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The Influence of Chelating Polyolefins on the Disproportionation of Propylene Catalyzed by WO_3 on Silica

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Addition of small amounts of polyolefins to the propylene feed increased propylene disproportionation conversion over a tungsten oxide on silica catalyst, and shortened the catalyst break-in period. These results are attributed to an increase in the number of active sites through modification by the polyolefins of the energy level distribution in the tungsten oxide centers.

INTRODUCTION

The disproportionation of propylene (to butenes and ethylene) catalyzed by tungsten oxide on silica has been the subject of several studies aimed at the clarification of its mechanism (*1*). Current experimental evidence (*1, 2*) gives substance to the idea that disproportionation takes place by way of a four-center complex formed by the reaction of two adjacently adsorbed propylene molecules. Marked gas phase mass transfer effects have been reported (*2-4*). These have been explained by Johnson (*3, 4*), who assumed that the catalyst surface contains widely separated very active sites and that the reaction is limited by site-localized diffusion effects. From the dependence of the catalyst activity on temperature and promoter (WO_3), Johnson also inferred that the catalyst surface is heterogeneous and that the number of active sites is a function of temperature and of promoter concentration (*4*).

We postulate that olefin disproportionation over the tungsten oxide–silica catalyst occurs through promotion of electrons from molecular orbitals comprising metal *d*-orbitals and olefin π-orbitals to levels comprising metal *d*-orbitals and olefin antibonding π-orbitals. The separation of these levels is a function of the metal *d*-orbital separation before coordination of the olefin to the metal. On a heterogeneous surface a broad distribution of metal energy levels is expected, depending on the localized interaction of the metal with the support. Consequently, at a given temperature, only some fraction of the sites may be active. The other sites, which give rise to a spectrum of progressively greater separations between the levels involved in the postulated electronic transitions, require proportionately higher temperatures for their activation. At low promoter concentration the tightest binding centers on the support, which give rise to the largest splitting of the metal orbitals, are occupied by the metal; as the concentration of the promoter increases, centers which interact more weakly with the metal also become occupied, and the spectrum of disproportionation sites broadens. This view is in accord with and provides a mechanism for Johnson's conclusion that the number of active sites increases with temperature and promoter concentration.

Since the reaction is limited by site-localized diffusion, any modification of the sites already operational, resulting in an increase of their activity, without a change in the experimental variables (temperature, pressure, and flow rate), should produce no significant increase in conversion. However, conversion can be increased by increasing the number of active sites through suitable modification of those sites not yet active under the experimental conditions. One way to accomplish this is by addition to the metal atom of ligands capable of decreasing the difference between the energy levels in question. It seemed to us that ligands with π-type orbitals which can combine with the upper d-orbitals of the metal and lower their energy would be best suited for this purpose. Because the catalyst is easily poisoned by polar compounds, it also appeared desirable to limit the choice of ligands to hydrocarbons. To test our views we have studied the influence of some chelating di- and triolefins (hereafter referred to as polyenes) and, for comparison, of some other hydrocarbons on the disproportionation of propylene catalyzed by tungsten oxide on silica.

Experimental Method

All tests, except one series, were done at atmospheric pressure in a continuous-flow system, with a fixed catalyst bed in a quartz reactor. The catalyst was supported in the reactor by a plug of quartz wool, and the space above the catalyst was filled with quartz chips to function as a preheater. The reactor was heated by an electric furnace constructed of quartz, so that color changes in the catalyst bed could be observed during the test. The temperature was measured at the center of the catalyst bed. A similar system with a stainless steel reactor was used for the series of experiments at 21.4 atm.

One cubic centimeter of catalyst, having 20–40 mesh size, was used in every test. The catalyst was activated in the reactor in a stream of dry air at 600°C for 1 hr and was then flushed with nitrogen for 20 min while being cooled to the temperature desired for the test. The propylene, before it entered the reactor, was passed through a rotameter and a drying tube containing activated Alcoa H-151 alumina and 10× mole sieves. The propylene flow rates are given in Tables 1–4; they are expressed in cc/min at 25°C and 1 atm. The additives (n-octane, benzene, and the polyenes) were introduced into the propylene stream at the reactor inlet by means of a syringe pump. The products were analyzed by v.p.c.; a 19-ft hexamethylphosphoramide column, a 12-ft polypropylene glycol column, and a 20-ft Silicone 703 column were used.

The catalyst was a 6.8% WO_3 on silica, which has already been described by Moffat *et al.* (*3*). The propylene was Phillips Polymerization grade. The additives were commercial samples; they were flushed with nitrogen to remove dissolved oxygen and were dried over 10× mole sieves.

Results

1,5-Cyclooctadiene (1,5-COD) was the only compound whose influence on propylene disproportionation was studied both at atmospheric pressure and at 21.4 atm. The effects produced by the addition of 1,5-COD to the propylene feed are illustrated by the data in the first three tables. The results given in Tables 1 and 2 show the influence of 1,5-COD on the induction period at atmospheric pressure and at 21.4 atm, respectively. Those given in Table 3 show the effects of 1,5-COD on propylene disproportionation conversions at various temperatures and at atmospheric pressure after the induction period. It is evident from these data that both at atmospheric pressure and at the higher pressure (a) the

TABLE 1
Effects of 1,5-COD on the Induction Period at Atmospheric Pressure[a]

Time on stream (min)	Propylene conversion (%) 1,5-COD[b] 0	1.0
5	6.2	40.6
11		42.2
13	24.4	
22	30.7	
30		40.7[c]
38	33.5	
50		38.7[c]
55	35.5	

[a] 500°C, propylene flow rate 50 cc/min.

[b] Mole percent in feed.

[c] 1,5-COD removed from the feed.

TABLE 2
EFFECTS OF 1,5-COD ON THE INDUCTION PERIOD AT 21.4 ATMOSPHERES[a]

Time on stream (min)	Propylene conversion (%) 1,5-COD[b]			
	0	0.04	0.2	0.4
5	2.7	7.9	16.0	24.5
20	10.5	24.4	35.5	42.3
35	17.3	30.0	41.4	44.3
50	18.6	20.6[c]	20.9[c]	16.9[c]
65	25.3	25.2[c]	23.1[c]	18.2[c]
80	41.7[d]			

[a] 413°C, Feed rate: 600 cc/min.
[b] Mole percent in feed.
[c] 1,5-COD removed from the feed.
[d] 0.2 Mole % 1,5-COD added to the feed.

induction period is reduced in the presence of 1,5-COD, (b) after the induction period the reaction is enhanced by 1,5-COD, and (c) the effects produced by 1,5-COD are temporary.

In addition to 1,5-COD, several other hydrocarbons were tested for their influence on propylene disproportionation over WO_3 on silica. These are listed in Table 4, where their effects on the propylene conversions after the induction period are reported. Their influence on the induction period at 500°C is shown in Fig. 1. All these tests were made at atmospheric pressure using a propylene feed rate of 50 cc gas/min. *n*-Octane was added to the feed at a rate of 0.5 cc liquid/hr; the other compounds were added at 0.17 cc liquid/hr, i.e., 2–3 wt % of the total feed, or 0.6–1.5 mole %, depending on the molecular weight of the additive. The propylene conversions reported were calculated on the basis of the propylene and propylene disproportionation products in the reactor effluents. The distribution of the propylene disproportionation products (ethylene, 1-butene, *trans*-2-butene , and *cis*-2-butene) observed when the additives were present was not significantly different from that obtained when propylene only was used.

The results shown in Table 4 and in Fig. 1 indicate that the additives tested fall into three classes: (a) compounds which did not affect the course of the disproportionation reaction (*n*-octane and benzene); (b) compounds which produced moderate increases in propylene conversion (1,5-hexadiene and

TABLE 3
EFFECTS OF 1,5-COD ON PROPYLENE DISPROPORTIONATION AFTER THE INDUCTION PERIOD AT ATMOSPHERIC PRESSURE[a]

Time on stream (min)	Temperature (°C)	1,5-COD in feed (mole %)	Propylene conversion (%)
0–90	500	0	
90	500	0	37
110	450	0	10
120	Addition of 1,5-COD was started		
130	450	4	43.4
165	400	4	43.1
180	350	4	43.0
195	300	4	23
215	Addition of 1,5-COD was stopped		
230	300	0	2.4
247	350	0	6.5
270	350	0	1.4
275	Addition of 1,5-COD was resumed		
288	350	4	39

[a] Propylene flow rate 45 cc/min.

TABLE 4
EFFECTS OF VARIOUS HYDROCARBONS ON PROPYLENE DISPROPORTIONATION AT ATMOSPHERIC PRESSURE[a]

Compound added (0.17 cc liquid/hr)	Propylene conversion (%)			
	350°C	400°C	450°C	500°C
None	Trace	1	5–10	30–40
n-Octane*			7	38
Benzene		1	11	38
1,5-Hexadiene		3	17	41
Dicyclopentadiene		4	19	42
1,5-Cyclooctadiene		14	35	43
1,3-Cyclooctadiene		12	40	44
1,5,9-Cyclododecatriene		10	40	40
1,4-Cyclohexadiene	7	42	43	42

[a] Propylene flow rate 50 cc/min.
[b] 0.5 cc liquid/hr.

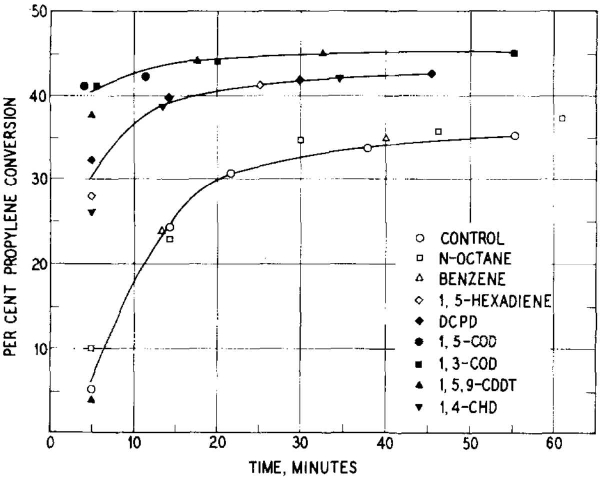

FIG. 1. Effects of various hydrocarbons on the induction period of the propylene disproportionation reaction at 500°C and atmospheric pressure.

dicyclopentadiene); and (c) compounds which enhanced significantly propylene conversions (1,4-cyclohexadiene, 1,5,9-cyclododecatriene, and 1,3- and 1,5-cyclooctadiene). The enhancement of the reaction always ceased when the additives were removed from the feed. It is clear from these results that the polyenes produced effects similar to those described for 1,5-COD.

The polyenes were generally consumed in the course of the reaction. This occurred both by thermal reactions, e.g., decomposition of the cyclooctadienes to butadiene, and catalytically by mutual double bond cleavage of the polyenes with propylene. While the catalytic reaction yielded only polyenes and monoolefins, the thermal reaction produced, in addition to polyenes, aromatic compounds, as by dehydrogenation of 1,4-cyclohexadiene. When this compound was passed over the catalyst, in the absence of propylene, at atmospheric pressure and at 44 cc gas/min, it was converted almost exclusively to benzene and hydrogen; the conversion was 99% at 500°C and 66% at 400°C. The results given in Fig. 1 and Table 4 show that benzene does not influence the disproportionation of propylene. Accordingly, 1,4-cyclohexadiene showed a pronounced enhancement of propylene conversion at 400°C, but a smaller effect at 500°C. These results also indicate that the higher propylene conversions were not produced by hydrogen.

We have also observed enhancement of propylene disproportionation by polyenes over other catalysts, e.g., by 1,4-cyclohexadiene over cobalt molybdate on alumina at 150°C, and by dicyclopentadiene over rhenium oxide on alumina at 38°C.

DISCUSSION

There is a good deal of evidence (*1*, *5*) to indicate that some reduction of the $WO_3 \cdot SiO_2$ catalyst occurs in developing its activity for disproportionation. The catalyst break-in period can be attributed in part to such a reduction by propylene. Accordingly, pretreatment of the catalyst with a reducing agent, such as hydrogen or carbon monoxide, shortens the induction period (*1*, *5*). A change in the color of the catalyst, from yellow (characteristic of stoichiometric tungsten trioxide) to blue (characteristic of substoichiometric tungsten trioxide with an O/W atom ratio of 2.95 or lower (*6*)) accompanies these pretreatments. Without pretreatment with a reducing agent, as in our experiments, a similar color change is observed when propylene is passed over the catalyst. That reduction accompanies these color changes was confirmed by an X ray diffraction analysis: after activation of the catalyst in dry air (1 hr at 600°C) the tungsten oxide was present as the stoichiometric trioxide; subsequent treatment of the catalyst with carbon monoxide at 600°C produced a substoichiometric trioxide of composition $WO_{2.2}$ to $WO_{2.90}$.

The reduction (if, in fact, it plays a direct role in promoting activity) may be needed mainly to form vacant coordination sites on the tungsten by removal of oxygen atoms, or to produce active metal species (e.g., formation of pentavalent tungsten), or both. Since the effects produced by the polyolefins are temporary, they must not arise from reduction or other permanent changes in the properties of the catalyst. Therefore, it seems unlikely that the induction period corresponds to formation of vacant sites; oxygen vacancies are probably present on the catalyst surface at the start of the induction period. Also the catalytic activity of the transition metal cannot be considered necessarily a function of the oxidation state of the metal. It seems conceptually more accurate to consider catalytic activity as a function of the energy levels of the metal ion. These levels can be adjusted by changes in the oxidation state of the metal and by changes in the nature of the ligands, in their number, or in their geometry. This view provides an explanation of how similar effects are obtained by prereduction of the catalyst and by addition of chelating polyolefins to the feed.

Within the concept of the four-center mechanism, we view the role of the metal mainly as that of providing a suitable framework for the transfer of electrons from the π-orbitals of the reactant olefins to their antibonding π-orbitals, from which the incipient σ bonds of the product molecules are formed. Since, even in the reduced catalyst, the oxidation state of the metal is high, the upper levels of the metal-olefin complex, arising from metal orbitals and olefin antibonding orbitals, must be empty or singly occupied. It seems reasonable then that disproportionation occurs not through shifts of the electronic density within molecular orbital levels of the metal-olefin complex, but by electronic transitions between these levels (see Introduction), and that a delicate balance in the relative position of these levels must be achieved. π-Bonding ligands, such as chelating diolefins, are expected to lower the energy values of the upper levels (into which the electrons are promoted) through interaction of their antibonding π-orbitals with the d-orbitals of the metal.* As a consequence, sites which are inactive for disproportionation in the absence of the diolefin may become active when the diolefin is coordinated to the metal; or, alternatively, coordination of the diolefin to an active site may facilitate the electronic transition and speed up the reaction. An increase in conversion in the latter case means that the electronic transition constitutes the slow step in propylene disproportionation, and mass transfer effects should not be observed. Since, under the conditions used in our experiments, severe mass transfer limitations are evident (*4*), the increase in conversion must be attributed to an increase in the number of active sites.

REFERENCES

1. BANKS, R. L., *Top. Current Chem.* **25**, 39 (1972).
2. LUCKNER, R. C., MCCONCHIE, G. E., AND WILLS, G. B., *J. Catal.* **28**, 63 (1973).
3. MOFFAT, A. J., JOHNSON, M. M., AND CLARK, A., *J. Catal.* **18**, 345 (1970).
4. MOFFAT, A. J., CLARK, A., AND JOHNSON, M. M., *J. Catal.* **22**, 379 (1971).
5. LUCKNER, R. C., AND WILLIS, G. B., *J. Catal.* **28**, 83 (1973).
6. GEBERT, E., AND ACKERMAN, R. J., *Inorg. Chem.* **5**, 136 (1966).
7. BEGLEY, J. W., AND PENNELLA, F., *J. Catal.* **8**, 203 (1967).

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* A similar, though less forceful, role is probably played by the propylene molecule. The influence of olefin coordination on the energy levels of a transition metal complex is illustrated by the calculations made for the olefin polymerization system titanium trichloride-aluminum alkyl (*7*).