A Selectivity Factor in Vapor-Phase Hydrocarbon Oxidation Catalysis

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Theoretical and experimental work is described which leads to a novel hypothesis for explaining the selectivity in heterogeneous vapor phase hydrocarbon oxidation catalysis. Two essential postulates of the hypothesis are:

1. The oxygen atoms must be distributed on the surface of a selective oxidation catalyst in an arrangement which provides for limitation of the number of active oxygen atoms in various isolated groups.

2. The metal-oxygen bond energy of the active oxygen atoms, at the conditions of reaction, must be in a range where rapid removal (hydrocarbon oxidation) and addition (regeneration by oxygen) is assured.

Monte Carlo methods are used to illustrate the distribution of isolated sites on catalytic surfaces under the dynamic conditions of hydrocarbon oxidation reactions. Differences in catalyst and process requirements between oxidation processes operating in an overall oxidizing or reducing atmosphere are discussed.

The field of heterogeneous vapor phase catalytic oxidation of hydrocarbons to useful oxygenated products has advanced rapidly in recent years. The selective oxidation of propylene to acrolein (*1, 2*), ethylene to ethylene oxide (*3, 4*), and various aromatics to dibasic aromatic carboxylic acids or anhydrides (*5, 6, 7*) represent cases of considerable commercial importance. In spite of this rapid, practical development the literature pertaining to fundamental studies of oxidation catalysis and to new theoretical approaches to the subject has not kept pace (*8*).

Many interesting questions are posed as a result of some of the more recent developments in heterogeneous oxidation catalysis. Why does one catalyst for the oxidation of propylene to acrolein demand a substantial stoichiometric excess of propylene relative to oxygen (*9*), while another catalyst may require just the reverse for selective oxidation (*10*)? Why do different oxidation catalysts yield different products under essentially identical conditions of process operation? For example it is possible to oxidize propylene to either acrolein or acetone (*11*), or to oxidize *n*-butylenes to either butadiene (*12*) or maleic anhydride (*13*), simply by selection of the appropriate catalysts.

A partial answer to these questions is provided by the work described here. It lies in the development of a generalized hypothesis of heterogeneous vapor phase catalysis which is consistent with experimental observation and capable of predicting the course and extent of various reactions. Two basic principles underlie the hypothesis:

1. Oxygen atoms must be distributed on the surface of a selective oxidation catalyst in an arrangement which provides for limitation of the number of active oxygen atoms in the various site groupings (site isolation).
2. The metal oxygen bond energy of the active oxygen atoms at the conditions of reaction must be in the range where rapid removal (that is hydrocarbon oxidation) and addition (that is regeneration by oxygen) is assured.

DISCUSSION

To be acceptable a general hypothesis of oxidation catalysis should be capable of at least qualitative explanation of the following:

1. Changes in activity and selectivity as a function of oxidation state of the catalyst.
2. Differences in activity and selectivity within families of salts of given acidic transition metal oxides.
3. Differences in activity and selectivity of the same average intermediate oxidation state of the same catalyst when it is achieved by reduction of a more highly oxidized state or by oxidation of a more reduced state.
4. Differences in activity and selectivity of an oxidation catalyst at given intermediate oxidation states which result when different reducing agents are employed to achieve them.
5. Changes in activity and selectivity of intermediate oxidation states which occur as a function of elapsed time from the instant of formation of these states by oxidation or reduction processes.

In the development of the hypothesis to be presented here it is instructive to consider two hypothetical oxidation catalyst surfaces and then to attempt to relate them to real catalyst systems. The first case to be considered is that of an oxidation reaction which is conducted with a large stoichiometric excess of hydrocarbon relative to oxygen. Since it is believed that the stoichiometry of the oxidation reaction on a molecular scale is of critical importance in determining the product selectivity relationships, it will be necessary to define the reaction more definitely. Certain assumptions will be made for purposes of simplification and illustration.

1. The reaction considered involves the catalytic conversion of propylene-oxygen mixture to acrolein and waste products.
2. The catalyst's uppermost, lowermost, and intermediate oxidation states can be realized under the reaction conditions by suitable adjustment of the reactant, oxygen-propylene, ratio. There is considerable basis in the literature for believing that molecular oxygen must become associated with the catalyst surface before it takes part in the hydrocarbon oxidation reaction (*3, 4, 5, 6*).
3. The ability of the lowermost oxidation state to oxidize propylene is so slight that it can be neglected. The uppermost and intermediate oxidation states are capable of oxidizing propylene.
4. Propylene can react with the catalyst surface to yield acrolein and water or it can react to produce the waste products 3 CO + 3 H_2O. The reaction to produce acrolein

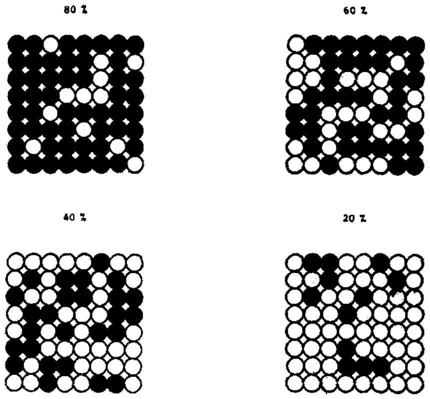


Fig. 1. Oxidation of reduced surface grid with oxygen.

and water has a stoichiometric requirement of two oxygen atoms and that to produce 3 CO + 3 H_2O requires six oxygen atoms (for simplification the side reactions to produce acrylic acid, acetaldehyde, acetic acid, and carbon dioxide are neglected).

5. The basic catalyst surface (for this example) is assumed to be a metal oxide in the lowermost oxidation state. It is approximated by a grid pattern in which a single layer of oxygen atoms can be added to form the uppermost oxidation state.

6. The relative stabilities of the various reactants and products toward oxidation are such that propylene will react to form acrolein or waste products with equal facility, while acrolein and carbon monoxide resist further oxidation (*14*).

Oxygen Regeneration

If the oxidized form of such a hypothetical catalyst is exhaustively reduced with a series of propylene slugs at the optimum temperature for reaction, the lowermost oxidation state of the catalyst is obtained. At this point a small slug of oxygen can be introduced, sufficient to restore about 20% of that removed in the reduction process. The problem now is to determine the distribution of this 20% active oxygen coverage of the inactive underlying surface. Since molecular oxygen is diatomic and the collisions with the surface will be randomly distributed, intuitively, the surface pattern produced by the 20% oxygen coverage will consist mostly of small isolated oxygen atom groups such as doublets and quadruplets and relatively few patches containing more than four oxygen atoms. Of course lateral diffusion effects have been ignored because only the surface configuration at the instant of regeneration is being considered here. Monte Carlo methods with random number tables (*15*) were employed to obtain distributions of isolated groups containing different numbers of oxygen atoms. Tables containing 50 by 50 digit grids were employed. These are randomly numbered tables with digits ranging between 0 and 9. A random pattern in which 20% of the grid is covered by incoming oxygen atom pairs is obtained by selecting a number such as zero, marking it out wherever it appears on the table, and then marking out a number adjacent to each zero on a random basis (such as the largest number neighbor). Alternatively each vertical and horizontal row of a 50 by 50 grid may be numbered (1 to 50) and random hits made on the grid in a sequence obtained by use of a random number list to select horizontal and vertical coordinates. An incoming pair that strikes an already occupied site is assumed to result in an ineffective collision. Similarly an incoming pair which strikes a vacant site without a vacant neighbor to accommodate the second oxygen also is assumed to result in an ineffective collision. This point is illustrated in Figure 1, although for purposes of simplicity 8 by 8 rather than 50 by 50 grids are shown. In addition to 20% oxidation of the reduced grid the cases of 40, 60, and 80% oxidation are also shown.

When a surface is contacted with propylene, it is assumed that the propylene molecule has an effective collision diameter equivalent to one grid location and its eight nearest neighbors. Then it is evident that the propylene can strike the surface and find itself in an environment consisting of a maximum of nine oxygen atoms and a minimum of zero. If these surface models are now contacted with a slug of propylene sufficient to remove only an infinitesimal amount of the reversible oxygen, the product distribution can be calculated (adhering to the previously stated restrictions). Sites containing two to five oxygen atoms are incapable of waste oxidation because they cannot supply the stoichiometric requirement of six oxygen atoms. Thus they will produce only acrolein plus water, which has a stoichiometric requirement of two oxygen atoms. Sites containing less than two oxygen atoms fail to supply the minimum stoichiometric requirement for even acrolein formation and will therefore be ineffective. All sites containing six or more oxygen atoms will react with propylene to produce the waste products, 3 CO + 3 H_2O. Since subsequent oxidation of the product acrolein and carbon monoxide is neglected, the final distribution is obtained by taking the ratio of the number of sites associated with two to five oxygen atoms to the number of sites associated with six or more oxygen atoms.

In Figure 2 the per cent of surface locations (including their eight nearest neighbor locations) which are associ-

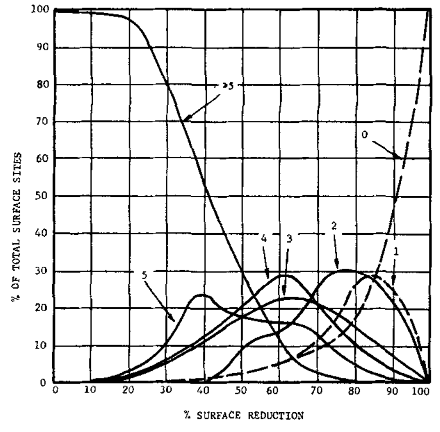


Fig. 2. Site population as a function of surface coverage (oxygen regeneration of reduced grid).

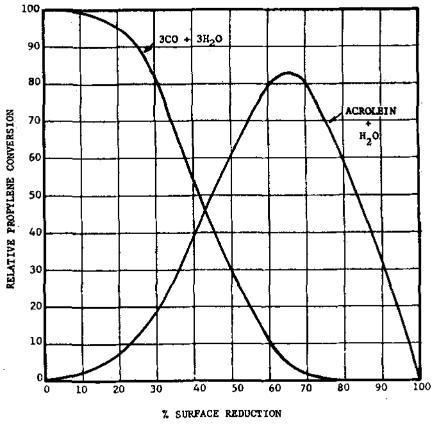


Fig. 3. Relative propylene conversion as a function of oxidation state (oxygen regeneration of reduced grid).

ated with zero, one, two, three, four, five, and six or more oxygen atoms is plotted as a function of surface coverage for the case of oxygen regeneration of a vacant surface. The highest concentration of selective atom sites (two to five oxygen atoms) is found in the range between 20 to 70% surface oxidation. This point is illustrated in Figure 3, where the anticipated relative activity for propylene oxidation is plotted as a function of oxidation state of the catalyst. The plot predicts that the acrolein activity should go through a maximum as the catalyst is progressively oxidized. It also predicts that the waste oxidation would rise rapidly with surface oxidation, becoming the predominant reaction at oxidation states greater than 70%. The change in selectivity with surface coverage of this model is illustrated in Figure 4. The relative production of acrolein decreases with increasing surface oxidation. The relative production of carbon monoxide and water increases slowly with surface oxidation at first but rises very rapidly as high values are approached.

This hypothetical example can be compared with a real catalyst which functions in a low oxidation state with a reactant feed which contains a large stoichiometric excess of propylene relative to oxygen. Just as in the model, the surface is relatively thinly populated in active oxygen. Thus there is a constant rain of propylene and oxygen molecules upon the surface with most oxygen molecules building into the surface momentarily in isolated atom pairs, but also being removed in pairs to produce acrolein plus water almost immediately by gas phase propylene molecules which strike them. The average life of oxygen atom pairs on the surface should be short enough to preclude extensive redistribution by lateral and bulk diffusion processes.

Now, if some of the restrictions which were placed on the model are relaxed (for example by permitting some of the product carbon monoxide to react further with surface oxygen to produce carbon dioxide with a stoichiometric requirement of one oxygen atom and some of the acrolein to react with sites containing four or more oxygen atoms to yield waste products), the quantitative distribution of products will be changed somewhat from the idealized description, but not greatly.

Propylene Reduction

If the hypothetical catalyst of the previous example is regenerated with molecular oxygen to its uppermost oxidation state, the gridlike surface will be completely filled with active oxygen atoms. Now suppose that a small slug of propylene is passed over the catalyst, and assume further that the same rules governing selectivity which were employed in the first example are still in effect. Again, random number tables are employed to determine the product distribution. Obviously at very high oxygen surface coverage almost every propylene molecule is assured of hitting a region of surface containing at least six adjoining oxygen atoms (stoichiometric requirement for waste oxidation), and the products of reaction will consist largely of carbon monoxide and water. If the reduction process is continued, by repeatedly passing small slugs of propylene over the catalyst the surface distribution of isolated single, double, triple, etc. oxygen atom sites will be observed to change greatly with the per cent of reduction.

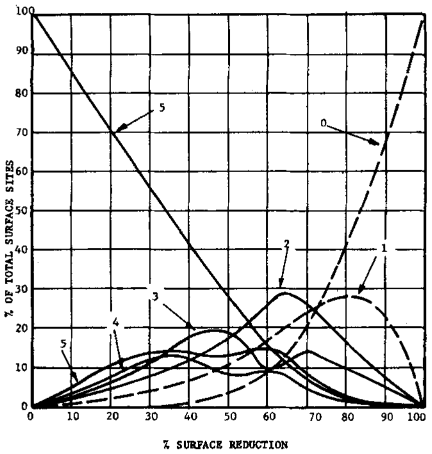


Fig. 5. Site population as a function of surface coverage (propylene reduction of oxidized grid).

In Figure 5 the per cent of surface locations of a grid model which are associated with zero, one, two, three, four, five, and six or more oxygen atoms is plotted as a function of surface coverage for the propylene reduction case. This plot is similar to that obtained previously for the oxygen regeneration of the reduced grid, but is not identical. Again grid locations with zero and one oxygen atom are taken as inactive, those associated with two through five oxygen atoms are capable of yielding acrolein plus water, while those associated with six or more oxygens are taken to yield waste oxidation products.

The manner in which the selectivity of this reaction changes with surface coverage of the model is illustrated in Figure 6. The selectivity for acrolein rises rapidly with reduction until about 80% selectivity is reached at 60% reduction. The curve then gradually rises to 100% selectivity at complete reduction.

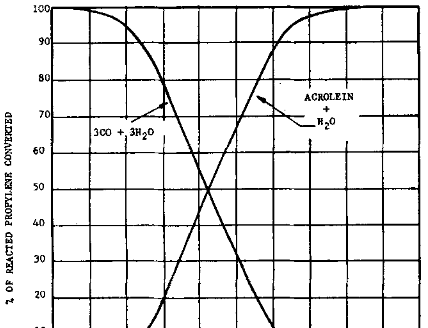


Fig. 4. Selectivity for propylene oxidation vs. surface coverage (oxygen regeneration of reduced grid).

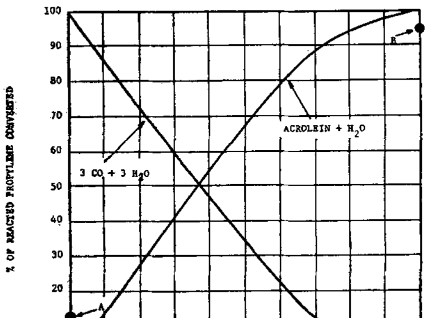


Fig. 6. Selectivity for propylene oxidation vs. surface coverage (propylene reduction of oxidized grid).

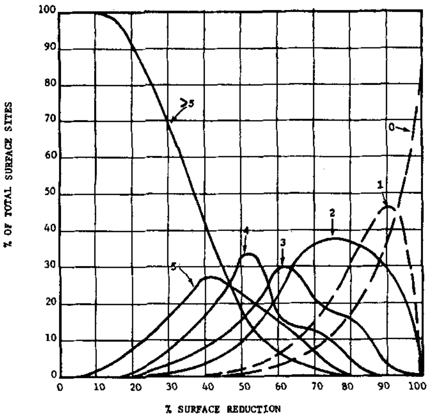


Fig. 7. Site population as a function of surface coverage (hydrogen reduction of oxidized grid).

Hydrogen Reduction

Instead of reducing the fully oxidized form of the catalyst to some intermediate oxidation state with propylene, a reducing agent such as hydrogen, which removes single oxygen atoms from the surface grid, can be employed. The distribution and population of sites as a function of oxidation state are somewhat different in this case.

Figure 7 illustrates the surface site population at various stages of reduction with hydrogen. If this figure is compared with that obtained with propylene as a reductant (that is Figure 5), the largest difference is noted at high oxidation states. At low surface reductions a propylene reduced grid is more selective for acrolein production than a hydrogen reduced grid. The opposite is true at high surface reductions. Oxygen regeneration of a reduced grid yields an intermediate acrolein selectivity at intermediate and low oxidation states.

Results

To test the hypothesis which has been developed here, a series of experiments were conducted with microreactor techniques (*16, 17*), with a silicon carbide supported copper oxide catalyst. Silicon carbide of 20- to 35-mesh particle size was impregnated with a copper nitrate solution, dried at 120°C. and calcined in air at 350°C. The final catalyst contained 0.4 wt. % copper oxide calculated as cupric oxide. The catalyst (3.9 g.) was charged to a stainless steel microreactor constructed of 3/8 in. thin wall tubing, 6 in. long. The charged reactor was immersed in a molten salt bath which was temperature controlled at 300 ± 0.5°C. Helium was passed through the reactor continuously at a rate of 70 ml./min. and then through vapor phase chromatographic columns and detectors. Three gas sampling valves were inserted in the helium line upstream of the reactor to provide for injection of small reactant gas slugs. The gas entering the reactor passed through a 6 in. length of 1/8-in. tubing to provide for preheat. The amounts of propylene, oxygen, oxides of carbon, acrolein, and water issuing from the reactor were determined by vapor phase chromatography.

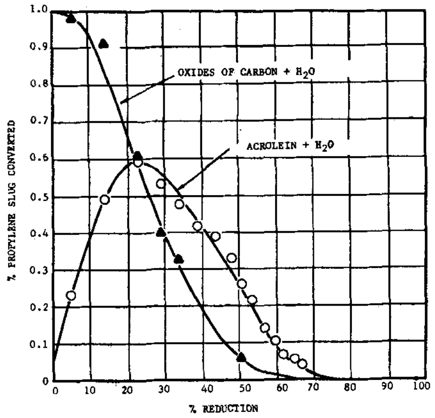
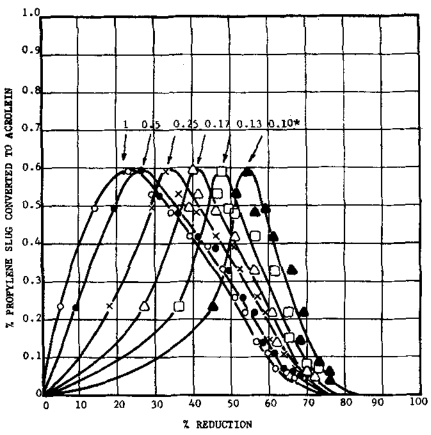


Fig. 8. Experimental propylene oxidation activity vs. catalyst oxidation state—copper oxide catalyst, 300°C. reaction temperature.



*Surface to bulk atom ratio

Fig. 9. Experimental propylene oxidation activity vs. oxidation state corrected to various surface to bulk atom ratios—copper oxide catalyst, 300°C. reaction temperature.

In one experiment a fully oxidized copper oxide catalyst (oxidized at 350°C.) was contacted with a 1-ml. slug of an equimolar mixture of propylene and oxygen at 300°C. The selectivity to acrolein in this reaction was 12%, which is in good agreement with the hypothesis (Figure 6, point *A*). In another experiment the catalyst was reduced with propylene until no further reduction was observed. At that point a 1-ml. slug of an equimolar mixture of propylene and oxygen was passed over this reduced catalyst. The selectivity to acrolein was found to be 95%, which is also in good agreement with the hypothesis (Figure 6, point *B*).

In order to determine the character of the experimental activity and selectivity for acrolein production as a function of the catalyst oxidation state over the full range of oxidation states, another experimental technique was employed. In this case a sequence of propylene slugs was passed over the catalyst and the amount of each propylene slug converted to acrolein or oxides of carbon was determined chromatographically. The oxidation state was related to the number of propylene slugs by back titration with oxygen slugs and independently by material balance of oxygen in the oxidation products from each propylene slug. In Figure 8 are plotted the mole per cent of each propylene slug converted to acrolein and to oxides of carbon as a function of the per cent reduction of the catalyst.

In devising the model with which to compare Figure 8, the finite thickness of the copper oxide crystals has to be taken into consideration. It will be assumed that the rate of diffusion from bulk to surface is slow relative to the time each gaseous propylene slug is in contact with the catalyst. Thus only the oxygen atoms in the surface layer will be eligible for reaction with a given propylene slug. However since the time between propylene slugs is much greater than the duration of a slug, it will be assumed that equilibration of oxidation state between the surface and the bulk will have been attained between successive propylene slugs. That these are good approximations with the catalyst employed was established by experiments in which the oxidation activity relaxation was determined

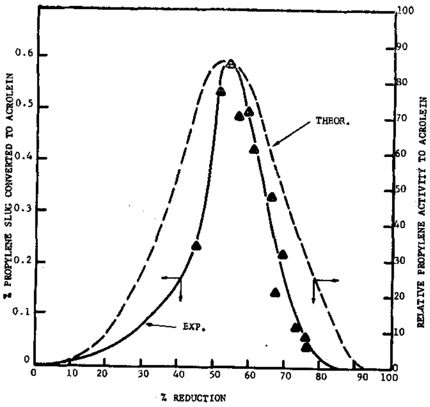


Fig. 10. Theoretical and experimental propylene conversion to acrolein as a function of catalyst oxidation state.

over several minutes at various oxidation states. The random diffusion process therefore results in an equilibrated surface essentially identical to a hydrogen reduced grid. In Figure 9 are plotted the data of Figure 8 for various atom layer thicknesses of the copper oxide crystals. It is seen that maximum activity for production of acrolein is shifted in the direction of lower oxidation state as the ratio of surface to bulk oxygen atoms decreases. From X-ray data and other considerations it is estimated that the ratio of surface to bulk oxygen atoms in the catalyst employed in these experiments is of the order of 0.1. In Figure 10 the activity curve for ten atom layers (from Figure 9) is compared with the model curve. A very reasonable similarity is evident.

Selective Catalysts at High Oxidation State

Although catalysts which display high selectivity for oxidation of hydrocarbons to useful products in a reduced oxidation state are extremely interesting, it is perhaps even more interesting to consider catalysts which display a high order of selectivity in an essentially completely oxidized state. In order to provide for selectivity in this case it is necessary to rely on a mechanism of site isolation which is based on a different concept than that of the randomness of gaseous molecular collision with the surface. One way of achieving active site isolation in metal oxide catalyst systems of high oxidation state is to take advantage of natural differences in reactivity of oxygen atoms in certain crystal structures. For example there may be several different metal-oxygen bond distances (and therefore bond energies) to consider in even a simple oxide system. Furthermore the most active of these oxygen atoms may appear as regularly spaced isolated groups in a field of less active oxygen atoms. A simple hypothetical case to consider is a crystal surface in which 20% of the oxygen atoms are very tenuously bound, while the remaining 80% are strongly bound and not readily available for hydrocarbon oxidation. The active oxygen atoms are distributed over the surface in regularly spaced isolated pairs. Again, using the propylene to acrolein reaction as in the previous examples and applying the same rules to govern reaction possibilities, one finds that the highest oxidation state of this catalyst is extremely selective for the production of acrolein.

Another interesting surface model is that of isolated rows of oxygen atoms, the rows being separated by a field of less active oxygen atoms. In this case the fully oxidized surface will lose oxygen atoms preferentially from the active rows during reduction with propylene. Accordingly a high order of selective oxidation will be observed at a relatively slight total surface reduction compared with the grid model.

Mars and van Krevelen (5) discuss the rowlike structure of vanadium pentoxide pertaining to the oxidation of aromatic compounds. They point out that in the vanadium pentoxide lattice two kinds of oxygen ions are distinguishable. The greater part of the oxygen is present in about the same plane as the vanadium ions. Two fifths of the oxygen ions however are arranged in planes parallel to and alternating with the first. They assume these latter oxygen ions to interact with the aromatic molecules at the surface and reason that the rate of oxidation depends on the concentration of these oxygen ions and on the amount of aromatic molecules adsorbed on or coming down to the surface from the gaseous phase.

If it is assumed that there is a simple chemical means for permanently rendering some of the active oxygen atoms in the rows to an inactive form, then permanently isolated site groupings containing small numbers of active oxygen atoms can be formed. For example this might be accomplished by less than stoichiometric reaction with another metal oxide which yields a nonreducible surface compound. If the inactive compound is formed, such that the rows are broken up into segments of random length, a catalyst which is very selective for oxidation of propylene to acrolein results.

Significantly, if small propylene slugs are passed over the fully oxidized forms of vanadium pentoxide, potassium oxide, and potassium metavanadate it is observed (*18*) that the vanadium pentoxide catalyst gives a substantial amount of oxidation to waste oxides of carbon, water, and only a small amount of oxygenated intermediate products, while the K_2O and KVO_3 give essentially no propylene oxidation to either waste or intermediate products. Thus inactive potassium oxide (from the standpoint of oxidation capacity) when reacted with active vanadium pentoxide produces a salt with essentially no oxidation capacity. If less than stoichiometric amounts of potassium oxide are reacted with vanadium pentoxide, the resulting compounds are observed to possess a capacity for the oxidation of propylene which decreases in a regular way with increasing potassium oxide addition. However the selectivity for the oxidation of propylene to acrolein of the resulting nonstoichiometric compounds actually increases as the ratio of potassium oxide to vanadium pentoxide is increased up to the stoichiometric point.

SUMMARY

In summary it is believed that experimental evidence supports the view that selective heterogeneous catalytic oxidation of hydrocarbons to oxygenated intermediates requires the following:

1. The oxygen atoms must be distributed over the surface of a selective oxidation catalyst in an arrangement which provides for limitation of the number of active oxygen atoms in the various site groupings. In general it is desired to provide at least enough active oxygen atoms at the isolated site to satisfy the stoichiometric requirement for the oxidation of the hydrocarbon to the desired product or to an isolable intermediate, but less oxygen than is required for complete oxidation to waste products. Active site isolation may be achieved in any of several possible ways, such as operation at an intermediate oxidation state in which the desired site groupings are maximized owing to the randomness of gas phase collisions with the surface, selection of metal oxides with naturally grouped active oxygen atoms in a field of less active oxygen atoms, and modification of an oxide surface by less than stoichiometric reaction with a reagent which permanently renders portions of it inactive.
2. The metal-oxide bond energy of the active oxygen atoms at the conditions of reaction must be in a range where rapid removal (that is hydrocarbon oxidation) and

addition (that is regeneration by oxygen) is assured. A very important means for adjusting the metal-oxygen bond energy of an oxide is by reacting it with another material to produce a new structure with modified bond energies and surface geometry (such as a series of vanadate compounds starting with the alkali vanadates and perhaps ending with heteropoly vanadic acids).

The experimental results described here are consistent with the proposed hypothesis, but there are obvious complicating factors. For example oxygen diffusion from bulk to surface and the reverse process tend to distort somewhat the site distributions of the surfaces from those described in the models. Also phase boundaries, dislocations, and other forms of surface disorder add further complications to the case of real surfaces. However in spite of these complications there is a clearly distinguishable correlation between the approximate surface configuration as described by the model and the selectivity factor in the oxidation of propylene to acrolein.

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Unsteady State Absorption of Carbon Dioxide by Dilute Sodium Hydroxide Solutions

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Rates of carbon dioxide absorption by 0.01, 0.05, and 0.1 molar sodium hydroxide solutions were measured at 25°C. for exposure times from 1.4 to 21.6 milliseconds with a laminar-jet technique. Absorption rates were calculated with a model based on one-dimensional diffusion occurring simultaneously with two consecutive irreversible chemical reactions. The resulting partial differential equations were solved with an IBM-709 computer. The calculated absorption rates agreed within 5% of the experimental values.

This work is part of an extensive study of the equilibrium, kinetics, and mass transfer characteristics of the system defined by the overall reaction

$$NaHS + CO_2 + H_2O \rightleftharpoons H_2S + NaHCO_3 \qquad (1)$$

The vapor-liquid equilibrium properties of this system have been reported previously (*18*) as have the reaction kinetics of the individual reactions which together give reaction (1) (*14, 15*). This study was concerned primarily with the unsteady state absorption of carbon dioxide by alkaline solutions. The following reactions were considered:

$$CO_2 + H_2O \underset{k_{r2}}{\overset{k_{f2}}{\rightleftharpoons}} HCO_3^- + H^+ \qquad (2)$$

$$CO_2 + OH^- \underset{k_{r3}}{\overset{k_{f3}}{\rightleftharpoons}} HCO_3^- \qquad (3)$$

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