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Oxydehydrogenation of Ethylbenzene to Styrene over Metal Pyrophosphates

1. Catalyst Composition and Reaction Variables

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A wide variety of metal pyrophosphate catalysts shows high selectivity for oxydehydrogenation of ethylbenzene to styrene which is superior to that of the orthophosphates or oxides. Whether the metal cation has only one valence state such as calcium or lanthanum or several states such as nickel or cerium has no effect on the activity. Surface treatment of common supports like alumina or silica with ammonium phosphates improves the selectivity and activity appreciably. The selectivity is sensitive primarily to the oxygen/ethylbenzene ratio and steam as a diluent permanently damages the catalyst. A variety of other alkyl aromatics can be oxydehydrogenated over these catalysts with good selectivity unless the product contains allylic or benzylic hydrogens or heteroatoms. A catalyst model is proposed in which a carbonaceous overlayer common to the various pyrophosphate substrates is the actual catalytic surface.

INTRODUCTION

The current process for dehydrogenation of ethylbenzene to styrene which has developed over more than four decades, although very selective for styrene, has some inherent limitations. Since it is an endothermic reaction and is limited by equilibrium, the conversion for practical steam/oil ratios is typically in the 40–60% range. Thus, the reaction and rather difficult separation of styrene and ethylbenzene are energy intensive. Also, the high temperatures required to give favorable conversion (>600°C) bring about severe cracking in the more complex alkylbenzenes. Thus, the application of this technology is rather limited.

The oxydehydrogenation reaction produces water rather than H_2 and as a result the reaction is exothermic. Therefore, conversions of nearly 100% are possible at much lower temperatures where many vinyl aromatics are stable.

For an economical process, the preferred oxidant is air if high selectivity can be maintained. Various promoters have been studied thoroughly, primarily halide (*1*) and sulfur (*2*) compounds, and while these have given high conversions and selectivities (>90%) a severe penalty is paid in terms of corrosion, recovery, recycle of the more expensive halides (bromine and iodine), and removal of impurities from the final product. As a result, these have not developed into commercial processes.

The key to oxydehydrogenation is a very selective catalyst, for three reasons. First, the process economics rapidly deteriorate when ethylbenzene is oxidized to carbon oxides. Second, formation of carbon oxides is extremely exothermic. Third, carbon oxides require large quantities of oxygen which then limits the conversion to styrene. The catalyst should be reasonably active in order to limit the reactor size, but too much activity can cause problems with heat transfer and runaway reaction. A factor which is not often discussed and yet is very important commercially is catalyst life which should be 1 year or more.

In this paper we will discuss the development of a family of condensed phosphate

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catalysts which are exceptionally good for oxydehydrogenation. Until fairly recently, bulk phosphates were seldom used as oxidation catalysts although phosphates as minor components in oxides were common. These phosphates are relatively inactive when compared with typical multivalent transition metal oxides. In fact, it is surprising that a single valent metal phosphate could have any oxidation activity.

EXPERIMENTAL

Catalyst Preparation

The best cerium phosphate catalyst was prepared according to a procedure described in detail by Alberti *et al.* (*3*). A solution of 1250 ml of $Ce(SO_4)_2$ (0.05 *M*) in 0.5 *M* H_2SO_4 was added dropwise over 7 h to an equal volume of 25% phosphoric acid preheated to 93°C. After complete addition, the solution was stirred and gently refluxed at 104°C for 20 h. The precipitate after cooling was filtered and washed free of sulfate.

A supported cerium phosphate on alumina was obtained by evaporating 16.3 g of $(NH_4)_2Ce(NO_3)_6$ onto 18.37 g of alumina (8.6 m^2/g), calcining at 400°C in air overnight to form CeO_2, and then impregnating with 6.8 g of 85% phosphoric acid. Typically, all the catalysts were calcined in air overnight at 550°C.

The alkaline earth and other metal phosphates were prepared as in the following example. Two hundred fifty milliliters of 1.2 *M* $Ca(NO_3)\cdot 4H_2O$ was rapidly added to 250 ml of 2.2 *M* $(NH_4)_2HPO_4$ (neutralized with nitric acid) with vigorous stirring in a blender. For the lanthanum and rare earth phosphates the oxides were dissolved in nitric acid and the pH of both solutions was adjusted to 0.9 before mixing. This minimized the formation of the hydroxides. The phosphate precipitates were filtered without washing, dried at 100°C, pressed, heated gently to 200–250°C to decompose the residual ammonium nitrates, and then calcined at 550°C for several hours.

In the case of the surface phosphatized calcium nickel phosphate catalyst (Dow Type A) (*4*), the typical procedure was to add 100 ml of 2.2 *M* $NH_4H_2PO_4$, which was neutralized with ammonium hydroxide, to 50 ml of catalyst. After 15 min this was drained, dried at 110°C, and heated to 400°C for 4 h and to 550°C for 2 h. Phosphoric acid was also used in place of the ammonium phosphate in some of the silica and alumina catalysts.

The DTA of the phosphatized Type A catalyst was similar to that of the precipitated $CaHPO_4\cdot 2H_2O$. This consisted of a strong endotherm at 185–210°C due to loss of ammonia and water and then a broader weak endotherm at 430°C with loss of water to form α-$Ca_2P_2O_7$ (*5*). At 600–625°C a sharp exotherm occurs which corresponds to formation of β-$Ca_2P_2O_7$.

Determination of cerium valence in the phosphates was obtained by dissolving in hydrochloric acid and KI under vacuum to avoid oxidation, iodometric titration, and analysis for total cerium by atomic absorption.

Apparatus

The apparatus for testing catalysts is shown in Fig. 1. The reactor was a Vycor tube (16 mm i.d.) with a concentric thermowell (6 mm o.d.) and the catalyst was typically 10–20 ml of 8- to 30-mesh particles. The ethylbenzene was delivered via a simple, inexpensive, but very reliable device which consisted of pressurizing it from a weighed tank through capillary tubing (0.127 mm i.d. by 1.6 mm o.d. stainless steel). The liquid stream was vaporized into the diluent/oxygen stream at a temperature below the atmospheric boiling point to avoid flashing. Vycor chips provided additional mixing before entering the reactor at 500–600°C.

Analysis

The reaction products were analyzed via a heated on-stream sample valve except for the mass balance experiments in which all

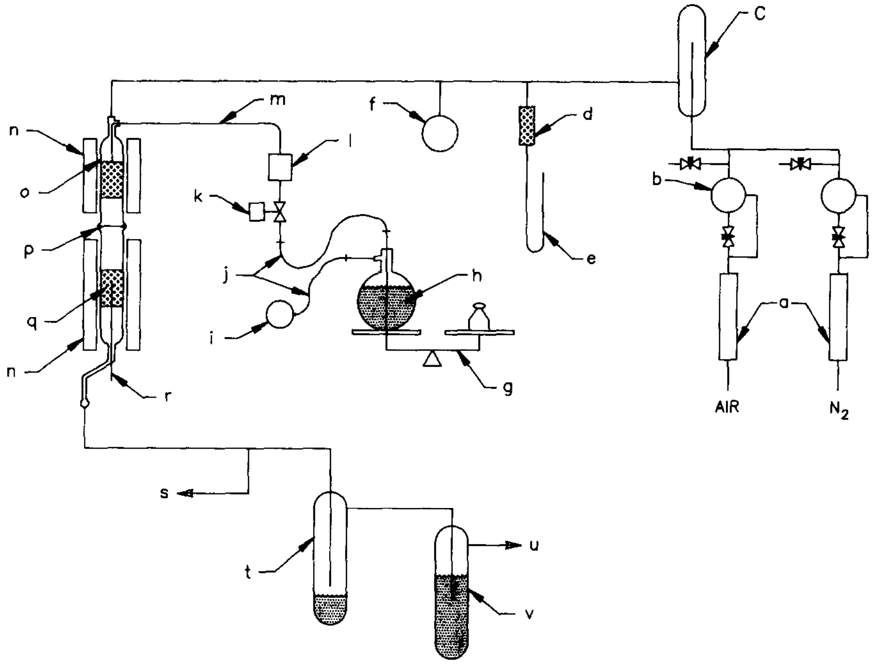

FIG. 1. Apparatus used to study oxydehydrogenation of ethylbenzene. (a) Rotameter, (b) flow regulator, (c) mixing bulb, (d) desiccant, (e) water manometer, (f) pressure switch, (g) balance, (h) ethylbenzene, (i) pressure controller, (j) flexible tubing, (k) pneumatic valve, (l) 60-μm filter, (m) 0.13-mm-i.d. capillary, (n) furnaces, (o) vaporizer, (p) o-ring joint, (q) catalyst, (r) thermocouple, (s) to GC sample valve, (t) cold trap, (u) vent, (v) bubbler (pressure control).

the vapors were condensed, weighed, and analyzed by gas chromatography. Analyses for the permanent gases, O_2, N_2, CO, and CO_2, were obtained by two columns in parallel, Porapak Q and 5A molecular sieve. The aromatic hydrocarbons were analyzed on Carbowax 20M + 2% KOH on Chromosorb P.

The solid infrared spectra were obtained on a Beckman IR-9 spectrometer with a split mull technique using Fluorolube/BaF_2 for 3800–1333 cm^{-1} and Nujol/AgCl for 1333–400 cm^{-1}.

The pyridine adsorption experiments for measuring acidities of the Type A catalysts were obtained using a Cahn RG electrobalance. The sample was suspended in flowing N_2 which was saturated with pyridine and then, after reaching constant weight in this stream at varying temperatures, the sample was purged with N_2 to measure chemisorbed pyridine.

RESULTS

Rare Earth Phosphates and Oxides

The initial screening experiments showed that the oxides of iron, lead, and tin produce $\leq 50\%$ selectivity to styrene even at low temperatures (400°C), whereas the corresponding phosphates were much more selective. A variety of titanium phosphates gave even better results at 430–450°C. A typical example is shown in Table 1. The next step was to synthesize a series of other tetravalent metal phosphates, e.g., of zirconium, tin, and cerium. Although these were rather inactive at 450°C, they maintained or even improved selectivity with increased temperature. In fact, cerium phosphate was really outstanding in both activity and selectivity. The nature of the phosphate groups in these catalysts was not determined.

The results given in Table 1 were based

TABLE 1

Cerium, Tin, Titanium, and Zirconium Phosphates as Oxydehydrogenation Catalysts for Ethylbenzene

Phosphate catalyst	Surface area (m^2/g)	T (°C)	Conversion (%)		Selectivity (%)		
			EB	O_2	Sty	CO	CO_2
Cerium	12.6	506	46.8	53.2	93.8	2.7	3.5
		550	65.5	83.0	90.9	4.5	4.6
		605	76.2	99.0	90.3	5.8	4.0
Tin	10.6	548	56.3	60.3	94.0	3.4	2.7
Zirconium	28.7	556	55.4	99.2	86.3	5.9	7.7
		550	12.1[a]	—	100	0	0
Titanium	17.2	450	34.4	74.0	81.7	7.3	11.0
Vycor	—	568	0.6	—	99.0	—	1.0

Note. O_2 = 10.6 cc/min; EB = 9.4 cc/min; He 167 cc/min; GHSV = 1120 h^{-1}.

[a] This experiment without O_2 present in feed.

only on styrene, CO, and CO_2 which were analyzed by GC and did not include coke or minor by-products; thus, these results are somewhat higher than those that a complete mass balance would show. The results on this basis reached an apparent optimum at 1–3 h on-stream and then the activity dropped off slowly over many hours. The original activity could be completely restored by burnoff in diluted air. Zirconium phosphate is not quite as selective as tin or cerium but still is remarkably good. Under dehydrogenation conditions, i.e., in the absence of O_2, the conversion reached only 12%, whereas under oxydehydrogenation conditions with O_2 present the conversion reached 55%. This suggests that dehydrogenation followed by oxidation of H_2 is only a minor part this reaction. Further evidence for this is that H_2 was not detected in the normal oxidation reaction and yet when H_2 was added to the feed over cerium phosphate, practically all of it survived. The blank run with Vycor chips gave almost no reaction.

Table 2 shows, first of all, a comparison of results over ceric oxide, cerous orthophoshate, and cerous pyrophosphate (reduced under reaction conditions). It is obvious that the selectivity increases in the order $O^{2-} < PO_4^{3-} < P_2O_7^{4-}$ and as a result more oxygen is available for ethylbenzene conversion to styrene; i.e., the activity is also greater.

The typical oxidation catalyst is generally thought to involve an oxidation–reduction cycle, i.e., a facile valence change, and for cerium this would involve Ce^{3+}–Ce^{4+}. A test for this hypothesis would be to substitute La^{3+} for Ce^{3+} since lanthanum has no stable 4+ state but nearly the same ionic size and chemistry as those of Ce^{3+}. The surprising result, shown in Table 2, is that $La_4(P_2O_7)_3$ (or even a mixed rare earth phosphate) behaves almost exactly like $Ce_4(P_2O_7)_3$. Again, the lanthanum orthophosphate is significantly less selective than the pyrophosphate.

Characterization of Cerium Phosphate Catalysts

The cerium phosphate catalysts were generally amorphous to X-ray diffraction except for the monazite formed at high temperatures. However, IR spectroscopy was effective in distinguishing the different phosphate groups and this led to a correlation with catalyst performance. Figure 2 shows a comparison of the spectra of a "poor" (low-selectivity) and a "good"

TABLE 2

A Comparison of Oxides, Orthophosphates, and Pyrophosphates of Cerium and Lanthanum

Catalyst	T (°C)	He : O_2 : EB	GHSV (h^{-1})	Conversions (%)		Selectivity (%)		
				EB	O_2	Sty[b]	CO	CO_2
CeO_2	554	15 : 1 : 1	1020	43.5	100	53.1	4.3	14.3
$CePO_4$	603	12 : 1.2 : 1	1080	49.1	100	79.0	10.4	10.6
$Ce_4(P_2O_7)_3$	550	7 : 1 : 1	675	71.4	100	89.1	5.7	5.2
$LaPO_4$	550	6.3 : 1 : 1	241	39.8	100	73.6	9.3	11.6
$La_4(P_2O_7)_3$	550	6.3 : 1 : 1	241	65.2	100	87.9	5.4	5.1
$(RE)_4(P_2O_7)_3$[a]	550	6.3 : 1 : 1	241	66.4	100	86.3	6.5	5.6

[a] Rare earth mixture (La 65%, Nd 27%, Pr 7%).

[b] Selectivities to benzene (16.8%) and toluene (11.5%) were unusually high.

(high-selectivity) catalyst. The significant bands were identified by preparing standards. The good catalysts show a strong, sharp absorption at 530–570 cm^{-1} which corresponds to the P–O bending mode of pyrophosphate (*6*). A strong absorption in the region 625 cm^{-1} is characteristic of the orthophosphate group and whenever this was strong, the catalyst was always poor in selectivity. A broad band at 1200–1300 cm^{-1} is related to the metaphosphates and this did not correlate simply with catalyst behavior. In fact, a strong meta band which requires a high P/Ce ratio seems to correlate more often with a strong orthophosphate region with low P/Ce; i.e., there is a

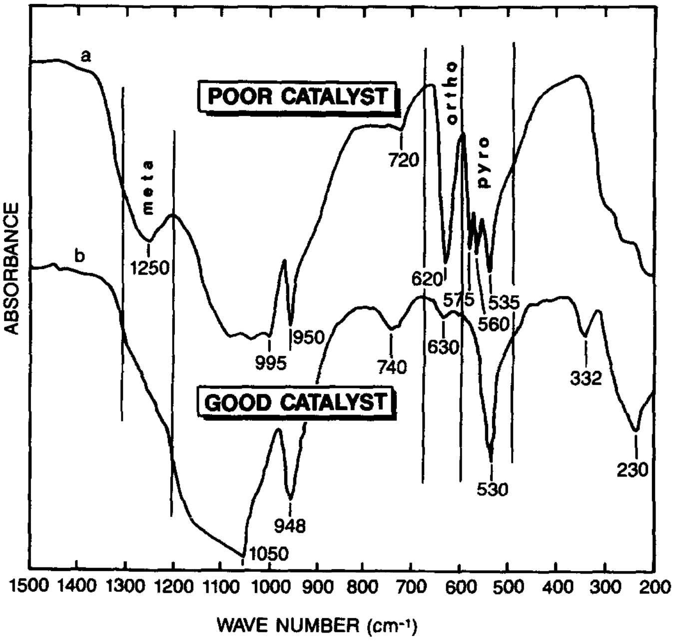

FIG. 2. IR spectra of typical "good" and "poor" cerium phosphate catalysts.

TABLE 3

Results from Alkali Metal and Other Metal Condensed Phosphate Catalysts

Compound	Surface area (m^2/g)	Conversion (%)		Selectivity (%)		
		EB	O_2	Sty	CO	CO_2
$Ca_5OH(PO_4)_3$	—	41.2	—	76.3	10.2	13.4
$Ca_2P_2O_7$[a]	22.0	45.2	—	81.9	5.2	12.9
$Ca_2P_2O_7$	6.2	67.4	95.3	92.5	4.5	3.1
$Mg_2P_2O_7$	35.4	70.5	100.0	92.8	2.8	4.4
$Sr_2P_2O_7$	2	63.9	89.0	90.7	4.1	5.2
$Ba_2P_2O_7$	1.2	28.5	40.3	92.6	3.7	3.7
$Ni_2P_2O_7$	—	65.9	100.0	90.1	4.1	5.8
$(Mg_{0.9}Ni_{0.1})_2P_2O_7$	—	70.6	100.0	88.9	4.5	5.3
$Al(PO_3)_3$	9.7	71.7	94.7	91.5	4.2	4.3
ThP_2O_7	—	53.5	100.0	86.3	5.5	8.3
$Zn_2P_2O_7$	—	45.8	100.0	82.3	3.9	12.8
$Fe_4(P_2O_7)_3$	—	8.5	18.2	81.9	5.9	12.3

Note. Conditions: He : O_2 : EB = 6 : 1 : 1, GHSV = 360 h^{-1}, T = 530°C.

[a] Reagent-grade $CaHPO_4 \cdot 2H_2O$ heated to 550°C. All the other catalysts were prepared by precipitation and calcination.

nonuniform distribution of phosphate groups.

The fresh, dried cerium phosphate catalyst has a P/Ce ratio in the range 1.6–1.85 which corresponds to $Ce(HPO_4)_2$ + excess $Ce(OH)_4$ (*3*). TGA and DTA indicate that at 200°C water of hydration is lost and at 430°C pyrophosphate begins to form slowly with loss of one more water. After samples are calcined at 550°C, IR shows the presence of CeP_2O_7 and trace amounts of $CePO_4$ (monazite), but the valence of cerium is still 4+. Above 650°C the catalyst loses both activity and selectivity and now monazite is observed by X-ray. At ≥800°C monazite dominates. Under reaction conditions at 550°C all the cerium is 3+ but still predominantly as pyro- or metaphosphate.

Alkaline Earth and Other Metal Pyrophosphates

The result on lanthanum pyrophosphate suggested the use of a wide variety of other pyrophosphate catalysts, some examples of which are shown in Table 3. All the alkaline earth pyrophosphates are selective; the particular strontium and barium compounds tested have lower surface areas and somewhat lower activities but these could very likely be optimized. Calcium pyrophosphate prepared from a reagent $CaHPO_4 \cdot 2H_2O$ was not as selective as our prepared sample and the orthophosphate, $Ca_5(OH)(PO_4)_3$ (apatite), was significantly less selective. One would expect ($Ni_2(P_2O_7)$) or the mixed $(Mg–Ni)_2(P_2O_7)$ to be a deep oxidation catalyst but apparently the phosphate group stabilizes the nickel as 2+. Phosphates of Al^{3+}, Th^{4+}, and Zn^{+} behave very much like the other phosphates. $Al(PO_3)_3$ is an example of a metaphosphate which is free of orthophosphates and has excellent catalytic properties.

Table 4 shows the results of coating typical supports such as silica and alumina with a phosphatized surface via H_3PO_4 or $NH_4H_2PO_4$. Under our conditions these supports alone are not very inert, but the phosphate treatment generates excellent selectivity. Similarly, a calcium nickel phosphate (Dow Type A catalyst) gives only 75.6% selectivity, whereas the phos-

TABLE 4

Surface Phosphatized Catalysts and Supports for Oxydehydrogenation

Catalysts	Surface area (m^2/g)	Conversion[a] % EB	Selectivity (%)		
			Sty	CO	CO_2
SiO_2 (Davison #59)	96	35.6	74.8	8.5	16.8
SiO_2 (Davison #70)					
$+H_3PO_4$ (1.5 *M*)	97.3	45.7	85.2	7.7	7.1
$+H_3PO_4$ (7.0 *M*)	5.1	46.2	90.8	4.8	4.4
$+NH_4H_2PO_4$	—	65.2	89.4	5.6	5.4
Al_2O_3 (Houdry 100S)	10	19.3	43.7	13.5	42.8
$+H_3PO_4$ (7.3 *M*)	4.7	60.0	84.9	6.3	8.8
$Ca_8Ni(PO_4)_6$ (Type A)	6	33.7	75.6	7.3	17.1
$+NH_4H_2PO_4$ (pH 7)	6	72.7	88.0	6.2	5.8
$Ca_8Ni(PO_4)_6$ + Cr_2O_3 (2%) (Type B)					
$+NH_4H_2PO_4$	6	70.7	88.7	5.6	5.8

[a] Same conditions as those described in Table 3.

phatized catalyst (Dow Type AP) gives 85–89% selectivity.

Figure 3 shows the effect of increasing molarity of the $NH_4H_2PO_4$ solutions which increases the phosphate content of the catalysts from 59.3 to 65.9%. Selectivity and conversion quickly reach a plateau at 0.44 *M*, which corresponds to around 61.6% PO_4^{3-} in the catalyst.

Figure 4 shows the performance of some

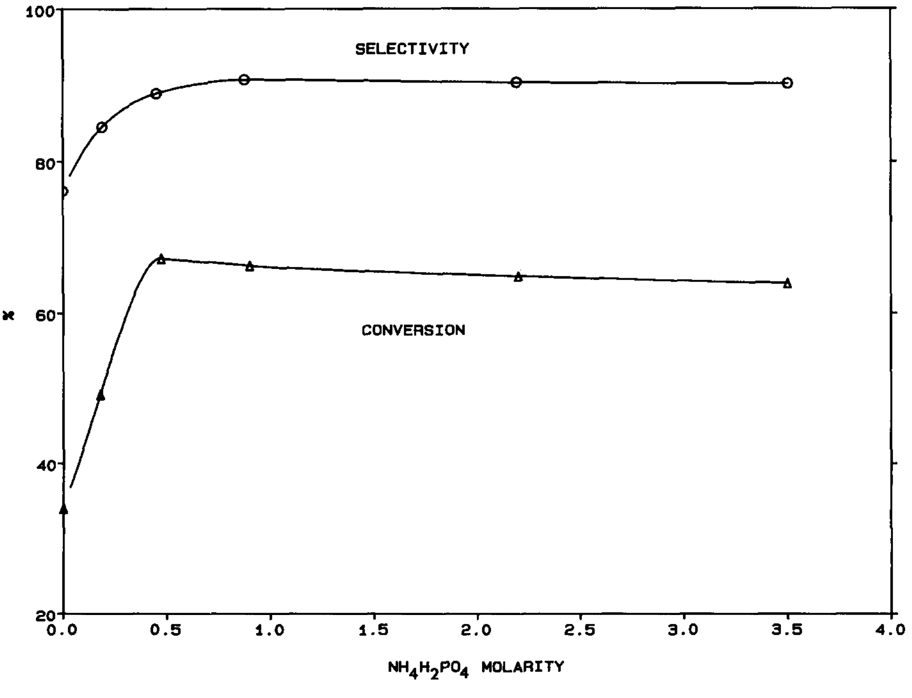

FIG. 3. Effect of molarity of $NH_4H_2PO_4$ solutions used to modify the Type A catalyst.

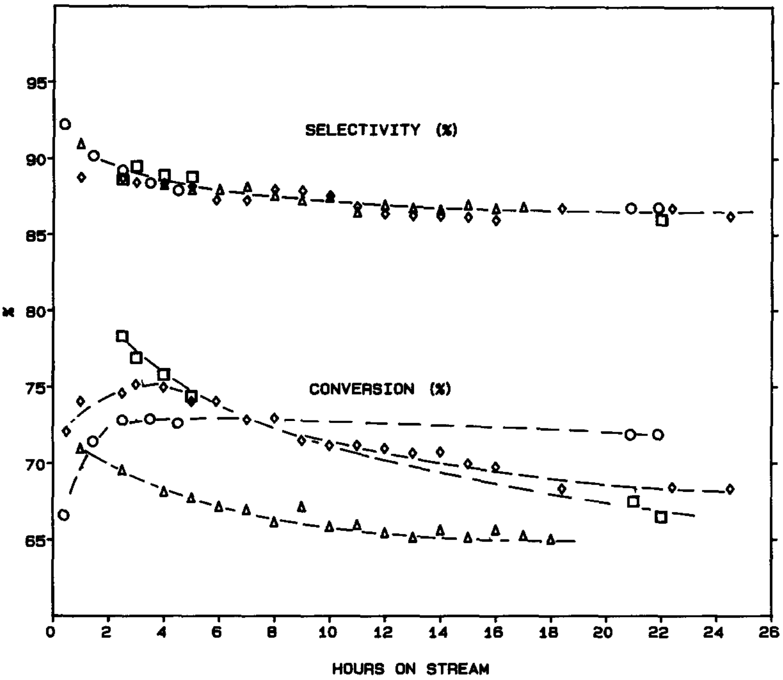

FIG. 4. Life studies of various selective phosphate catalysts; cerium pyrophosphate (◇); Type AP (○); calcium pyrophosphate (△); magnesium pyrophosphate (□).

of our best catalysts over 24 h. Although the selectivities remain nearly constant after the first 3–4 h, the activities drop off with time. The exception is the phosphatized calcium nickel phosphate (Type AP) which appears to go through an initial activation and then levels off at a value higher than the rest. In fact, in a scaled-up reactor, this catalyst gave only minor losses in activity over 50 days on-stream with one burnoff at which time it was shut down.

Reaction Variables

The effects of temperature, O_2/EB feed ratio, and dilution were explored only briefly in order to optimize the conversion and selectivity. As Table 5 shows, in Experiments A and B, a 13°C increase in temperature has no effect on selectivity. Conversion of ethylbenzene remained constant due to complete oxygen conversion at both temperatures. Increasing the O_2 from 10.6 to 15.0 cc/min in Experiments B and C does increase conversion and yield with a drop in selectivity to styrene. Lowering the temperature to 500°C with high O_2 (C) reduces conversion and yield but improves the selectivity to styrene only slightly. Decrease in diluent flow (or increase in reactant concentration) increases conversion with almost no loss of selectivity (D and E). This brief treatment indicates that for this particular system the optimum in selectivity and yield corresponds to the conditions in Experiment A or B with O_2/EB = 1. In subsequent experiments the diluent/EB was 6 rather than 15 with no adverse effect.

The effect of steam is shown in Table 6. Substituting steam for helium inhibits the reaction and promotes deep oxidation to carbon oxides. Furthermore, the catalyst does not completely recover when the steam is removed. We believe that this is due to loss of phosphate groups from the surface as evidenced by the transformation of the cerium pyrophosphate (P/Ce = 1.6) into monazite (P/Ce = 1).

TABLE 5

Effect Temperature, O_2/EB, and Dilution on Oxydehydrogenation over Cerium Pyrophosphate

Exp. No.	T (°C)	O_2 (cc/min)	He (cc/min)	Conversion[a] (%) EB	Selectivity (%)			Yield[b] % Sty
					Sty	CO	CO_2	
A	535	10.6	150	72.6	89.1	5.7	5.2	64.8
B	548	10.6	150	72.8	89.0	5.9	5.0	64.8
C	534	15.0	150	80.2	85.1	6.9	8.0	68.3
D	500	15.0	150	67.2	86.5	5.8	7.7	58.1
E	502	15.0	86	73.2	85.1	6.3	8.6	62.3

[a] EB flow = 10 cc vapor/min.; 20 cc catalyst.

[b] Yield is defined here as styrene per ethylbenzene fed, or conversion × selectivity to styrene.

Material Balances

Material balance experiments were carried out for cerium phosphate catalyst for ethylbenzene, chloroethylbenzene, and *t*-butylethylbenzene and an example for ethylbenzene is shown in Table 7. This is based on feed and product weights, gas flows, and GC analysis. The residue content was obtained by vacuum distillation and the coke by carbon oxide analysis during burnoff. The weight, carbon, and oxygen balances are 98.6%. When the residue, coke, and minor products in the material balance are accounted for, the selectivity to styrene drops to 84.4%. A material balance from Dow Type AP at the miniplant scale gave very similar results and more detailed product analysis gave the following selectivities (based on carbon) to products:

Styrene	84.3%
Carbon dioxide	6.74
Carbon monoxide	6.41
Residue	0.69
Toluene	0.65
Benzene	0.61
Phenol	0.51
Benzoic acid	0.39
Benzaldehyde	0.16
Benzofuran	0.12
Acetophenone	0.07

TABLE 6

Effect of Steam on the Activity of Cerium Pyrophosphate

Diluent		Conversion (%) EB	Selectivity (%)		
He (cc/min)	H_2O (cc/min)		Sty	CO	CO_2
103	0	72	88.0	7.5	4.8
40	60	47	78.6	10.6	10.7
103	0	63	84.5	8.9	6.5
		After burnoff			
40	60	49	79	10.4	10.6

Note. O_2 = 15.3 cc/min; Ar = 48.0 cc/min; EB = 3.5 g/h (13.5 cc/min); 10 cc catalyst.

TABLE 7

Mass Balance for Ethylbenzene to Styrene over Cerium Pyrophosphate at 538°C for 4.6 h

Conversion	
Ethylbenzene	71.9%
Oxygen	91.0
Selectivities	
Styrene	84.4%
Carbon monoxide	4.87
Carbon dioxide	5.14
Residue[a]	0.85
Coke[b]	2.85
	98.13%
Balances	
Weight	98.63
Moles	
Carbon	98.65
Oxygen	98.62

Note. Conditions: He : Ar : O_2 : EB = 7.2 : 3.5 : 0.8 : 1; GHSV = 690 h^{-1}.

[a] Nonvolatiles in the liquid product.

[b] Coke evaluated as polystyrene.

Table 8 gives a survey on other alkyl aromatics which were tested on cerium pyrophosphate or Type AP catalysts. The Group I materials all give high conversions and selectivities. Those in Group II are less selective because the vinyl products also have an allylic or benzylic hydrogen which can be further oxidized. In Group III, nitrogen, sulfur and oxygen groups generally give poor results; however, thiophene gives a significantly higher conversion with modest selectivity. The conversion of Group III compounds dropped off much more rapidly with time than the hydrocarbon groups. Butene gives surprisingly poor selectivity to butadiene.

DISCUSSION

Under the conditions of high temperature (450–600°C) and low space velocity (GHSV = 200–1100 h^{-1}) many materials which are normally considered to be inert for oxidations have, in fact, reasonably high activity and selectivity for oxydehydrogenation of ethylbenzene. Examples of this are alumina, silica, and alumina silicates which give complete oxygen conversions and as high as 75% selectivity. In general, phosphate catalysts are more selective than the corresponding oxides and we have found a significant improvement with pyrophosphates, especially in the surface layers. The condensed phosphate surface is the dominant factor since the cation has little or no effect. Whether the catalyst contains nickel, aluminum, lanthanum, or calcium, the catalytic behavior is surprisingly similar.

One reason for the unique selectivity of the pyrophosphate might be its ability to form a phosphate ester with a phenethanol intermediate. Alcohols can react with pyrophosphates in this way and the ester can be decomposed at rather low temperatures to give styrenes (*7*). Thus, the oxidation may be "trapped" at the alcohol (or phosphate ester) state in much the same way that oxidation of olefins in acetic acid or acetic anhydride traps the alcohol as the organic acid ester which is relatively stable to further oxidation (*8*).

However, this leaves the question of activation of oxygen. How is oxygen adsorbed or activated on pure calcium pyrophosphate? One could invoke trivalent phosphorus but this would probably not be stable enough to contribute. We would expect that a multivalent cation like nickel or cerium would influence the P^{3+}–P^{4+} transition and thus significantly alter the catalyst performance. A more likely explanation is that oxygen associated with an active carbonaceous layer deposited on the pyrophosphate surface is the true catalyst.

The oxydehydrogenation activity of various acidic catalysts has received increasing attention in recent years. Tagawa *et al.* (*9*) studied silica alumina, tin oxides, and phosphates and concluded that moderate acid strength is the key factor. Removal of strong acid sites by addition of sodium acetate improved the selectivity but excessive sodium deactivated the catalyst. A similar conclusion was reached by Fiedorow *et al.* (*10*) with alumina where small amounts of sodium ion did not affect activity even

TABLE 8

Oxydehydrogenation of Other Alkyl Aromatics

Feed	Catalysts	T (°C)	Conversion[a] alkyl aromatics	Selectivity vinyl aromatic
Group I				
Ethylbenzene	Ce-P	538	73.8	90.7
	AP	532	75.0	89.5
o,p-Chlorobenzene	Ce-P	537	76.5	87.5
	AP	540	64.5	81.0
p,t-Butylbenzene	Ce-P	536	73.3	85.1
	AP	500	52.1	77.8
1- and 2-Ethylnaphthalene	Ce-P	545	78.3	90.3
	AP	500	51.0	82.7
m-Diethylbenzene	Ce-P	531	62.2	88.8[b]
	AP	500	53.4	74.4[c]
Group II				
n-Butylbenzene	Ce-P	550	51.2	85.0[d]
o,p-Ethyltoluene	CeP	537	52.8	79.6
	AP	500	36.4	67.7
Isopropylbenzene	Ce-P	537	56.7	74.2
Group III				
2-Ethylpyridine	Ce-P	555	31.1	67.1
	AP	500	37.9	48.9
2-Ethylthiophene	AP	464	78.8	79.5
3-Ethylphenol	AP	458	57.7	64.4
1-Butene	Ce-P	550	27.4	72.9

[a] Typical conditions: cerium pyrophosphate (Ce-P) GHSV = 873 h^{-1}; He : Ar : O_2 : alkyl aromatic = 10 : 24 : 1.2 : 1; Type AP GHSV = 195 h^{-1}; He : O_2 : alkyl aromatic = 6 : 1 : 1.

[b] Ethylvinylbenzene, 64.5%; divinylbenzene, 24.3%.

[c] Ethylvinylbenzene, 59.9%; divinylbenzene, 14.5%.

[d] *cis*-1-phenylbutene-1, 7.3%; *trans*-1-phenylbutene-1, 20.2%; 1-phenylbutadiene-1,3, 31.5%; naphthalene, 26.0%.

though the strong acid sites would have been removed. Echigoya *et al.* (*11*) found that introducing acidity into silica by addition of either magnesium or zirconium correlated well with oxydehydrogenation activity. Pyridine in the feed which would adsorb on strong acid sites at these temperatures did not affect the oxidation reaction.

However, in earlier work, Alkhazov *et al.* (*12*) proposed that the important factor is not the acidity per se but rather the particular kind of carbonaceous deposit on these acid sites. Various aluminas initially showed widely different activities but eventually reached a common state which they suggest is a surface with carbonaceous residue. Emig and Hofmann (*13*) compared data on a wide variety of published catalysts and found very similar yields. A typical cracking catalyst gave no oxydehydrogenation product for 3 h on-stream and then activity and selectivity rose sharply to reasonably high values. Similarly, the activity of zirconium phosphate was initially low according to pulse experiments. Then the activity rose over the first 3 h and dropped off slowly in excellent agreement with our results in Fig. 4.

There is convincing evidence that carbon by itself is active under these conditions. Earlier work at Dow by Allen *et al.* (*14*) showed that typical carbons give good activity and selectivity for this reaction and they went on to use coked silica; however, the performance was erratic and the yields were not economical. More recently, Al-

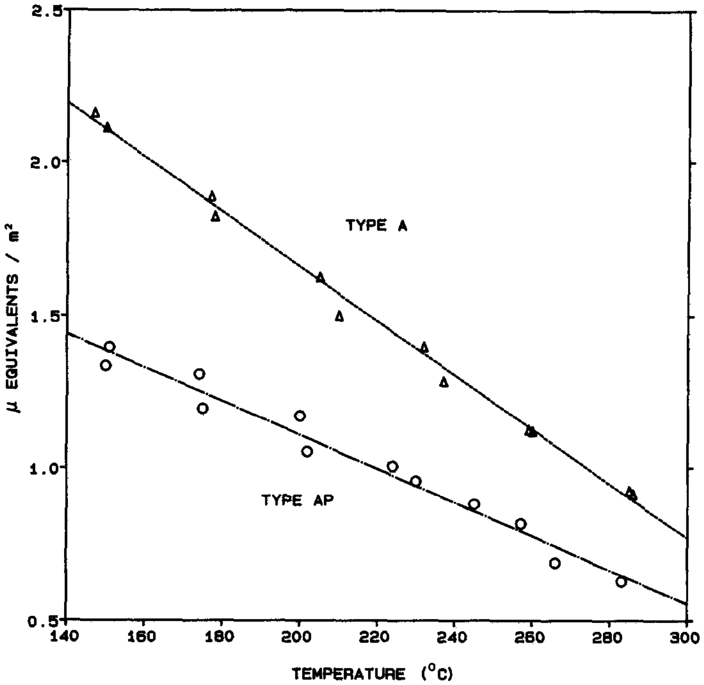

FIG. 5. A comparison of surface acidity between Type A and Type AP by chemisorption of pyridine vs temperature.

khazov *et al.* (*12*) tested carbons and found good properties except that there was loss of activity with time. Several investigators (*10, 12, 13*) actually separated the carbon layer from its catalysts and found it to have catalytic properties very similar to those of the support + carbon. In all cases the optimum carbon residue contained a low H/C ratio and elemental analysis for C–H–O gave excellent agreement with that of polynaphthoquinone which Iwasawa *et al.* (*15*) showed to be very selective for oxydehydrogenation. IR analysis of the coke on alumina by Fiedorow (*10*) also revealed quinone bands at 1650 cm^{-1}.

The pyrophosphate group is unique in that the carbonaceous layer which is deposited on it is particularly selective for oxydehydrogenation and is clearly superior to that on orthophosphates or oxides. The reason for this is that pyrophosphate provides a rather narrow distribution of moderate acid sites which are conducive to a continuous layer of carbon. For the examples of precipitated phosphates which decompose to pyrophosphates the surface naturally forms a uniform pyrophosphate surface. The surface treatment with phosphate covers up strong acid sites and replaces them with pyrophosphate groups. As Fig. 5 shows, phosphate treatment removes some of the acid sites of Type A catalyst including those which adsorb pyridine at the higher temperatures, i.e., the strong acid sites. More work needs to be done on characterization of the distribution of acidity on these phosphate catalysts in order to clarify this hypothesis. Alumina is known to have strong acid sites and compared with the phosphate-treated catalysts, which one would expect to have lost these sites, it is far less selective. The result on silica gel is surprising because it is generally considered to be neutral although impurities may generate strong acidity.

Our model for this catalyst, then, is a pyrophosphate substrate with a thin carbonaceous layer on the surface which is the actual catalytic surface. This overlayer may have properties of a typical carbon or it may have chemical properties which are influenced by the phosphate groups beneath it. Very likely this layer is not continuous or static but is continually being burned off and replaced; and certain sites, which are particularly active for burnoff such as strong acids or impurities, may never see a protective coating of carbon but would contribute to carbon oxide formation. The deposition and burning of this carbonaceous layer is discussed in more detail in Part 2 of this paper.

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REFERENCES

1. Manell, R. M., and Bajars, L., U.S. Patent 3,247,273 (April 19, 1966).
2. Adams, C. R., and Jennings, T. J., *J. Catal.* **17,** 157 (1970).
3. Alberti, G., Costantino, U., DiGregorio, F., Galli, P., and Torracca, E., *J. Inorg. Nucl. Chem.* **30,** 295 (1968).
4. Britton, E. C., Dietzler, A. J., and Noddings, C. R., *Ind. Eng. Chem.* **43,** 2871 (1951).
5. Rabatin, J. G., Gale, R. H., and Newkirk, A. E., *J. Phys. Chem.* **64,** 491 (1960); Parodi, J. A., Hickok, R. L., Segelken, W. G., and Cooper, J. R., *J. Electrochem. Soc.* **112**(7), 688 (1965).
6. Petrov, K. I., Vasil'eva, V. P., and Pervykh, V. G., *Russ. J. Inorg. Chem.* **11**(8), 981 (1966).
7. Cherbuliez, E., "Organic Phosphorus Compounds" (G. M. Kosolapoff and L. Maier, Eds.), Vol. 6, pp. 224 and 335. Wiley, New York, 1973.
8. Bryant, D. R., McKeon, J. E., and Ream, B. C., *J. Org. Chem.* **33**(11), 4123 (1968); Onoda, T., and Wada, K., U.S. Patent 4,033,999 (July 5, 1977).
9. Tagawa, T., Hattori, T., Murakami, Y., Iwayama, K., Ishida, Y., Uchida, H., (a) *J. Catal.* **71,** 257 (1981); (b) **75,** 56 (1982); (c) **75,** 66 (1982); (d) **79,** 47 (1983); (e) *Appl. Catal.* **2,** 67 (1982).
10. Fiedorow, R., Przystajko, W., Sopa, M., and Dalla Lana, I. G., *J. Catal.* **68,** 33 (1981); Fiedorow, R., Gut, W., Przystajko, W., Sopa, M., "Wybrane Zagadnienia z Fizykochemii Ukloadow Homo- I Heterogennych," UAM Seria Chemia, No. 43, 59, 1982. [C.A. 98: 217594e]
11. Echigoya, E., Sano, H., and Tanaka, M., "Eighth International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 623. Dechema, Frankfurt-am-Main, 1984.
12. Alkhazov, T. G., Lisovskii, A. E., Safarov, M. G., Dadesheva, A. M., Lapin, V. B., Kurbanov, N. A., Feizullaeva, Sh. A., Ismailov, Yu. A., Gulakhmedova, T. Kh., (a) *Kinet. Katal.* **13**(2), 509 (1972); (b) **13**(6), 1504 (1972); (c) **14**(5), 1182 (1973); (d) **17**(2), 434 (1976); (e) **19**(3), 605 (1978); (f) **19**(3), 611 (1978); (g) *React. Kinet. Catal. Lett.* **12,** 189 (1979); (h) *Kinet. Katal.* **23**(5), 1140 (1982).
13. Emig, G., and Hofmann, *J. Catal.* **84,** 15 (1983); U.S. Patent 4,400.568 (Aug. 23, 1983).
14. Allen, R. H., Alfrey, T., Jr., and Yats, L. D., U.S. Patent 3,487,564 (Feb. 24, 1970).
15. Iwasawa, Y., Nobe, H., and Ogasawara, S., *J. Catal.* **31,** 444 (1973).