

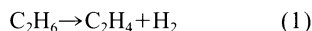
High Selectivities to Ethylene by Partial Oxidation of Ethane

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At least 85 percent selectivity to ethylene at greater than 70 percent conversion can be obtained by partial oxidation of ethane by adding large amounts of H₂ to the reaction mixture and using a platinum-tin catalyst operating at 950°C with a contact time of $\sim 10^{-3}$ seconds. This system almost totally shuts off the reactions that form undesired CO and CO₂, which fall from 20 percent without H₂ to 5 percent when H₂ is added. Although a 2/1 H₂/O₂ mixture should be explosive at high temperatures, no flames or explosions occur in the presence of ethane. The successive reactions on the catalyst generate more H₂ than used in the feed, so with recycle no additional H₂ would be needed. These results are unexpected because ethylene is a nonequilibrium product and entropy considerations argue that all reaction channels open at high temperatures so the products should approach equilibrium, which predicts only a few percent ethylene. This process is promising for the replacement of steam cracking in the production of ethylene.

Ethylene is the major intermediate in the chemical industry, with more than 25 billion kilograms produced in the United States annually (1). Ethylene is produced almost exclusively by steam cracking in which alkanes are heated to $\sim 800^\circ\text{C}$ in alloy tubes in a furnace to cause homogeneous pyrolysis; a typical reactor configuration is sketched in Fig. 1A. These plants operate with a residence time in the heated tubes of ~ 1 s and typically produce $\sim 85\%$ selectivity to ethylene at $\sim 60\%$ conversion of ethane. Undesired products are fed back into the furnace to be burned to provide much of the required heat, so that modern olefin plants, although highly energy efficient, necessarily convert $>10\%$ of the ethane into CO₂, a major greenhouse gas. Because the flame in the tube furnace has a high peak temperature, these processes inevitably produce significant pollutants such as NO_x.

The overall reaction for ethane to ethylene can be written as



although many other products such as acetylene, other olefins, and benzene are formed through this homogeneous free-radical chain reaction. Particularly troublesome in steam cracking is the formation of carbon on the tube walls. Although the addition of steam reduces the rate of carbon formation, these reactors must be shut down periodically to burn off accumulated carbon.

Catalytic dehydrogenation on metal ox-

ides (2) has been explored as an alternative to steam cracking because of its potentially higher selectivity to a single olefin, but selectivities reported are comparable to those in steam cracking only at low conversions.

Oxidative dehydrogenation (3) offers considerable advantage to these dehydrogenation processes because oxidation reactions are much faster than the reaction time required for steam cracking or catalytic dehydrogenation. Further, because the overall reaction is exothermic, no process heat is needed, thus simplifying the reactor. We have shown previously (4) that the reaction



using a Pt-coated ceramic foam monolith produces up to 65% ethylene selectivity at 70% ethane conversion and $>99\%$ O₂ conversion. We also found that use of Pt-Sn rather than Pt increased the selectivity to $\sim 70\%$ (5). Patents (6) suggest that the addition of H₂ with noble-metal catalysts can give slightly increased performance in oxidative dehydrogenation.

We now report that the combination of Pt-Sn with appropriate amounts of H₂ gives olefin selectivities higher than 85%. This improvement occurs by preferential oxidation of H₂ to H₂O initially in the catalyst, which removes the O₂, prevents alkane oxidation, and provides the necessary temperature for short contact time dehydrogenation with high selectivity and conversions.

In these experiments we add large amounts of H₂, typically in a 2/1 H₂/O₂ ratio at above atmospheric pressure. This experiment should be dangerous because H₂/O₂ mixtures are flammable or explosive over a wide range of compositions, even with inert dilution, especially at high temperatures and in the presence of a Pt catalyst. However, we found that H₂ addition to a 2/1 C₂H₆/O₂ mixture gave no evidence of

homogeneous reactions. We also note that the process can produce more H₂ than is fed by the successive dehydrogenation of C₂H₆, so that with recycle the process could require no net import of H₂.

This process appears to occur by mechanisms very different from conventional homogeneous and surface processes because both homogeneous and Pt-catalyzed oxidation processes yield considerable deep oxidation to CO and CO₂. These results suggest new technologies for chemical synthesis by suitable design of catalysts and by operating under extreme conditions.

Catalysts in these experiments consist of α -alumina foam monoliths, 18 mm in diameter and 10 mm long, on which 1 to 5% by weight of Pt and Sn were deposited from aqueous salt solutions. Because the surface areas were less than 1 m²/g, these loadings formed thick films and large particles on the alumina surface after heating to decompose the salts.

The catalyst was sealed in a quartz reactor tube with alumina cloth. Ethane, O₂, and H₂ were fed at a total pressure of 1.2 atm at 25°C and with a flow rate of 3 to 10 liter/min. The catalyst was ignited with a Bunsen burner flame, after which the burner was removed and the reaction zone insulated to achieve nearly adiabatic conditions. Alumina heat shields on both sides of the catalyst prevented axial radiation losses. Catalyst temperatures were between 900° and 950°C, which was within $\sim 20^\circ\text{C}$ of the calculated adiabatic temperature for the conversions and selectivities observed. Products were analyzed by gas chromatogra-

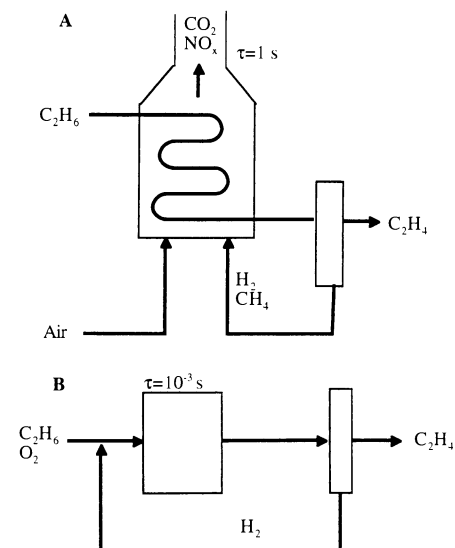


Fig. 1. Sketches of (A) conventional steam cracking reactor configuration to produce ethylene by homogeneous reaction of ethane and (B) by oxidative dehydrogenation with product H₂ recycle. The latter would be more than 10 times smaller, simpler to operate, and produce less CO₂ and pollutants.

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phy, which detected all reactants and products up to C_4 species. Selectivities (fractions of ethane converted to different product molecules) were calculated on a carbon atom basis. For mass spectrometric analysis, gas samples were collected and analyzed by calibrating against known gas mixtures.

Figure 2 shows plots of selectivities and conversions in typical experiments at $C_2H_6/O_2 = 2/1$ as a function of H_2 added to the reaction mixture, plotted as H_2/O_2 . Without H_2 , the selectivity with Pt alone was $\sim 65\%$ and with Pt-Sn, the selectivity was $\sim 70\%$. Of the 30% carbon in ethane that does not form ethylene in the absence of H_2 , $\sim 20\%$ oxidized to CO and CO_2 , 5% formed CH_4 , and $\sim 5\%$ formed other products with multiple bonds, such as acetylene and butylenes. When H_2 was added with Pt alone, the selectivity to ethylene increased by $\sim 5\%$ and the methane increased slightly. How-

ever, when H_2 was added with the Pt-Sn catalyst, the selectivity to ethylene rose to $>85\%$, and the other olefin products are $\sim 5\%$ to give a total selectivity to valuable products of $\sim 90\%$. Table 1 compares partial oxidation results using Pt and Pt-Sn catalysts with H_2 addition to the steam cracking process. It is seen that with H_2 addition, Pt-Sn catalyst gives comparable ethylene selectivity to steam cracking at higher conversion using a much smaller reactor.

We have repeated these and similar experiments on many catalysts with different supports, metal loadings, and metal ratios, and all of the results were consistent with the results shown. The selectivities and conversions varied by no more than 5% with variations of metal loading from 0.1 to 10%. These results show that the total surface area of the catalyst was unimportant and that the exposed oxide from the alumina did not have a harmful effect.

Preheating the reactants increased conversion while slightly lowering selectivities. The catalysts exhibited only a few percent decline in conversion and an even smaller decrease in ethylene selectivity over more than 20 hours of operation. Deterioration in performance was accompanied by loss of volatile Sn from the catalyst as indicated by surface analysis, although its evaporation rate from the intermetallic compound was less than that calculated from the vapor pressure of Sn. The lost activity could be restored to its initial value by replenishing the Sn in the catalyst. Although solid carbon is thermodynamically stable for these compositions and temperatures, we observed no carbon accumulation on the catalysts during more than 100 hours of operation.

These experiments suggest that the improved selectivities to olefins and the corresponding reduction of CO and CO_2 result from the consumption of O_2 by H_2 . This leaves ethane dehydrogenation as the dominant reaction, rather than the direct attack of O_2 on ethane, which these experiments suggest must otherwise produce $\sim 20\%$ CO and CO_2 .

We have varied the flow rate of gases through these catalysts over a wide range and have used different catalyst geometries to examine the dependence of reactor performance on residence time. We find that the conversions and selectivity to ethylene are nearly independent of flow rate over a factor

of 10 variation in flow rate. In these and other experiments we find that the performance is essentially unchanged for total contact times of the gases as low as 500 μs , which is further evidence that purely homogeneous reactions do not explain these results.

To further test the roles of H_2 loss by oxidation and its production by dehydrogenation of ethane, we replaced H_2 by D_2 and examined deuterium in the products by mass spectrometry. We observed that most of the water was formed from deuterium, and that most of the hydrogen in the product was from ethane. We also observed little deuterium in the ethylene or other hydrocarbon products. These results strongly suggest that the process in fact involves the simple unimolecular and bimolecular steps suggested here, either on the surface or in the gas.

We also examined these Pt-Sn catalysts after use by scanning electron microscopy (SEM) and x-ray diffraction (XRD). As shown in Fig. 3, all of the metal particles are fairly large and all particles contain both Pt and Sn with no isolated Pt dispersed on the alumina. No face-centered cubic Pt metal crystalline phases were seen in XRD on the used catalyst, only Pt_3Sn and PtSn phases. This confirms that the active catalyst is Pt-Sn compound crystals with no free Pt remaining that is not accompanied by Sn.

High selectivity to a particular nonequilibrium product is usually only obtained at low temperatures in order to focus a reaction along a particular reaction path, and this selectivity usually occurs only at low reactant conversion. High temperatures usually produce many products because entropy effects cause all reaction channels to open, and the products should approach equilibrium. We observe $>85\%$ olefin selectivity and $<5\%$ CO and CO_2 with H_2 addition on PtSn. This system is therefore capable of focusing the reaction path almost exclusively along the reaction channels that produce C_2H_4 and H_2O , while simultaneously producing large amounts of H_2 by decomposition of C_2H_6 . Attack of the ethane by O_2 to cause C-C bond scission is strongly suppressed.

Qualitatively, this process must involve first the oxidation of H_2 to H_2O , which generates heat and removes O_2 , followed by dehydrogenation of C_2H_6 to produce C_2H_4 and H_2 , and all of these reactions occur within $\sim 10^{-3}$ s. Possible mechanisms to explain

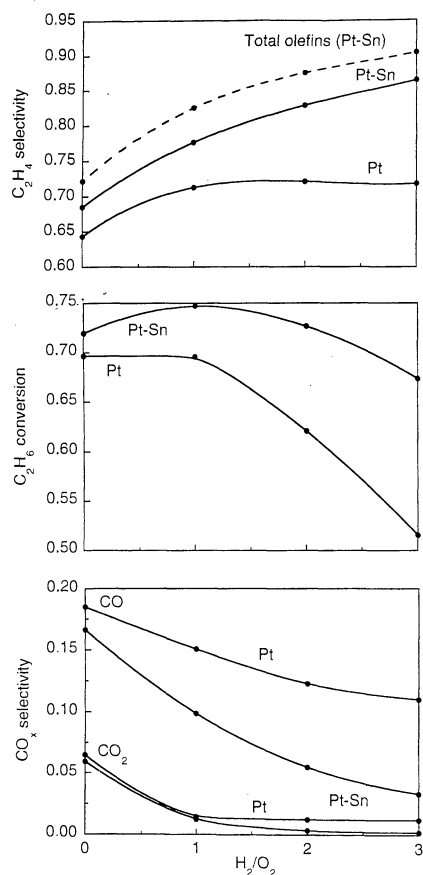


Fig. 2. Plots of experimental carbon atom selectivities to different products and ethane conversion as a function of H_2 addition in a monolith reactor with Pt and Pt-Sn catalysts on α -alumina foams at an C_2H_6/O_2 ratio of 2/1. Selectivities are defined as percentages of carbon atoms in C_2H_6 converted to particular products. Selectivities to desired products as high as 90% can be obtained with 70% ethane conversion. The CO and CO_2 fall to less than 5%, showing that addition of H_2 with this catalyst almost completely suppresses oxidation of the alkane to these products.

Table 1. Comparison of partial oxidation of ethane with steam cracking.

Process	Feed (moles)				C_2H_4 selectivity (%)	C_2H_6 conversion (%)	Time (s)
	C_2H_6	O_2	H_2	H_2O			
Steam cracking	2	0	0	2	85	60	0.1
Pt	2	1	0	0	64	69	10^{-3}
Pt-Sn + H_2	2	1	2	0	83	73	10^{-3}

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these results are (i) purely catalytic reactions on the Pt-Sn surface, (ii) purely homogeneous reaction, and (iii) catalytic H_2 oxidation followed by homogeneous ethane decomposition. We will consider each of these mechanisms and show that, while each gives partial interpretation of results, none appears to be totally satisfactory.

The adsorption of C_2H_6 , O_2 , and H_2 and most product species has been fairly well characterized on Pt from experiments on single crystals under well-defined conditions (7). These results are consistent with surface catalytic reactions in which C_2H_6 adsorbs dissociatively to form C_2H_5 , which then further dehydrogenates on the surface by β -H elimination to form rapidly desorbing C_2H_4 . Addition of H_2 should by this picture give minor changes with slightly more H_2O and less CO and CO_2 .

Surfaces of Pt-Sn have been characterized by adsorption of most of these species under well-defined conditions by depositing Sn on single crystals of Pt to mimic the surfaces of the Pt_3Sn and $PtSn$ phases (7). These experiments show reduced saturation coverages and lower adsorption energies of all species upon addition of Sn to Pt surfaces.

Our results suggest that, on the PtSn surface, the rate of the reaction $H_2 + O_2 \rightarrow H_2O$ is enhanced or the decomposition of C_2H_6 is

retarded. Our experiments at very high flow rates suggest that the overall rates of these processes appear to be just as high on PtSn as on Pt, and thus the rate of H_2O formation may be enhanced on PtSn. Further experiments and models of the surface reaction steps are necessary to quantify these reaction steps.

A purely homogeneous mechanism does not appear to be capable of describing these results. The homogeneous reaction steps and their rates have been thoroughly characterized (8) to explain pyrolysis and combustion of alkanes, both of which occur through free-radical intermediates. For ethane, these reactions can be simplified as $C_2H_6 \rightarrow C_2H_5 \cdot \rightarrow C_2H_4$ where $C_2H_5 \cdot$ is the gaseous ethyl radical species. We have simulated the purely homogeneous reaction process by incorporating the 3500 elementary steps of ethane pyrolysis and combustion (8). We assumed an instantaneous temperature step from 25° to $950^\circ C$ at the catalyst entrance for $C_2H_6/O_2/H_2$ compositions of 2/1/2, 2/1/0, and 2/0/0 and calculated all of the species concentrations versus time. Results of mole fractions versus time are shown in Fig. 4 (inset). Without H_2 addition, the selectivity of ethane oxidation to ethylene is predicted to be no more than $\sim 70\%$, and with H_2 added the selectivity rises only to 75% at 70% C_2H_6 conversion.

In Fig. 4, we show the experimental results of Fig. 2 (thicker lines), plotted as ethylene selectivity versus C_2H_6 conversion. Curves are shown for Pt with and without H_2 and for Pt-Sn

with and without H_2 . Also shown are predicted curves by the homogeneous reactions from the calculations shown in the inset (thinner lines). It is seen that homogeneous oxidation with added H_2 ($C_2H_6/O_2/H_2 = 2/1/2$) or without added H_2 ($2/1/0$) does not predict the high selectivities observed.

Pyrolysis of C_2H_6 without O_2 (2/0/0) predicts selectivities approaching 90%, in agreement with experiments. This result suggests a mechanism for the oxidation process in which Pt-Sn preferentially catalyzes the surface H_2 oxidation reaction and then homogeneous pyrolysis dehydrogenates C_2H_6 to C_2H_4 . In this model, it is assumed that all O_2 reacts rapidly with the surface hydrogen, and then the C_2H_6 pyrolyzes homogeneously to give predicted selectivities. The adsorption of olefins on Pt is weakened by addition of Sn (7), which could be a factor in reducing further reactions of C_2H_4 .

However, the mechanism of surface H_2 oxidation followed by homogeneous C_2H_6 pyrolysis does not agree with the time scales observed in the experiments, which are also indicated in Fig. 4. Although homogeneous oxidation processes occur within 1 ms at $950^\circ C$, an order of magnitude longer time is required to attain the C_2H_6 conversions observed in the absence of O_2 .

We therefore conclude that none of these mechanisms explains the experimental results completely. The extremely short reaction times argue for surface processes, whereas the ethyl-

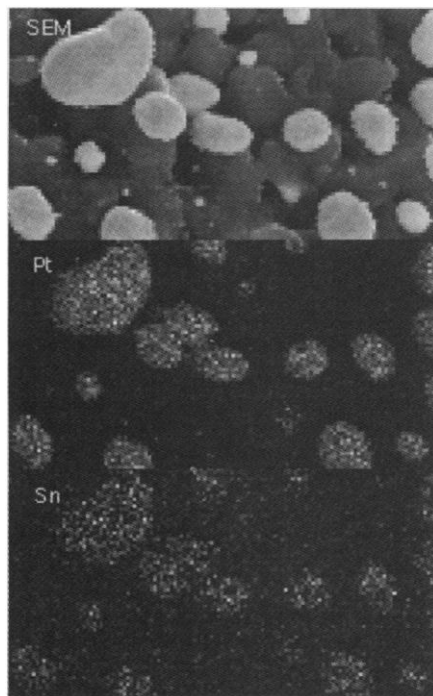


Fig. 3. Scanning electron microscope images of Pt-Sn catalyst particles on α -alumina monoliths after use in the reactor for ~ 5 hours. Particles are large ($\sim 1 \mu m$ diameter) single crystals with individual facets evident. All particles contain both Pt and Sn, indicating that no free Pt metal is formed on this catalyst. Bar, $2 \mu m$.

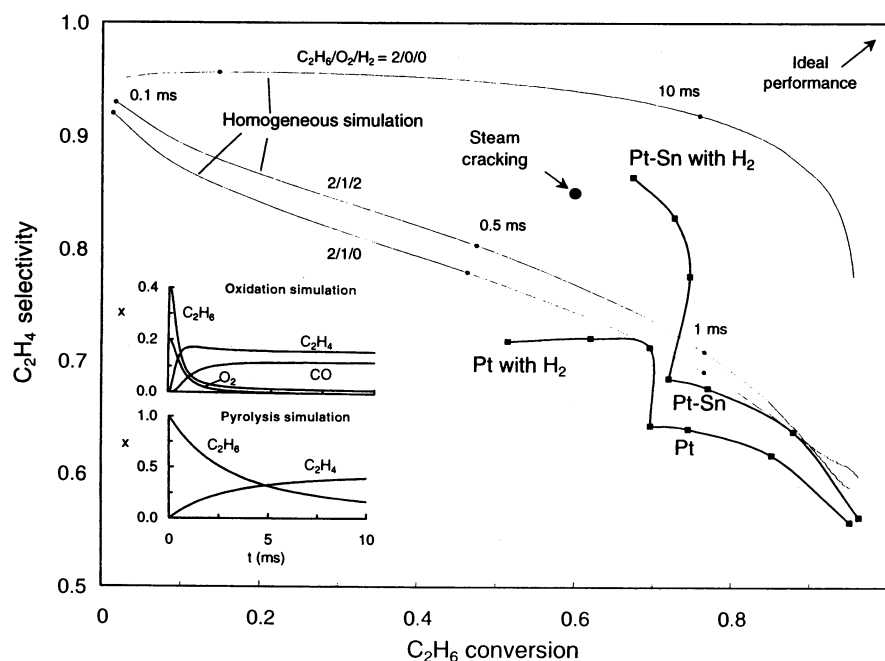


Fig. 4. Selectivities of ethane dehydrogenation to ethylene versus ethane conversion. Squares indicate experimental results giving ethylene selectivity and conversion above those in steam cracking of ethane (large dot) by using a Pt-Sn catalyst with H_2 addition. Also shown are predictions assuming only homogeneous reactions. (Inset) Calculated mole fractions versus time with O_2 (upper) and without O_2 (lower). The selectivity rises considerably above that predicted by homogeneous reaction in the presence of O_2 , and the time for the experimentally observed conversion is far shorter than predicted by homogeneous pyrolysis in the absence of O_2 .

ene selectivities are consistent with homogeneous reactions in the absence of O_2 . Further experiments and simulation would be required to distinguish between these mechanisms.

This system is an example where extreme conditions can be used to produce a very high selectivity to a single product at high temperatures in a very efficient reactor configuration, even though thermodynamic equilibrium predicts mostly solid carbon and only a few percent ethylene. The process operates by combining the fast surface oxidation reactions on a modified Pt surface with homogeneous and heterogeneous dehydrogenation

processes. We have shown that homogeneous reactions alone cannot account for the observed results, but the specific role of homogeneous reaction steps, if any, has not yet been determined. We suggest that extreme conditions such as these may provide the environments to carry out similar reactions to produce chemicals with high efficiency, more efficient energy use, and less pollution.

References and Notes

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Localization-Delocalization Transition in Quantum Dots

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Single-electron capacitance spectroscopy precisely measures the energies required to add individual electrons to a quantum dot. The spatial extent of electronic wave functions is probed by investigating the dependence of these energies on changes in the dot confining potential. For low electron densities, electrons occupy distinct spatial sites localized within the dot. At higher densities, the electrons become delocalized, and all wave functions are spread over the full dot area. Near the delocalization transition, the last remaining localized states exist at the perimeter of the dot. Unexpectedly, these electrons appear to bind with electrons in the dot center.

The problem of electron localization has remained a prime focus of experimental and theoretical research over the past 40 years. In 1958 Anderson (1) showed that, in one dimension and in the presence of an arbitrary disorder potential, an electron diffuses over only a finite length. A subsequent milestone in localization theory was the scaling hypothesis (2). A scaling law connects the properties of a system with the properties of its subsystems of smaller sizes. Scaling theory used conductivity as the only parameter needed to characterize a disordered system. This basic assumption originated from Thouless and Edwards (3, 4) and linked the dc conductivity of a finite disordered system with the sensitivity of electron energy levels to a modification of boundary conditions.

The dependence of a particular electronic state energy on boundary conditions reflects the probability density for an electron's wave function to reside at the boundary and thereby reveals the likelihood of permeating the bound-

ary. Despite all the success of the scaling theory, it is the theory developed for noninteracting systems. Here, we use Thouless's intuitively clear approach to localization to study the properties of a confined interacting electron droplet. We monitor how the energies to add single electrons to a quantum dot change as we vary the potential at the dot's edges.

In most quantum dot experiments (5, 6), a dot is weakly connected to two macroscopic leads. Applying a positive (negative) potential to a closely placed gate electrode increases (decreases) the number of electrons on the dot. At the particular gate potential at which an electron is added to the dot, the number of electrons on the dot can fluctuate by one, allowing single electrons to be added to the dot from one lead and to depart the dot through the other. The conductance through the dot displays a peak for these values of the gate voltage and remains zero for other values (5, 6). Note that if electrons cannot be transported through the dot, no conductance peak can be observed. Our method of single electron capacitance spectroscopy (SECS) displays a peak in the sample capacitance each time an electron is added to the dot (7). Because of the geometry (Fig. 1A) of our samples and because SECS measures charge rather than conductance, even electrons added to states localized within the dot are de-

tected in SECS measurements. SECS can thereby sense electrons even in dots that are electrically insulating. For high electron densities, both conductance and capacitance measurements yield similar results. Because of electron repulsion, more energy is required to add subsequent electrons to the dot. Charge in the dot behaves nearly as classical charge on a metallic disk, and electron additions appear nearly periodically with gate voltage (Coulomb blockade).

SECS measurements have shown (7, 8) that the low-density regime appears entirely different. Not only is the addition spectrum highly nonuniform, but peaks from subsequent electron additions can form pairs and bunches, apparently indicating that an unknown mechanism has eliminated the repulsive interaction between the two (or more) electrons. The pairing phenomenon arises both in large ($>0.8\text{-}\mu\text{m}$ diameter) disordered dots in which electrons are likely localized at random traps and in smaller ($<0.5\text{-}\mu\text{m}$ diameter) but more ordered dots. This investigation demonstrates that in the latter case the low-density system in quantum dots actually bifurcates into two subsystems: a central core and a periphery. The pairing phenomenon arises from an apparent and unexplained cancellation of the Coulomb repulsion between electrons in these two regions.

These dots are fabricated within an AlGaAs-GaAs heterostructure (Fig. 1A) described in (7, 8). The essential layers, from the substrate to the surface, are a conducting substrate of GaAs serving as the only contact lead to the dots, a AlGaAs tunnel barrier, an active GaAs layer where electrons are accumulated, and a blocking AlGaAs layer. On the top surface a small CrAu top gate was formed by electron beam lithography. This top gate was used as a mask for wet or reactive ion etching to completely deplete the active GaAs layer outside the covered region and therefore to produce the quantum dot below the top gate. Then a thin film of CrAu was evaporated over the formed structure. This film was thin enough to break at the edges of the previously fabricated top gate (9)

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