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Oxidation over $MgCrFeO_4$ and $ZnCrFeO_4$ Catalysts

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In a previous paper, it was reported that $MgCrFeO_4$ and $ZnCrFeO_4$ are very effective catalysts for the oxidative dehydrogenation of butenes to butadiene. This paper reports the evaluation of these catalysts for the oxidative conversion of a variety of other hydrocarbons. It was found that whenever a conjugated product can be formed it is the predominant product. When there is no possibility for dehydrogenation only complete combustion occurs. In contrast to what has been observed with another oxidation catalyst, bismuth molybdate, oxygenated hydrocarbons are not formed in detectable amounts.

These ferrite catalysts are effective for producing isoprene, 2,3-dimethylbutadiene and methacrolein via oxidative dehydrogenation and for the production of high single pass yields of styrene using SO_2 as the hydrogen acceptor.

INTRODUCTION

In a previous paper (*1*) results for the oxidative dehydrogenation of butenes to butadiene over magnesium chromium ferrite ($MgCrFeO_4$) and zinc chromium ferrite ($ZnCrFeO_4$) catalysts were reported. This work showed that the substitution of Cr^{3+} for iron in the lattice of the binary spinels, $MgFe_2O_4$ and $ZnFe_2O_4$, greatly increased the efficiency of the catalyst for oxidative dehydrogenation. It was also shown that the $ZnCrFeO_4$ catalyst was far more selective for this reaction than either α-Fe_2O_3 or $\alpha(Fe,Cr)O_3$. Subsequent work by Massoth and Scarpiello (*2*) has shown that incorporation of Cr^{3+} in the spinel lattice greatly increases the stability of the $ZnCrFeO_4$ against bulk reduction by both hydrogen and butene.

The oxidative dehydrogenation of butene over $MgCrFeO_4$ and $ZnCrFeO_4$ was postulated to proceed via a redox cycle involving Fe^{3+} and Fe^{2+}, with the active hydrocarbon intermediate being an allylic C_4 radical complexed with Fe^{3+}. The active adsorbed oxygen species was postulated to be an O^- radical ion (*1, 2*).

This paper reports our studies on the oxidative conversion of various unsaturated hydrocarbons, some of which contain polar atoms, using $MgCrFeO_4$ and $ZnCrFeO_4$ catalysts. Also a study of the dehydrogenation of ethylbenzene using SO_2 as the hydrogen acceptor was conducted using these ferrite catalysts.

EXPERIMENTAL

Materials

$MgCrFeO_4$ and $ZnCrFeO_4$ catalysts were prepared by coprecipitation from the nitrate salts with NH_4OH. Detailed methods of preparation have already been reported (*3, 4*).

The organic reagents were obtained from various suppliers. In all cases the purity was better than 99%.

Three oxidizing gases were used. C.P. grade oxygen was obtained from Air Products. A blend of oxygen and argon or nitrogen in an 85/15 mole ratio was prepared by Air Products. C.P. grade sulfur dioxide was obtained from Matheson Gas Products.

Apparatus and Procedure

In these experiments an organic reagent, an oxidizing agent, and a diluent were passed continuously over a fixed catalyst bed contained in a tubular reactor. The effluent from the reactor was passed through a trap maintained at 0°C by a wet ice bath. The gases passing through the trap, as well as the liquid retained in the trap, were analyzed by GLC and/or mass spectroscopy.

Three reactors were employed. A 22 × ¾ in. stainless steel reactor was used for the reactions of oxygen with the olefins, toluene, and ethylbenzene. A 17 × ¾ in. quartz reactor was used with isobutyric acid, isobutyraldehyde, and isobutyronitrile; and a 20 × 1 in. quartz reactor was used to react sulfur dioxide with ethylbenzene. The reactors were heated by electric furnaces regulated by Thermoelectric temperature controllers. Temperatures within the catalyst bed were measured with a moveable iron-constantan thermocouple located in a concentric thermowell running the length of the reactor.

The reactors contained a 10-cc catalyst bed. The void space above and below the catalyst bed was filled with 6–8 mesh silicon carbide. For reactions with oxygen, the 10 cc bed contained 5.0 cc of 10–20 mesh catalyst particles, diluted with 5.0 cc of 10–20 mesh silicon carbide. For the dehydrogenation of ethylbenzene using sulfur dioxide, 10 cc of 10–20 mesh catalyst were used without dilution.

Water and liquid organic reagents, supplied respectively by a Milton Roy Minipump and a Harvard Infusion Pump, were vaporized and mixed in an independently heated chamber. Gases were supplied from pressurized cylinders at rates measured by rotometers. Except where otherwise stated, the diluent used in these experiments was steam.

Product Analysis

Steam and liquid products were condensed in the 0°C trap. Light gases passed through the trap. The liquid products were analyzed by GLC. The chromatographic peaks were initially identified by combined GLC–mass spec analysis. In the reactions of isobutyraldehyde, isobutyric acid, and isobutyronitrile the reactants and products were slightly soluble in water. Consequently, the organic and aqueous phases were combined into one phase by the addition of methanol or isopropanol. In the reaction of ethylbenzene with sulfur dioxide, a weighed amount of *n*-decane was added to the liquid product as an internal standard.

The gases passing through the 0°C trap were analyzed by both GLC and mass spec. Nitrogen or argon, present in the feed, served as an internal standard.

RESULTS

Table 1 lists the various hydrocarbons whose oxidation was studied using $MgCrFeO_4$ and $ZnCrFeO_4$ catalysts. The conversion-selectivity* values given represent those which result in the maximum yield per pass of desired product. It can be seen that:

1. Wherever a conjugated product can be formed by oxidative dehydrogenation, it is the predominant product.
2. Where there is no possibility for dehydrogenation, i.e., isobutene and toluene, carbon oxides and water are the only products observed.
3. Using oxygen, ethylbenzene is selectively dehydrogenated to styrene at low conversions; however, with SO_2 selectivity is good even when conversion is high.
4. Isobutyraldehyde is selectively dehydrogenated; however, isobutyronitrile and isobutyric acid are not.
5. In no cases are oxygenated hydrocarbons formed in detectable amounts using these ferrite catalysts.

The remainder of the results section considers these reactions in more detail.

Dehydrogenation of Olefins

Table 2 shows conversion and selec-

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* Conversion = mole% reactant converted to all products.

Selectivity

$$= \frac{\text{mole\% reactant converted to desired product}}{\text{mole\% reactant converted to all products}}.$$

TABLE 1
CONVERSION OF VARIOUS HYDROCARBONS USING $MgCrFeO_4$ AND $ZnCrFeO_4$ CATALYSTS

Catalyst	Hydrocarbon	Oxidant	Temperature °C	% Conversion	Products and selectivities
$MgCrFeO_4$	Butene-2	None	460	25	88% Butene-1, 12% Butadiene
	Butene-2	O_2	360	63	93% Butadiene, 7% CO_2
	Isobutene	O_2	350	5	100% CO_2
	2-Methylbutene-2	O_2	350	16	90% Isoprene, 10% CO_2
	2,3-Dimethylbutene-2	O_2	375	21	92% 2,3-Dimethylbutadiene, 8% CO_2
	2-Ethylbutene-1	O_2	375	6	69% 2-Ethylbutadiene, 31% CO_2
	Toluene	O_2	400	6	100% CO_2
	Ethylbenzene	O_2	400	20	77% Styrene, 23% CO_2
	Ethylbenzene	SO_2	600	94	85% Styrene, 9% Thianaphthene
	Isobutyraldehyde	O_2	350	68	88% Methacrolein
$ZnCrFeO_4$	Butene-2	None	460	31	89% Butene-1, 11% Butadiene
	Butene-2	O_2	350	54	94% Butadiene, 6% CO_2
	Isobutene	O_2	350	6	100% CO_2
	2-Methylbutene-2	O_2	350	23	89% Isoprene, 11% CO_2
	2,3-Dimethylbutene-2	O_2	375	36	89% 2,3-Dimethylbutadiene, 11% CO_2
	2-Ethylbutene-1	O_2	375	19	83% 2-Ethylbutadiene, 17% CO_2
	Ethylbenzene	O_2	400	30	80% Styrene, 20% CO_2
	Ethylbenzene	SO_2	600	97	87% Styrene, 11% Thianaphthene
	Isobutyraldehyde	O_2	350	65	87% Methacrolein
	Isobutyronitrile	O_2	425	58	28% Methacrylonitrile, 15% Methacrolein
	Isobutyric acid	O_2	400	27	20% Methacrylic acid

tivity data obtained from the oxidation of the various olefins over $MgCrFeO_4$. Because of differences in the space velocities of the olefins, the pseudo zero order rate constants for diene formation and CO_2 formation are given. Butene-2 is more reactive than the other hydrocarbons listed and gives a higher selectivity to diene. The 2-methylbutene-2 is less reactive than butene-2 and gives a somewhat lower selectivity to diene at the higher conversions. It should be noted that in going from butene-2 to 2-methylbutene-2 not only does the rate of formation of diene increase but also the rate of formation of CO_2. The oxidative dehydrogenation of 2,3-dimethylbutene-2 and 2-ethylbutene-1 was of particular interest as a route to the corresponding diolefin monomers. The oxidative conversion of 2,3-dimethylbutene-2 over $MgCrFeO_4$ gives a high selectivity to the diene even at moderately high conversion. At 32% conversion, a selectivity of 89% is obtained. 2,3-Dimethylbutene-2 is slightly less reactive than 2-methylbutene-2 for both diene and CO_2 formation. The oxidative dehydrogenation of 2-ethylbutene-1 over $MgCrFeO_4$ is a relatively slow and nonselective reaction even at temperatures above 375°C. Although this compound is far less reactive than 2,3-dimethylbutene-2 with respect to diene formation, it shows a slightly higher rate for CO_2 formation.

The relative reactivities of the various hydrocarbons over $ZnCrFeO_4$ (see Table 3) are in general similar to those found over $MgCrFeO_4$. However, there are some exceptions. Both 2,3-dimethylbutene-2 and 2-ethylbutene-1 are more reactive over $ZnCrFeO_4$ as compared with $MgCrFeO_4$.

In a previous paper (*1*) it was reported

TABLE 2

OXIDATIVE CONVERSION OF VARIOUS HYDROCARBONS USING $MgCrFeO_4$ AS THE CATALYST

Olefin	T°C	Conversion mole%	Selectivity diene mole%	Selectivity CO_2 mole%	$K_0 \times 10^3$ diene	$K_0 \times 10^3$ CO_2
Isobutene	325	1	—	100	—	1.1
	350	5	—	100	—	7.0
	400	10.2	—	100	—	14.3
Butene-2	300	12	90	10	15.0	1.6
	325	28	93	7	36.8	2.7
	363	63	93	7	83.4	6.1
2-Methylbutene-2	325	8	89	11	10.7	1.4
	350	16	90	10	21.8	2.3
	375	30	87	13	39.2	4.4
	400	36	85	15	47.2	8.6
2,3-Dimethylbutene-2	325	6	94	6	7.8	.5
	375	21	92	8	26.4	2.3
	400	32	89	11	39.0	4.7
2-Ethylbutene-1	325	1	60	40	1.0	0.7
	375	6	69	31	7.2	3.2
Ethylbenzene	325	3	90	10	4.6	0.3
	350	5	88	12	7.6	0.6
	375	9	84	16	12.8	1.6
	400	20	77	23	25.9	4.8
Toluene	350	.4	—	100	—	0.8
	375	1	—	100	—	1.9
	400	6	—	100	—	11.5

that for the oxidative dehydrogenation of butene-1 and butene-2 over the ternary ferrites, double bond isomerization occurred at a much slower rate than the rate of diene formation. It was then shown that only in the absence of gas-phase oxygen did double bond isomerization approach equilibrium and in the absence of oxygen isomerization occurs via butene adsorption on a reduced iron site. With higher olefins a definite inverse relationship is observed between the rate of diene formation and the rate of isomerization. Table 4 lists the relative space time yields of diene and isomers for the various hydrocarbons using the ternary ferrite catalysts. With these catalysts, the extent of double bond isomerization increases proportionally with the decrease in the rate of diene formation.

In Tables 2 and 3 data are also given for the oxidation of isobutene. The main point of interest is that no methacrolein is formed; the only products being carbon oxides and water.

Ethylbenzene Dehydrogenation

The oxidative dehydrogenation of ethylbenzene is a reaction of considerable interest because of the possibility of high per pass yields of styrene. The data given in Table 2 show that over the ferrite catalysts the reaction is slow at moderate temperatures and selective only at low conversions. At high conversions there is a sharp decrease in selectivity. The only nonselective products formed over $MgCrFeO_4$ were benzene, toluene, and carbon oxides. It is also interesting to note that for toluene oxidation over the ferrite catalysts, the only products formed were carbon oxides and water. Again, no oxygenated products such as benzaldehyde or benzoic acid were detected.

With $MgCrFeO_4$ and $ZnCrFeO_4$ high se-

TABLE 3
OXIDATIVE CONVERSION OF VARIOUS HYDROCARBONS USING $ZnCrFeO_4$ AS THE CATALYST

Olefin	T°C	Conversion mole%	Selectivity diene mole%	Selectivity CO_2 mole%	$K_0 \times 10^3$ diene	$K_0 \times 10^3$ CO_2
Isobutene	300	1	—	100	—	1.3
	325	2	—	100	—	3.0
	350	6	—	100	—	8.3
Butene-2	275	4	98	2	5.9	.07
	300	24	94	6	32.9	2.0
	325	46	95	5	63.1	3.0
2-Methylbutene-2	325	12	91	9	15.8	1.8
	350	23	89	11	31.7	3.8
	375	35	85	15	45.5	8.0
2,3-Dimethylbutene-2	325	13	94	6	17.0	1.1
	350	24	93	7	30.3	2.3
	375	36	89	11	43.4	5.4
2-Ethylbutene-1	325	3	77	23	3.8	1.2
	350	12	77	23	16.0	4.7
	375	19	83	17	26.0	5.3
Ethylbenzene	350	7	85	15	10.0	1.3
	375	26	80	20	34.0	6.6
	400	30	80	20	38.9	7.1
	425	32	77	23	41.0	9.72

lectivities could only be obtained at low oxygen-to-ethylbenzene ratios. Therefore, a series of experiments was carried out for the oxidation of ethylbenzene–styrene mixtures using $ZnCrFeO_4$ at low oxygen concentrations. The purpose of these experiments was to determine if styrene was strongly inhibiting the conversion of ethylbenzene to styrene. In these experiments all variables were held constant except the initial concentrations of ethylbenzene and styrene. Results of these experiments are shown in Table 5. These data clearly show that as the mole fraction of styrene increases the conversion of ethylbenzene to styrene rapidly decreases while the conversion to CO_2 remains fairly constant which indicates that the oxidative dehydrogenation of ethylbenzene to styrene over the ternary ferrites is indeed limited by styrene inhibition.

TABLE 4
DOUBLE BOND ISOMERIZATION AND DIENE FORMATION USING $MgCrFeO_4$ AND $ZnCrFeO_4$ CATALYSTS AT 325°C

Catalyst	Reactant	Relative yield of diene	Relative yield of isomers
$MgCrFeO_4$	Butene-2	100	2.3
	2-Methylbutene-2	21.1	29.1
	2,3-Dimethylbutene-2	24.0	26.9
	2-Ethylbutene-1	5.4	82.7
ZnCrFeO	Butene-2	100	10.1
	2-Methylbutene-2	24.6	20.0
	2,3-Dimethylbutene-2	16.9	21.5
	2-Ethylbutene-1	2.3	60.0

Styrene can sometimes be produced from ethylbenzene with much higher selectivity by using sulfur dioxide rather than oxygen as the hydrogen acceptor. Both $ZnCrFeO_4$ and $MgCrFeO_4$ as well as other ferrites are good catalysts for this reaction (*5*). Table 6 shows some typical product distributions. At 94% ethylbenzene conversion, the selectivity to styrene is 87 mole%. The major by-product is thianaphthene. The per pass yields of styrene and thianaphthene are plotted against ethylbenzene conversion in Fig. 1. Conversion was varied

TABLE 5
OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE–STYRENE MIXTURES OVER $ZnCrFeO_4$[a]

Cycle no.	Ethylbenzene X_0	Styrene X_0	Conversion[b] mole%	Yield styrene[c] mole%	Yield CO_2 mole%
1	1	0	17.6	15.2	2.1
2	.842	.154	9.8	6.8	2.3
3	.762	.227	6.2	3.7	2.2
4	.716	.270	5.6	3.2	2.3
5	.676	.309	2.0	0	2.0

[a] Reaction temperature = 425°C and $C_8/O_2 = 3$.
[b] Net increase in styrene, benzene and CO_2.
[c] Net increase in styrene.

by changing the temperature, space velocity or catalyst age with the same result. As conversion increases, the yield of styrene reaches a maximum of 83 mole% at 94.5% conversion. Thereafter, the yield of thianaphthene increases sharply with a corresponding decrease in styrene yield.

Degradation products are obtained only in minor amounts when using sulfur dioxide. About 1% of the ethylbenzene is dealkylated to give benzene or toluene. When the benzene ring is broken, the major product is carbon disulfide; carbonyl sulfide and carbon dioxide are found in lesser amounts. The sum of these three compounds generally corresponds to less than 3% of the ethylbenzene converted.

In the course of the reaction, a carbonaceous residue is deposited on the catalyst surface. This may correspond to as much as 2% of the reacting ethylbenzene on a fresh catalyst. As a result, the catalyst is slowly deactivated as shown in Fig. 2. $ZnCrFeO_4$ and $MgCrFeO_4$ may be repeatedly restored to their original activity by burning off the carbonaceous residue with air. The use of steam or air rather than nitrogen as a diluent does not significantly retard the aging process. The oxygen in the air is completely consumed in the combustion of ethylbenzene and styrene rather than the carbonaceous residue.

TABLE 6
PRODUCTS OF ETHYLBENZENE DEHYDROGENATION USING SO_2

Catalyst	$ZnCrFeO_4$	$ZnCrFeO_4$	$MgCrFeO_4$
N_2/EB/SO	4/1/1	10/1/1	4/1/1
LHSV	0.5	0.3	0.5
Temperature °C	600	600	600
% Ethylbenzene Conversion	96.5	94	94
Selectivities			
Styrene	84	87	86
Thianaphthene	11.2	9.1	9.3
Benzene	0.4	0.3	0.3
Toluene	0.6	0.5	0.4
CS_2	2.5	2.2	1.9
COS	0.2	0.2	0.2
CO_2	0.2	0.2	0.2
Coke	1.6	1.1	1.4
Total	100.7	100.6	100.7

The apparent activation energy for

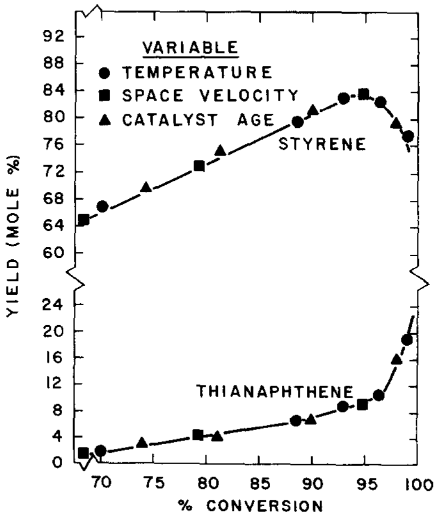


FIG. 1. Product yields versus conversion, variable ● temperature, ■ space velocity, ▲ catalyst age.

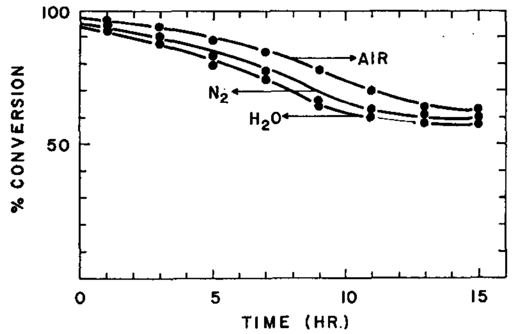


FIG. 2. Percent conversion as a function of time using $ZnCrFeO_4$ (1.8 m^2/g) with nitrogen, air, and steam as diluents.

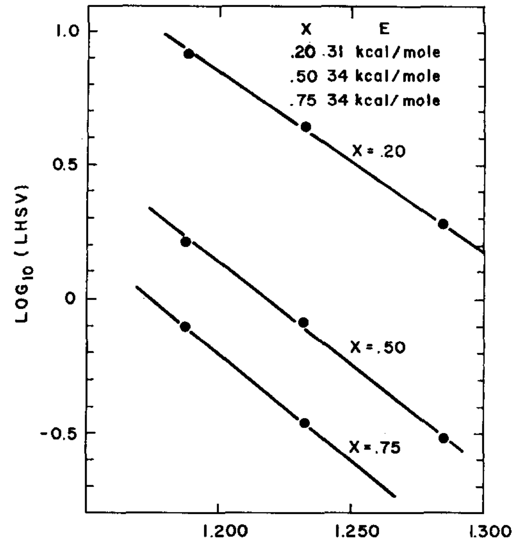


FIG. 3. Arrhenius plots, $N_2/EB/SO_2 = 10/1/1$.

ethylbenzene disappearance was estimated using a freshly regenerated sample of $ZnCrFeO_4$. Figure 3 shows an Arrhenius plot of the log of the space velocity required to achieve a given ethylbenzene conversion versus the reciprocal of the absolute temperature. The average value of the activation energy obtained from the Arrhenius plots is 33 kcal/mole.

Dehydrogenation of Hydrocarbons Containing Polar Groups

To further explore the catalytic properties of $ZnCrFeO_4$ and $MgCrFeO_4$, the oxidative reactions of isobutyraldehyde, isobutyronitrile and isobutyric acid were investigated. If only the oxidative dehydrogenation took place the expected products would be methacrolein, methacrylonitrile and methacrylic acid, respectively.

With $ZnCrFeO_4$ and $MgCrFeO_4$, isobutyraldehyde is selectively oxydehydro-

TABLE 7

VARIATION OF ISOBUTYRALDEHYDE CONVERSION WITH TEMPERATURE, CONTACT TIME AND OXYGEN RATIO USING $ZnCrFeO_4$ AND $MgCrFeO_4$ CATALYSTS

Catalyst	Temperature °C	C_4H_8O/O_2	Contact time sec	C_4H_8O Conversion mole%	Selectivity to methacrolein
$ZnCrFeO_4$	300	1.5	0.27	13.1	77.4
$ZnCrFeO_4$	300	1.0	0.53	21.5	72.1
$ZnFrFeO_4$	300	1.5	0.53	17.0	75.3
$ZnCrFeO_4$	300	1.5	1.06	25.3	75.9
$ZnCrFeO_4$	325	1.0	0.53	35.3	81.6
$ZnCrFeO_4$	325	1.5	1.06	44.2	83.7
$ZnCrFeO_4$	325	1.5	0.53	28.6	82.9
$ZnCrFeO_4$	325	2.0	0.53	25.9	83.8
$ZnCrFeO_4$	325	3.0	0.53	23.2	87.1
$MgCrFeO_4$	325	1.5	0.53	19.7	80.2
$MgCrFeO_4$	325	1.5	1.06	36.9	82.4
$ZnCrFeO_4$	350	1.5	0.53	40.8	86.5
$ZnCrFeO_4$	350	1.5	1.06	65.3	87.1
$MgCrFeO_4$	350	1.5	0.53	36.7	85.8
$MgCrFeO_4$	350	1.5	1.06	68.1	88.0
$H_2O/C_4H_8O = 10$					

genated to methacrolein. The variation of the isobutyraldehyde conversion with temperature, oxygen ratio and contact time using the ferrite catalysts is given in Table 7. The data show that as the isobutyraldehyde-to-oxygen ratio is increased, the conversion decreases and the selectivity to methacrolein increases. Also, at a constant isobutyraldehyde-to-oxygen ratio and contact time, both the conversion and selectivity from 75.3 to 86.5% at 300–350°C, respectively, cannot be explained and is opposite to the results obtained for the oxidative dehydrogenation of olefins to diolefins over the same catalyst. As would be expected, the isobutyraldehyde conversion increased with increasing contact time. The selectivity is essentially invariant over the range evaluated at each temperature studied. These data show the best conditions to dehydrogenate isobutyraldehyde to methacrolein are 350°C with a contact time of 1.06 sec. Also, there appears to be very little difference between the activities of $ZnCrFeO_4$ and $MgCrFeO_4$ catalysts under conditions where maximum per pass yields are obtained. The nonselective products in all cases were carbon monoxide, carbon dioxide, and propylene. These products all arise from the oxidation of isobutyraldehyde since experiments run in the absence of oxygen showed no thermal decomposition.

The oxidative conversion of isobutyronitrile to methacrylonitrile using $ZnCrFeO_4$ and $MgCrFeO_4$ catalysts proceeded at moderate selectivity. Figure 4 gives the data obtained for this reaction. Over the temperature range evaluated, the conversion remained low and the selectivity to noncombustion products was rather high, i.e., $>60\%$. It was interesting to find that the only other major product besides methacrylonitrile was methacrolein.

Experiments were carried out to determine if isobutyric acid could be oxidatively converted to methacrylic acid using ferrite catalysts. Figure 5 gives conversion values and methacrylic acid yield as a function of reaction temperature. From these data, it is obvious that the oxidative reaction does not take place to a great extent and that complete combustion is the main reaction.

Discussion

It has been shown by Adams (*6*), that when olefins having higher molecular weights than butene are oxidized over bismuth molybdate, selectivities are high at low conversions, but decline rapidly at higher conversions. He attributed this to the fact that selective oxidation reactions are inhibited by the reaction products, while the nonselective formation of carbon oxides is only slightly inhibited. This effect is most marked when aldehydes as well as dienes are produced. The low yields of isoprene obtained in the oxidative dehydrogenation of 2-methylbutene-1 and

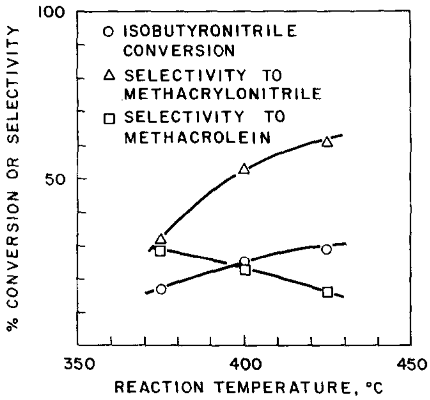


Fig. 4. Oxidative conversion of isobutyronitrile at various temperatures using $ZnCrFeO_4$.

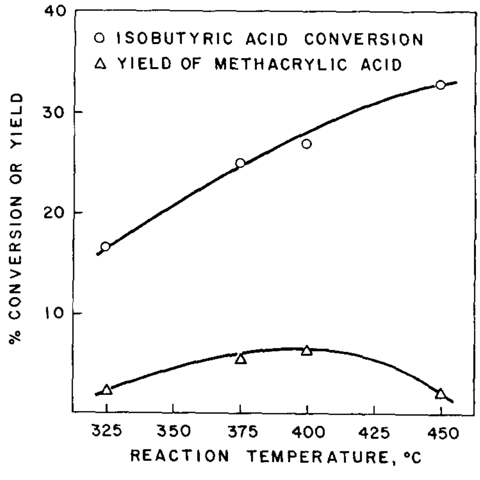


Fig. 5. Oxidative conversion of isobutyric acid at various temperatures using $ZnCrFeO_4$.

2-methylbutene-2 over bismuth molybdate is explained by the fact that substantial amounts of saturated and unsaturated five carbon aldehydes are formed and these inhibit the dehydrogenation reaction.

With the ternary ferrites, oxygenated compounds other than carbon oxides are not formed in the oxidation of olefins in detectable amounts. One would expect that in the absence of these inhibitors relatively high yields of C_5 and C_6 dienes could be obtained by the oxidative dehydrogenation of methyl and dimethyl butenes. As we have shown, this is indeed the case. However, with 2-ethylbutene-1, low selectivities are obtained even at moderate conversions. This would appear to result from the tendency of this molecule to undergo carbon–carbon scission under oxidation conditions to produce ethylene and butenes, and not from any strong inhibition by reaction products. The only hydrocarbon to show strong inhibition by-product over the ternary ferrites is ethylbenzene. In this case one would expect the completely conjugated styrene to be very strongly adsorbed on these catalysts and inhibition expected.

While the ternary ferrites are efficient catalysts for the dehydrogenation of C_4, C_5, and C_6 olefins, there is a decrease in reactivity and selectivity to diene as the number of carbons in the olefin increases. The decrease in reactivity is accompanied by an increase in the extent of double bond isomerization in the unreacted olefins. However, in no case was the isomerization more than 39% of equilibrium.

The following reaction scheme has been previously proposed for the oxidative dehydrogenation of butene over $ZnCrFeO_4$ (*1*):

$$\square + C_4H_8 + Fe^{3+} + O_a^- \rightarrow (C_4H_7 \cdot Fe)^{3+} + OH^- \tag{1}$$

$$(C_4H_7 \cdot Fe)^{3+} + O_l^{2-} \rightarrow C_4H_6 + Fe^{2+} + OH^- \tag{2}$$

$$2OH^- \rightarrow H_2O + O_l^{2-} + \square \tag{3}$$

$$Fe^{2+} + 1/2O_2 \rightarrow Fe^{3+} + O_a^-. \tag{4}$$

Here $\square$ is an anion vacancy, O_a^- is an adsorbed radical ion, O_l^{2-} is a lattice oxygen, $(C_4H_7 \cdot Fe)^{3+}$ is a complex of Fe^{3+} and an allylic radical. If the reaction of the higher olefins follows this same scheme, the results presented here would indicate that for the higher olefins step 2 becomes slower relative to step 1 and reversal of step 1 gives rise to the increased extent of double bond isomerization. This is consistent with the idea that the decrease in reactivity of the higher olefins is due to the increasingly strong adsorption of their resultant dienes. On the other hand, it is a possibility that the higher olefins inhibit the reoxidation of Fe^{2+} to Fe^{3+} giving rise to a decrease in reactivity and an increase in double bond isomerization due to adsorption of olefin on an Fe^{2+} site.

As stated previously the oxidative dehydrogenation of ethylbenzene over the ternary ferrites appears to be strongly inhibited by styrene, giving good selectivity only at low conversions. Similar results have been reported for bismuth molybdate, with benzaldehyde being one of the nonselective products (*6*). Neither benzaldehyde, nor any other oxygenated hydrocarbons, were detected as by-products when ethylbenzene was oxidatively converted over the ternary ferrites. This again demonstrates the great difference between the oxidative properties of the ternary ferrites and bismuth molybdate.

It appears that high yields of styrene cannot be obtained by dehydrogenating ethylbenzene with gas-phase oxygen as the hydrogen acceptor regardless of the catalyst.

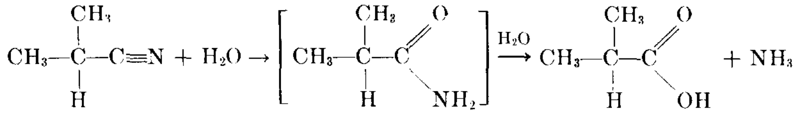
Styrene can be produced at high single pass yields using sulfur dioxide as the hydrogen acceptor over the ternary ferrite catalysts. Sulfur dioxide is a weaker oxidizing agent than oxygen, thus the temperature of dehydrogenation must be in the 550 to 650°C range. Even at these high temperatures high selectivities are obtained with $ZnCrFeO_4$ and $MgCrFeO_4$ and as reported using bismuth molybdate (*6*) and calcium nickel phosphate catalysts (*7*). The major coproduct formed at high conversions is thianaphthene, which is formed by the reaction of styrene with SO_2 or other sulfur compounds. The yield of thianaphthene as a function of ethylbenzene conversion shown in Fig. 1 is typical of that found with a number of other catalysts. In fact, thianaphthene would most likely form over any surface within this temperature range from relative high concentrations of styrene and SO_2.

In this reaction, the ferrite catalysts lose activity with time due to the formation of a carbonaceous residue on the catalyst. This is true for the other catalysts reported for this reaction also. Thus, any commercial process utilizing SO_2 would have to be cyclic. A proposed commercial styrene scheme utilizing SO_2 has been reported by Esso—Scientific Design (*8*), where periodically the reaction feed has to be interrupted so that carbon deposits can be removed by burning with a dilute oxygen stream. The ternary ferrite catalysts reported in this paper are outstanding in their ability to be repeatedly regenerated without loss of activity or attrition. One sample of $ZnCrFeO_4$ was regenerated forty-two times without any type of change.

The activation energy for ethylbenzene dehydrogenation with SO_2 over the ternary ferrites is 33 kcal/mole, which is approximately 11.5 kcal/mole lower than conventional ethylbenzene dehydrogenation over a chromium-promoted iron oxide catalyst (*9*). It appears that in addition to removing the equilibrium limitations on ethylbenzene dehydrogenation by reacting with the liberated hydrogen, sulfur dioxide lowers the activation energy of the process by actually participating, in its adsorbed form, in the hydrogen abstraction step.

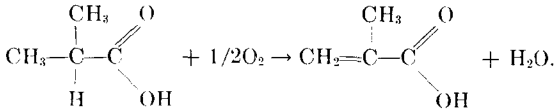
The oxidative dehydrogenation of isobutyraldehyde proceeded at high selectivities to methacrolein using the ternary ferrite catalysts at moderate conversion levels. It has been reported that methacrolein can be prepared from isobutyraldehyde by conventional dehydrogenation over supported metal catalysts (*10, 11*), by the direct reaction with arsenic, antimony, and bismuth oxides (*12, 13*), and by oxidative dehydrogenation over bismuth phosphomolybdate (*14, 15*). In all cases poor selectivities were obtained. With $ZnCrFeO_4$ and $MgCrFeO_4$ very high selectivities can be obtained at moderate conversion levels and at relatively low temperatures.

The formation of methacrolein from isobutyronitrile was unexpected. To our knowledge this is the first time this reaction has been reported. One might predict that the nitrile would hydrolyze to give isobutyric acid,



$$CH_3-\underset{H}{\overset{CH_3}{C}}-C\equiv N + H_2O \rightarrow \left[CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-NH_2\right] \xrightarrow{H_2O} CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH + NH_3 \qquad (5)$$

which in turn would be oxydehydrogenated to yield methacrylic acid.



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH + 1/2O_2 \rightarrow CH_2=\overset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OH + H_2O. \qquad (6)$$

However, $ZnCrFeO_4$ does not catalyze the hydrolysis reaction. When oxygen was eliminated from the feed, and only steam and isobutyronitrile were passed over the catalyst, there was no reaction. Also, there is no reaction when oxygen and isobutyronitrile are passed over the catalyst in the absence of steam. The fact that isobutyraldehyde is obtained as a by-product suggests that the nitrile is first converted to isobutyraldehyde oxydehydrogenated to yield methacrolein.

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