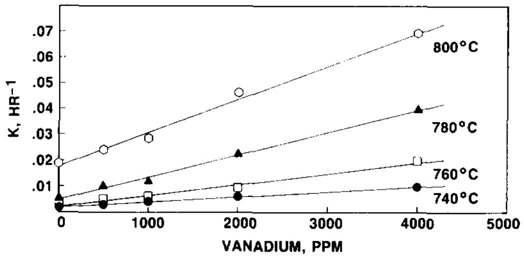

FIG. 3. Rate constants versus vanadium concentration at 0.20 wt% Na_2O.

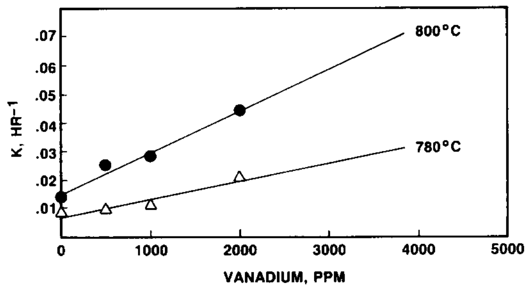

FIG. 4. Presteaming temperature has minimal effect on rate measurements.

An experiment was made to show that steam is necessary as a reactant. Presteamed LZ-Y82 was impregnated with 2000 ppm vanadium and then steamed 4 h at 760°C. This caused the crystallinity to decrease by 11% so it should be adequate to disperse the vanadium. The sample was then heated in dry air at 760°C for an additional 100 h. No further change in the crystallinity could be detected. From our kinetic measurements we would have predicted the zeolite to be 50% converted in 30 h in the presence of 1 atm of steam.

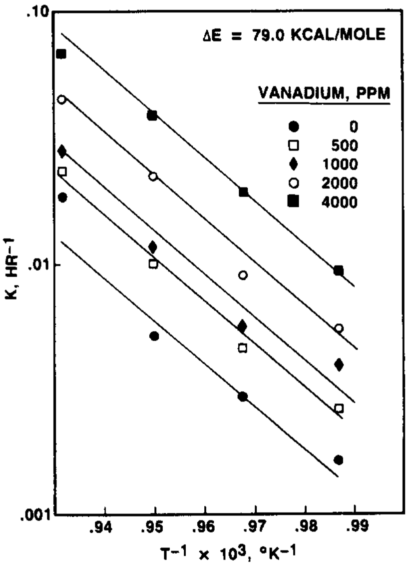

FIG. 5. Effect of temperature on reaction rate at 0.20 wt% Na_2O.

Most of the theoretical basis for the interpretation of solid-state kinetics was developed by Avrami almost 50 years ago (*16–18*). The theory is based on a model involving nucleation followed by growth. Nucleation is usually considered to be a heterogeneous process occurring at defects such as impurities and grain boundaries. Once activated the nuclei grow until phase transformation is complete. The process can be visualized as a random distribution of points growing into overlapping spheres limited by the boundaries of the crystal. There are limitations in the original Avrami treatment that have been dealt with by Cardew and co-workers (*19*). This group addressed the effects of crystal size and developed a theory that, under certain circumstances, allows one to obtain kinetic data for both the nucleation and growth parameters and to make meaningful studies on powders. The most information that one can expect from solid-state kinetic data is the relative rates of nucleation and growth. Under the limiting cases where this ratio approaches either infinity or zero one obtains only the nucleation rate or the growth rate. When the process is nucleation controlled the kinetic data can be displayed as a simple first-order plot. If there is no induction period the line will pass through the origin. The slope of this line, usually called the first-order rate constant, is also equal to the reciprocal of the nucleation time constant. It is important to note that the results will be essentially the same whether the nuclei are randomly distributed on the surface or within the interior of the crystal. Although the kinetic results can identify nucleation as the rate limiting step, they do not yield any information on the mechanism of nucleation. It is very tempting to draw conclusions about reaction mechanisms as one would with results from homogeneous kinetic studies. However, this is not often warranted. It must be remembered that the model for solid-state reactions is not based on transition state theory. Even obedience of the rate data to the Arrhenius equation does not necessarily confirm the dominance of a single rate controlling step (*25*). In the present case where the activation energy does not change as vanadium is added to the system and the kinetic results show that the reaction is nucleation limited, it is very tempting to relate the preexponential or frequency factor to the number of nucleation sites. However, the limitations on drawing conclusions on reaction mechanisms from solid-state kinetic data are such that this is probably not justified. References (*25*, *26*) provide a good introduction for those wishing to read more about this problem.

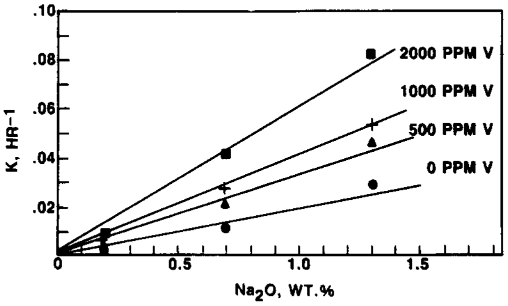

FIG. 6. Effect of sodium on reaction rates at constant vanadium. Reaction temperature is 760°C.

The literature was searched for solid-state reactions analogous to the USY–steam system that had been studied kinetically. It was hoped that a case would be found where there was kinetic proof of a catalyzed solid-state phase transformation. However, a computer search never found the words catalyst and phase transformation linked in any way. Most of the kinetic data in the literature involve either the sintering of two reactants to make a product or a thermal decomposition with a gaseous byproduct. There is very little data on simple high-temperature phase transitions. The most analogous system found was the transition of titania from the anatase to the rutile structure. It takes place between 400 and 1000°C and has an activation energy of 90 to 120 kcal/kmole. The value depends on the method of preparation and purity of the starting samples. The system has been extensively studied by Rao and co-workers who found the reaction to be nucleation rate limited (*20–22*). First-order rate constants at 760°C are about 0.1 h-1. Both the rate constants and the activation energies are in the same order of magnitude as those measured for the USY–steam system. Another system somewhat analogous to the USY–steam system is the transition of tetragonal to monoclinic zirconia. The rate of this reaction is influenced by impurities but the kinetic data do not identify any of these as catalysts. In a study using highly purified samples, the rate was found to be nucleation limited above 570°C and growth limited below this temperature (*23*). The activation energy where the reaction is nucleation limited is 138 kcal/mole and is only 17.8 kcal/mole where the reaction is growth limited. High activation energies seem to be typical for nucleation-limited phase transitions. These need not always be high temperature reactions as the transformation of grey to white tin, which takes place between 30 and 36°C, can have an activation energy of 60 kcal/mole. Further refinement of this data to calculate an activation energy for spontaneous nucleation yielded a value of 120 kcal/mole (*24*). The literature search confirmed that the kinetic results from the present study were reasonable for a nucleation-limited solid-state phase transformation.

B. Effect of Ion Exchange on Reaction Rates

The effect of sodium level on the steam stability of USY was also addressed. The results, plotted in Fig. 6, show that at several levels of vanadium the rate constants are directly proportional to the sodium level. Extrapolation of the data in Fig. 6 to zero sodium leads to the conclusion that USY with extremely low sodium levels would have very high vanadium tolerance. This must be verified by experiment. Temperature response data for two levels of sodium on vanadium-free zeolite are plotted in Fig. 7. The activation energy is about the same as that measured for the low sodium

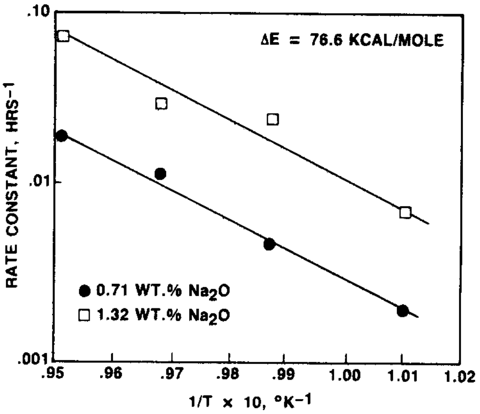

FIG. 7. Effect of temperature on vanadium free USY at 0.71 and 1.32 wt% Na_2O.

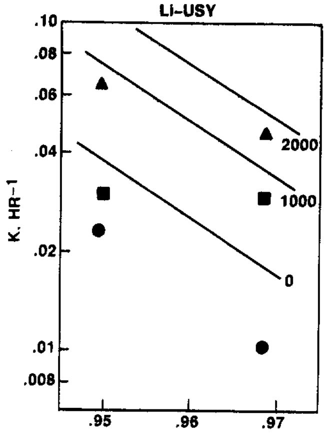

FIG. 8. Effect of lithium exchange on reaction rate.

LZ-Y82 system with vanadium as the catalyst. It is clear that the role of sodium is very similar to that of vanadium. Both catalyze the steam destruction of USY. There is some synergism between the two catalysts. This is evident from Figure 6. If there were no synergism, the slopes of all the lines would be the same and the data would plot as a series of parallel lines.

If we compare the slopes of the 0 ppm vanadium line in Fig. 6 with the 760°C line in Fig. 3 we can make an assessment of the relative strength of the two catalysts. The results of such a comparison, given in Table 1, show that the two metals have about equal activity. This is true whether the active species is calculated as the metal or the oxide. Since we do not have a zero sodium example with vanadium, this type of assessment is confounded by any synergy from the 0.20 wt% Na_2O that is present. The challenge is to devise a mechanism that can accommodate such chemically different species as catalysts to the same reaction and to explain why there is synergism between them.

TABLE 1

Comparison of Sodium and Vanadium as Catalysts

Active species	K/1000 ppm at 760°C
Na	0.0027
Na_2O	0.0020
V	0.0038
V_2O_5	0.0021

The effect that other cations can have on the reaction rate was also investigated. Potassium-exchanged USY could not be distinguished from sodium exchanged USY when the results were compared on an equal molar basis. Lithium is slightly less effective than sodium as a catalyst. This is shown in Fig. 8 where the lines are those predicted for USY containing sodium at the same molar equivalent. The points are the actual data from the kinetic measurements using the lithium-exchanged zeolite. Figure 9 shows that rare earth exchange of USY does not change the rate of reaction. The lines in Fig. 9 are from the kinetic data obtained for presteamed LZ-Y28 containing 0.20 wt% Na_2O and the points are from the kinetic measurements with USY containing 5.4 wt% RE_2O_3.

CREY was also tested. In order to eliminate any effect of sodium, the comparison with USY was made at the same level. The results, shown in Fig. 10, are somewhat surprising. At this sodium level, which is typical for CREY in commercial catalysts, CREY is more steam stable than USY. USY-containing catalysts are usually con-

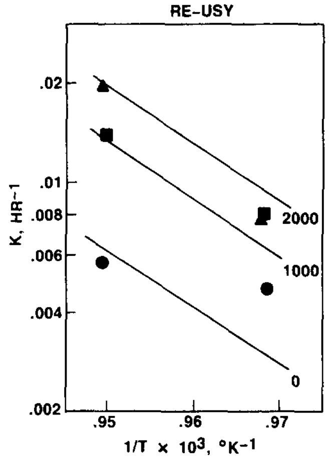

FIG. 9. Effect of rare earth exchange on reaction rate.

sidered to be more steam stable than CREY-containing catalysts. This is because, in typical catalysts, USY almost always contains less than 0.9 wt% Na_2O. The fact that the slopes of all of the lines in the figure are about the same shows that there is little difference in the vanadium tolerance of the two zeolites. In this comparison CREY appears to be more vanadium tolerant than USY because it is inherently more steam stable at this high sodium level. These results, along with those on USY in Fig. 9, indicate that rare earths do not take a direct part in the reaction between vanadium and Y zeolites. The formation of rare earth vanadates is a by product, occurring after the zeolite is destroyed.

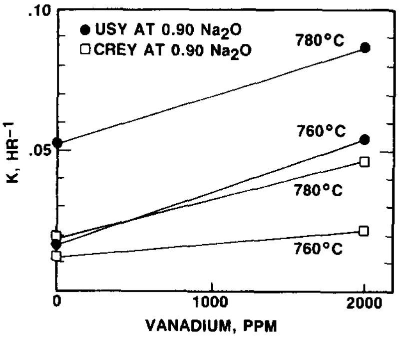

FIG. 10. Comparison of USY and CREY zeolites at 0.90 wt% Na_2O.

TABLE 2

Steam Stability of Silicalite in the Presence of Sodium and Vanadium

	wt%			
	0	0.5	1.0	1.5
Na_2O				
Surface area (m^2/g)				
Calcined 4 h at 538°C	401	308	227	174
Steamed 4 h at 760°C	354	7	1	4
Vanadium				
Surface area (m^2/g)				
Calcined 4 h at 538°C	418	430	407	402
Steamed 4 h at 760°C	349	284	211	181
First-order rate constant, h^{-1}	0.0414	0.104	0.164	0.200

C. *Steam Stability of Silicalite*

Data on the stability of silicalite in the presence of both sodium and vanadium are given in Table 2. The concept behind this experiment was to determine the vanadium tolerance of a zeolite that is essentially free of alumina. Faujasites that contain the least amount of framework alumina are usually the most steam stable. From this it is often inferred that steam destabilization is accomplished via some form of dealumination reaction. Vanadium does not attack silicalite in dry air. The surface areas are essentially unchanged after 4 h at 760°C. However, vanadium does attack silicalite in the presence of steam. By taking the calcined surface area as being directly proportional to the starting zeolite concentration and the steamed surface area as being proportional to the unconverted zeolite, one can calculate crude first-order rate constants. These constants are plotted in Fig. 11. As with USY, the rate constants for the vanadium-catalyzed reactions extrapolate to the rate constant for the vanadium-free reaction. The slope of the line is almost threefold higher than that in Fig. 3 for USY at the same temperature and vanadium loading. These data show that silicalite is less tolerant of vanadium than USY and that the attack on a zeolite crystal by

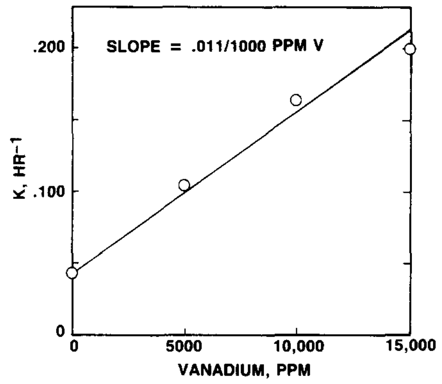

FIG. 11. Vanadium tolerance of silicalite at 760°C.

steam in the presence of vanadium can involve a Si–O bond. However, the effect of soda on silicalite is different enough from its effect on Y zeolites that the analogy with vanadium is weakened. Silicalite has considerably less sodium resistance than USY in both dry air and steam. The difference is great enough to imply a different mechanism. The destruction of silicalite in dry air is consistent with some sort of sintering mechanism. This could be providing a parallel path for the destruction silicalite in addition to the vanadium–steam route.

D. Proposed Reaction Pathway

Examination of LZ-Y82, that had been impregnated with 2 wt% vanadium, by both secondary ion mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) showed that the surface concentration of vanadium, both after calcining and after steaming, was about 2 to 3 times higher than would be expected from the bulk concentration. A surface enrichment of only threefold does not preclude some of the vanadium migrating into the interior of the zeolite particles. However, depth profiling experiments with X-ray photoemission and low-energy ion scattering clearly indicate the enrichment of vanadium +5 on the external surface of both the calcined and steamed zeolites. Based on luminescence studies any vanadium on the calcined sample that is inside the zeolite crystal is likely to be present as VO+2 ions (*27*). However, after steaming the vanadium is almost all in the +5 state. If it was in the form of vanadic acid in the presence of steam, the vanadium should now be largely in an anionic form and would have no driving force to penetrate the zeolite.

The silicalite experiment shows that steam destruction need not proceed by dealumination and the kinetic evidence from the Y zeolite studies strongly indicates that the reaction is not proceeding via a dealumination step. The three or four tetrahedral alumina sites per unit cell remaining in steamed USY would presumably be randomly distributed throughout the zeolite crystals and be protected from a species that prefers a surface location. Approximately 4500 ppm vanadium is needed to provide a vanadium atom for each alumina site per unit cell. Even though the vanadium is quite mobile and we are dealing with average values on the number of sites, it seems unlikely that the rate of reaction would be directly proportional to vanadium concentration at very low levels if nucleation was taking place at the site of framework alumina atoms. The rare-earth-exchanged USY had about 3 times the number of framework aluminum atoms but had essentially the same reaction rate with steam as LZ-Y82 both in the presence and absence of vanadium. The fact that CREY and USY show the same vanadium tolerance when CREY has almost 5 times as many framework aluminum atoms per unit cell is also inconsistent with framework alumina being the site of attack by vanadium.

In spite of our ignorance about the detailed mechanism of the base reaction, it is possible to propose a mechanism that is consistent with the known facts and that can explain why such chemically different species as vanadium and sodium could act the same catalytically. If vanadium has difficulty penetrating the zeolite crystal, it may be limited to primarily taking part in a surface reaction. Vanadium, either as oxide or in some partially hydroxylated form, would be a weak base and could react with the hydroxyl groups on the surface of the zeolite. This would have a destabilizing effect on any adjacent Si–O–Si bond which would make it more amenable to hydrolysis by steam. A sodium ion could react with a hydroxyl group in a similar manner. Even though sodium atoms can move throughout the entire zeolite crystal, there would not be any Si–OH groups in the interior except at the sites of crystal defects which would be potential nucleation sites. The catalytic effects of both vanadium and sodium should be similar because with either material the rate of nucleation would be limited by the number of total hydroxyl groups which are present. Since most of the hydroxyl groups are on the exterior surface, the two metals would have nearly the same catalytic activity. The proposal that Si–OH groups are the sites of attack is also consistent with the reduced steam stability of a small particle Y zeolite which would have a high surface to volume ratio (*28*). This proposal does not account for the synergism observed between vanadium and sodium as catalysts. The occurrence of either sintering or melting is often a problem in experiments of this type and could give an effect similar to synergism. However, in the experiment to show the necessity of steam, there was no detectable change in the LZ-Y82 after 100 h at 760°C. This indicates that steam is necessary for the synergistic effect just as it is for the uncatalyzed reaction and that it is not a melting or sintering phenomena as this would take place in dry air. Understanding synergism is often quite difficult and will require more information than the present study can provide.

CONCLUSIONS

This study clearly shows that the reaction taking place in the presence of either vanadium or sodium is the steam destruction of zeolite. Steam is a necessary reactant and the role of vanadium and sodium are that of catalysts. The present study is believed to be the first kinetic proof of a catalyzed solid-state phase transition. Both sodium and vanadium have about the same activity as catalysts and there is some synergism between them. From the solid-state kinetic results we can conclude that both materials enhance the rate of nucleation but the results do not give any direct information as to how this takes place. As a catalyst, potassium is about equal to sodium and lithium is slightly less active. Rare earths do not change vanadium tolerance. Their effect is an indirect one of changing the base steam stability of the zeolite. XPS results show that vanadium does not uniformly penetrate the zeolite crystal suggesting that the attack may be predominantly at the surface. This result, along with the poor vanadium tolerance of silicalite and the fact that vanadium tolerance is not a function of unit cell size, strongly indicates that the point of attack is not at the tetrahedral alumina site in the zeolite framework. A more probable site of attack is at a Si–OH bond. This would also be true in the absence of vanadium and should cause us to reevaluate our thinking on the mechanism of the uncatalyzed reaction of zeolites with steam.

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