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Dehydrogenation—The First Step in the Cracking of Isopentane over Silica–Alumina Cracking Catalysts

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Earlier work has shown that at low conversions, dehydrogenation is the main primary reaction when isopentane is passed over a silica–alumina catalyst, and that the resulting pentenes largely determine the products and kinetic parameters of cracking (Garten, Ph.D. Thesis, Johns Hopkins University, 1967). Results reported here indicate that the dehydrogenating activity of the catalyst is intrinsic and not the result of trace impurities. Further, the dehydrogenation activity is not related to the ability of the catalyst to hydrogenate ethylene in a hydrogen–ethylene mixture. The latter activity appears to be the result of catalyst impurities, probably iron, and is easily poisoned by hydrogen sulfide. These observations agree with the conclusion from previous work (Garten, 1967) that at least for isopentane cracking, the traditional "secondary reaction" role accorded to the corresponding olefins should be supplanted by considering dehydrogenation of the paraffinic feed as the major primary reaction of cracking, the breaking of the carbon–carbon bond being a subsequent step to dehydrogenation.

INTRODUCTION

In cracking reactions over acidic oxide catalysts, olefin formation is generally accepted as a consequence of the β-scission of initially formed carbonium ions which decompose into primary carbonium ions and olefins (*2*). Thus, olefin formation follows breaking of the carbon–carbon bond, and the reactions of the olefins have been treated as secondary reactions of the cracking system (*3*). Direct formation of olefins by dehydrogenation of paraffins is not considered characteristic of an uncontaminated catalyst. Voge *et al.* (*4*) state that dehydrogenation of paraffins to olefins occurs to only a minor extent and does not play a significant role in determining the product distribution of cracking. Previous work by Garten (*1*), however, has shown that dehydrogenation is the primary reaction when isopentane or normal pentane is passed over a silica–alumina cracking catalyst, and that the resulting pentenes strongly influence the cracking pattern. A probable reason that the dehydrogenation reaction has been so long ignored is that at the moderate to high conversions at which cracking is normally studied, the pentenes constitute a negligible fraction of the cracking products. Because of the important role dehydrogenation appears to play in cracking, it was decided to study this reaction more closely and try to determine whether dehydrogenation is indeed an intrinsic characteristic of the catalyst or the result of trace impurities. Since iron is the main impurity which might be responsible for dehydrogenation, special attention was focused on the influence of this element. The main mode of attack was to study the activity and product distribution of several silica–aluminas for the cracking of isopentane and the hydrogenation of ethylene both before and after poisoning with hydrogen sulfide.

EXPERIMENTAL

The gases used in these experiments were all of at least 99.5% purity and except

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for the hydrogen and chromatograph carrier gases, they were dried by passage over silica gel dessicant and/or Drierite. The hydrogen was Matheson "Zero Gas," hydrogen with less than 0.5 ppm hydrocarbon impurities. The ethylene and hydrogen sulfide were further purified by several freeze, pump, and thaw cycles. The isopentane was obtained from the Phillips Petroleum Company and had a stated purity of 99.99%. It was further purified by passage through a mercuric sulfate–sulfuric acid trap to remove olefins (*1*). After being put into the cold trap the isopentane was also degassed.

Three catalysts were used in this study. The main catalyst (also used by Garten) was a commercial silica–alumina catalyst obtained from the Davison Chemical Company and designated as #980. It was used either as pellets 3/16 in. in length and diameter or ground to 8–14 mesh. The manufacturer gave an analysis of 13.21% alumina, 86.44% silica, 0.03% iron, 0.02% sodium oxide, and 0.3% sulfate. The BET surface area of the catalyst is 390 m^2/g. The second catalyst used was a highly pure silica–alumina catalyst furnished by Keith Hall (Mellon Institute) and designated DSA-3. It was made by neutral hydrolysis of aluminum isopropoxide and tetraethylorthosilicate and contained only 1 ppm iron. The highest impurity levels reported were about 10 ppm each of copper, magnesium, and lead. The particle size was 20–50 mesh. The surface area was not measured, but is assumed to approximate that of the similarly prepared catalyst DSA-1 with a reported BET area of 280 m^2/g (*5*). The third catalyst used in this study was made by treating porous glass under vacuum at about 100°C with a concentrated aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ (71 g/25 cm^3) (*6*). After being dried for an extended period at 135°C and then calcined at 525°C during the regular pretreatment, the catalyst should contain about 7% alumina. The porous glass was obtained from the Corning Glass Company (#7930) and was through 30 mesh. Before impregnation it was leached for 15 hr in 1 *N* nitric acid solution to remove metallic impurities, rinsed thoroughly with distilled water, and dried at 135°C. Just prior to impregnation, it was evacuated at 300°C. The final catalyst (which will be referred to as the "porous glass" catalyst) had a BET surface area of 108 m^2/g.

The basic system for the kinetic studies was a conventional glass circulation system which has been described in detail elsewhere (*1*). The system, however, was modified so that an external stream of helium could be flowed over the catalyst and either isopentane in a cold trap at 0°C or a 2 cm^3 pulse of ethylene–hydrogen mixture could be picked up by the helium. In the flow runs, the time of contact was varied by changing the helium flow and/or the amount of catalyst (the 980 catalyst varied between 2 and 28 g).

For the cracking (all flow) runs the catalyst temperature was 450°C. The effluent gas was sampled with a syringe and analyzed chromatographically using a Perkin Elmer column V, di-2-ethylhexyl sebacate, and bis-(2-methoxyethyl) adipate, at room temperature and a flame ionization detector. The catalyst pretreatment consisted of a 6 hr oxidation at 525°C by oxygen saturated with water vapor at room temperature followed by a short evacuation and overnight flushing with helium at 60 cm^3/min and 500°C.

For all ethylene hydrogenation runs, a mixture of 20% ethylene and 80% hydrogen was used at a total pressure of from 200 to 400 mm Hg. In the pulse runs, ethylene and ethane were determined by channeling the reaction mixture directly into a chromatograph equipped with an alumina column at 70°C and using a thermal conductivity detector. During the circulation runs, samples of about 0.25 cm^3 were diverted into the chromatograph at roughly 5-min intervals using a conventional glass sample loop and helium carrier gas. The catalyst pretreatment varied somewhat, but always involved a 6 hr oxidation (wet or dry), usually at 525°C, followed by overnight evacuation to 10^{-6} mm Hg at the same temperature. The reaction temperature was 456°C.

RESULTS AND DISCUSSION

The results presented in Tables 1 to 3 show that the product distribution obtained by passing isopentane over the three silica–alumina catalysts are all very similar. Furthermore, they agree with the results obtained by Garten in that they indicate that at low conversions, the principal products are pentenes. Thus using catalyst 980 Garten found that at 0.6% conversion 80 mol of pentenes was formed per hundred moles of isopentane converted, whereas we obtained 80 mol of pentenes at a conversion of 0.12% (Table 1). For the DSA-3 catalyst, 87 mol of pentenes was formed per 100 moles of iso-

TABLE 1

Product Distribution for Cracking Isopentane at 450°C over Catalyst 980, DSA-3, and Porous Glass Compared to Blank Run (Thermal or Homogeneous Reaction)[a]

	Run number					
	CD5-1	CS4	CP2-1	#53[b] (Garten)	CS8-1	CB5-3 (thermal)
Compound $\geq C_6$	—	—	—	—	—	—
3-Methylpentane	—	1.5	0.5	—	—	—
2-Methylpentane +2,3-dimethylbutane	—	2	0.5	—	—	~6.5
2-Methyl-2-butene	42	20	39	—	40	~6.5
cis-2-Pentene	5.5	3	5	—	6.5	~5
trans-2-Pentene	11	6	9.5	—	13	~2.5
2-Methyl-1-butene	13.5	8	6.5	—	19.5	~2.5
1-Pentene	—	1.5	2.5	—	Small	Small
n-Pentene	—	7.5	~1.3	5.5	Small	Small
cis-2-Butene	2	1.5	2	—	4	6
trans-2-Butene	2.5	2	3	—	6	11.5
2-Methylpropylene + 1-butene	—	3.5	4.5	—	3.5	31
n-Butane	2	2.5	1	6.5	Small	Small
2-Methylpropane	15[c]	22	13	59	2.5	6.5
Propylene	8.5	18	14	9	5	13
Propane	1.5	5	1.5	24	0.4	13
Ethylene + ethane	8	18	11.5	14	5	19.5
Methane	15	14	18	Not determined	14.5	46
Time of contact (t_c),[d] (sec)	44	4.5	30	~54	0.14	4.5
% conversion	0.37	2.7	2.0	48	0.12	0.013
Mole% olefins[e]	73	60	74	~19	84	61
Mole% Pentenes	57	29	47	Very small	65	13
% converted carbon as pentenes	72	39	63	—	80	23
Type of catalyst	DSA-3	980	Porous glass	980	980	Blank

[a] The 3-methyl-1-butene peak was always obscured by the isopentane peak and assumed small.

[b] This run was done in a circulaton system.

[c] Other results indicate that hydrogenation of thermally produced 2-methyl-propylene is the cause of this large figure.

[d] Based on total volume occupied by catalyst for easy comparison with Garten's data. The true t_c is about $\frac{2}{3}$ the given value.

[e] The entire C_2 fraction is considered olefin for easy comparison with Garten's data. Generally, 80% of the C_2 fraction is ethylene.

TABLE 2

Effect of H_2S Poisoning on the Product Distribution on Passing Isopentane over 980 Catalyst at 450°C

	Run number		
	CS6-1 (poisoned)	CS6-2 (poisoned)	CS9-1 (poisoned)
	(moles)/100 mol converted)		
Compound $\geq C_6$			0.13
3-Methylpentane	—	0.5	1.2
2-Methylpentane + 2,3-dimethylbutane	—	0.5	2
2-Methyl-2-butene	29.5	23.5	1.5
cis-2-Pentene	4.5	4	0.2
trans-2-Pentene	7.5	7	0.3
2-Methyl-1-butene	8	8	0.4
1-Pentene	3.5	2	0.1
n-Pentane	2	5	6
cis-2-Butene	2	1.5	0.4
trans-2-Butene	2.5	2	0.7
2-Methylpropylene + 1-butene	4.5	3.5	1
n-butane	—	2.5	8.5
2-Methylpropane	9.5	17.5	63
Propylene	27.5	19.5	5.5
Propane	1.5	6.5	30.5
Ethylene + ethane	27	19.5	12.5
Methane	12	18	5.0
Time of contact (t_c),[a] (sec)	3	3	44
% conversion	1.6	1.4	43
Mole% olefins[b]	82	64	16
Mole% pentenes	38	32	2
% converted carbon as pentenes	53	45	3

[a] See footnote *d* in Table 1.

[b] See footnote *e* in Table 1.

pentane coverted at a conversion of 0.06% (Table 3) and for the catalyst made from porous glass, 63 mol at a conversion of 2% (Table 1). As seen in Tables 1 and 2, the yield of olefins and especially pentenes drops dramatically as the conversion increases. In Table 1, the DSA-3 and porous glass catalysts can be compared to catalyst 980 at similar conversions.

The poisoning runs in Table 2 show that the pretreatment of catalyst 980 with hydrogen sulfide for an hour had no appreciable effect on either the rate of reaction or the product distribution. Certainly the results do not give any indication that pentenes are being formed by dehydrogenation of pentanes over a metallic impurity.

It should be mentioned that the amount of hydrogen sulfide picked up by catalysts 980 and DSA-3 in the pretreatment could not have been taken up only by the impurities present; some of it must have been retained by the silica–alumina. Thus, catalyst 980 retained 1.7×10^{-5} mol of H_2S whereas the iron content amounted to only 1×10^{-5} mol. On the DSA-3 catalyst, the iron impurity would have held only 10^{-8} mol of H_2S whereas 1×10^{-5} mol was taken up.

From these results it appears reasonable to conclude that pentenes are formed due to the intrinsic activity of the three silica–alumina catalysts and not due to the action of metallic iron as an impurity.

It was known from previous experiments that catalyst 980 is a good catalyst for hydrogenating ethylene to ethane. Thus, Hightower and Emmett (*7*) reported that at 372°C the ethylene in a hydrogen–ethylene mixture was 90% converted to ethane. The time of contact was about 12 sec. However, it has also been reported that when radioactive ethylene is added to a stream of cetane being cracked over catalyst 980 at 372°C, very little of it is built into the higher hydro-

TABLE 3

Activity and Effect of H_2S poisoning on product distribution from Passing Isopentane over DSA-3 Catalyst at 450°C

	Run number	
	CD4 (poisoned)	CD3
	(moles/100 mol converted)	
Compound $\geq$C6	—	—
3-Methylpentane	—	—
2-Methylpentane +2,3-dimethylbutane	—	—
2-Methyl-2-butene	62	46
cis-2-Pentene	4	6
trans-2-Pentene	13	13
2-Methyl-1-butene	21	20
1-Pentene	~2	~2
	Very small ↓	Very small ↓
Time of contact (t_c)	3.1	4.5
% conversion	0.026	0.06[a]
% converted carbon	~100	87

[a] A second unpoisoned run extrapolates to a percentage conversion of 0.026 at $t_c = 3.1$ sec. This is typical of the experimental spread at these low conversions.

carbons and only a small fraction of it is converted to ethane. These observations suggested that the iron impurities were responsible for the hydrogenation activity of catalyst 980 for ethylene–hydrogen mixtures. To verify this, catalyst 980 was studied with respect to its ability to hydrogenate ethylene and the effect of hydrogen sulfide, a well-known poison for iron (*8*, *9*), was determined. The results are shown in Fig. 1. Hydrogen sulfide reduced the initial rate of reaction about 40-fold. The partial pressure of ethylene was, of course, falling off rapidly over the unpoisoned catalyst so that the rate of hydrogenation decreased with time. The specific rate (per m^2) of hydrogenation over fresh catalysts was about 1/20th as great on the porous glass catalyst as on the 980 catalyst and about 1/500th as large on the highly pure DSA-3 catalyst.

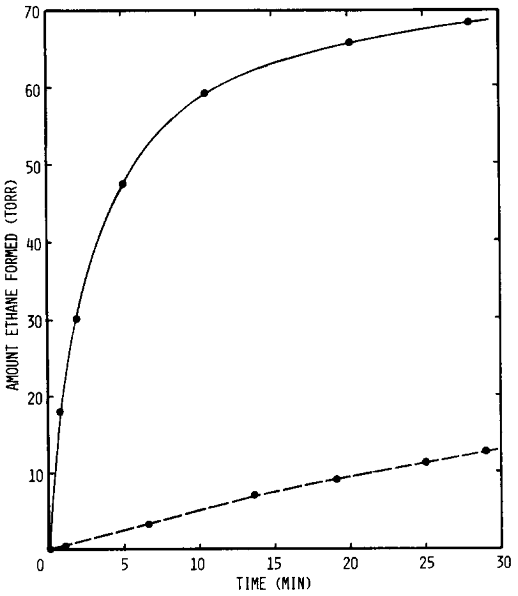

FIG. 1. The effect of H_2S poisoning on the activity for the hydrogenation of ethylene on catalyst 980. The solid line is for run 24 with a fresh catalyst, and the dashed line is for run 27 with a poisoned catalyst. The volume of the recirculating system is 290 cm^3, the effective volume of the catalyst at the reaction temperature of 456°C is 5.6 cm^3, the initial total pressure was 413 Torr, and the catalysts were pretreated at 525°C using wet oxygen.

The question naturally arises as to whether the ethylene–ethane ratio in the product of isopentane cracking shows any dependence on the amount of iron impurity present. Although the ratio is not shown in the present tables, actually it varied from values in the range 2 to 7 over the three catalysts without any apparent relationship to the iron impurity. This made it seem likely that during the cracking process, the iron impurity would become so poisoned that it would lose its activity for the hydrogenation of ethylene. To confirm this, a pulse of ethylene–hydrogen was passed over a cracking catalyst that had just been used for isopentane cracking. The activity for hydrogenation was only a few percent as large as on the fresh catalyst.

All of these data combine to indicate that the formation of pentenes is an intrinsic activity of silica–alumina catalysts. Presumably, pentenes are formed by the breaking of the initial pentyl carbonium-ion into a proton on the catalyst plus a pentene molecule. On the other hand, the hydrogenation of ethylene in a hydrogen–ethylene mixture presumably takes place on an impurity, probably on iron.

The question also arises as to whether there is any contribution of homogeneous or thermal cracking in the present experiments. As shown in Table 1, an experiment was done with the regular reactor without a catalyst being present. The homogeneous reaction is only about 1/300th as fast as the catalytic rate over catalyst 980 and only gives about 1/5th as much pentenes. Hence, in most runs the contribution of the homogeneous reaction is completely negligible and even over catalyst DSA-3, in which the homogeneous rate is about 1/3 of the catalytic rate, the contribution of the homogeneous reaction would have been only about 5% of the pentenes.

CONCLUSION

A study has been made of the initial product distribution of isopentane cracking and the activity for the hydrogenation of ethylene of three silica–alumina cracking catalysts. The results support Garten's assertion that pentenes are the main primary products of isopentane cracking. The activity for dehydrogenation has been shown to be an intrinsic characteristic of the catalysts, and hence the observed product distribution is not the result of trace impurities. The activity for hydrogenating in a hydrogen–ethylene mixture is, however, not intrinsic and is probably caused by the iron impurity.

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