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Removal of Coke Precursors with Hydrogen: Studies with Alternating Pulses of Propane and Hydrogen

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The time scale of coke formation on the surface of a supported chromia catalyst, during the dehydrogenation of propane at 1200°F, has been studied. The reactor feed consisted of alternating pulses of propane and hydrogen. For switching frequencies as high as 1 sec^{-1}, the catalyst bed did not destroy the pulsed nature of the feed.

A model of residue formation is discussed which involves growth of unsaturated oligomers, which upon reaching a critical size can no longer be regenerated with hydrogen. The time required for the development of such a species is found to be of the order of 1 sec.

It is well known that the presence of hydrogen reduces the rate of formation of carbonaceous residues on catalyst surfaces used in hydrocarbon reactions. Little is known of the ability of hydrogen to remove residue already formed. Rohrer and Sinfelt (*1*), have demonstrated the ability of hydrogen carrier gas to remove deactivating residues formed during passage of a hydrocarbon pulse over a Pt/Al_2O_3 catalyst. The reactivation process, however, was not studied as a function of time of exposure to hydrogen and hydrocarbon. The present study is addressed to determining the time scale of residue formation on a catalytic surface. Propane dehydrogenation over supported chromia was used as a model reaction.

When a catalytic surface is contacted with a propane pulse at sufficiently high temperature, dehydrogenation to propylene will occur and will be accompanied by formation of carbonaceous residue or precursors thereof. A model of precursor growth, using C_3^{2-} units, leads to sequential formation of C_6^{2-}, C_9^{2-}, C_{12}^{2-}, etc. Cyclization and further alkylation of side chains and rings will eventially yield the polynuclear aromatic structure of coke. The intercession of a hydrogen pulse can lead to the saturation of aliphatic doublebonds. Conversion of aromatics to naphthenes is precluded due to the thermodynamic stability of the former at higher temperatures. The conversion of an olefinic oligomer to a paraffinic one will interrupt polymerization and lower the binding energy to the surface. Smaller saturated oligomers will be capable of desorption. Larger ones will not, and upon resumption of the propane pulse with concomitant lowered hydrogen partial pressure, will dehydrogenate and resume polymeric growth.

This simplified model implies that the efficacy of the hydrogen pulse will be critically dependent upon the duration of the propane pulse. If the latter is sufficiently short, precursor oligomers will be small and capable of removal by a hydrogenation–desorption mechanism.

In order to test this model, propane dehydrogenation was carried out over a supported chromia catalyst using alternating pulsed feeds of propane and hydrogen. A propane pulse, of duration τ_{C_3}, was fed to the reactor and was followed by a hydrogen pulse of duration τ_{H_2}, then back to propane, etc. Switching frequencies as high as 1 sec^{-1} were employed, i.e., $\tau_{C_3} = \tau_{H_2} = 1$ sec. This was accomplished by the use of two-position, double air-piloted valves, for both hydrogen and propane. These were controlled by a four-way solenoid valve, which was actuated by an electrical timer. The arrangement was such that when propane was feeding to the reactor, hydrogen was vented, and vice-versa.

The catalyst employed was chromia supported on a sintered (80 m^2/g) deacidified alumina. The support was prepared by impregnating β-alumina trihydrate with $CsNO_3$ solution and drying and calcining 8 hr at 1600°F. The support was impregnated with CrO_3 solution, and dried and calcined 4 hr at 1000°F. The mole ratio in the finished catalyst ($Cr:Cs:Al_2O_3$) was 10:5:100. This catalyst is characterized by high selectivity for dehydrogenation.

It is obvious that for sufficiently short pulses, smearing will occur in the catalyst bed. This will effectively convert the pulsed feed into a blended feed. In an effort to establish conditions in which alternating pulse operation is feasible, propane and hydrogen were fed into a reactor and the effluent led through a thermal conductivity cell. The cell output was displayed on an oscilloscope and Polaroid pictures taken. The stainless-steel reactor (17/32 in. i.d.) was charged with 20 cm^3 supported chromia catalyst. The total volume of the reactor was 42 cm^3. A preheat section consisted of 12 cm^3 porcelain beads, and a postcatalyst section consisted of 10 cm^3 porcelain beads. Catalyst and bead particles were 10–40 mesh.

Figure 1 gives reactor–effluent composition at two different switching frequencies. Flow rates of both gases were 20 liters/hr (lowering to 10 liters/hr gave slightly more smearing), and catalyst temperature was 600°F. It is clear that for switching frequencies ≤ 0.5 sec^{-1}, the effluent retains its pulsed character. A check at a frequency of 1 sec^{-1} could not be made, as the volume of the thermal conductivity cell produced a blending effect.

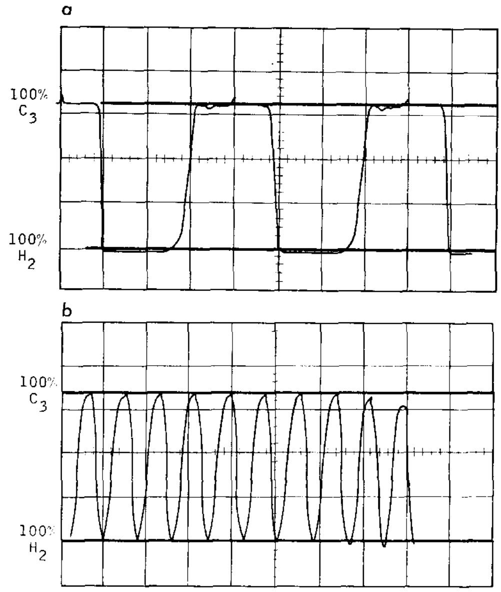

FIG. 1. Trace of oscilloscopic display of thermal conductivity of reactor effluent using alternating pulsed feed of C_3 and H_2. (a) Switching frequency = 1/10 sec^{-1}; (b) Switching frequency = 1/2 sec^{-1}.

Table 1 presents data from propane dehydrogenation runs at 1200°F. In all cases, 15 cm^3 of supported chromia catalyst, (20/40 mesh particles), was used. Following a hydrogen pretreatment at 1200°F for .5 hr, a blended feed of propane and hydrogen, each at 20 liters/hr, was introduced. A significant hydrogenolytic activity was present at first, but this attenuated far more rapidly than the dehydrogenation activity. Thus, after about 140 min on blended feed, selectivity to propylene was at least 86 mole %. At this point, the blended feed was ceased and the run continued either with: (1) pure propane feed at 20 liters/hr; (2) alternating pulsed feed, propane and hydrogen, each at 20 liters/hr, $\tau_{C_3} = \tau_{H_2} = 5$ sec; (3) the same as (2), except $\tau_{C_3} = \tau_{H_2} = 1$ sec. "Time on C_3" values for runs (2) and (3) are calculated as half the elapsed clock time, corresponding to actual exposure to hydrocarbon.

Figure 2 presents data from the three runs, commencing with the switch from blended feed. The "relative activity" values represent mole percent conversion to C_3^{2-} relative to that observed just prior to

TABLE 1
CONVERSION AND SELECTIVITY VS TIME ON C_3 WITH SUPPORTED CHROMIA AT 1200°F

Time on C_3, min	Conversion, mole %	Selectivity to C_3^{2-}, %
Blended feed	Run 1	
23	43.1	82
30	38.0	86
56	30.6	91
96	22.0	93
133	17.4	92
138		
Pure C_3	Switch to pure C_3	
165	24.5	88
192	16.9	86
220	12.6	83
250	9.5	81
300	6.4	80
320	6.2	81
Blended feed	Run 2	
5	56.6	63
12	48.4	87
50	34.8	91
103	27.5	91
133	25.2	91
143		
Pulsed feed	Switch to $\tau_{C_3} = \tau_{H_2} = 5$ sec.	
159	41.1	90
180	33.3	91
204	27.4	91
218	24.4	90
232	21.6	89
	Run 3	
7	63.4	59
137	21.7	86
140		
Pulsed feed	Switch to $\tau_{C_3} = \tau_{H_2} = 1$ sec.	
150	39.6	83
165	40.8	83
225	33.0	85
270	27.8	85

switching from blended feed. This normalization serves to correct for the difference in activities observed during the blended feed portion of these three runs.

If the curves in Fig. 2 are extrapolated back to the time of switching (from blended feed), the conversion is seen to approximately double due to this switch. Thus, the reaction order with respect to propane is about unity. Curve 3 indicates this response to the same extent as curve 2. This demonstrates that pulse smearing is not significant even at the switching frequency of 1 sec^{-1}, although this could not be directly shown by effluent–thermal conductivity measurements.

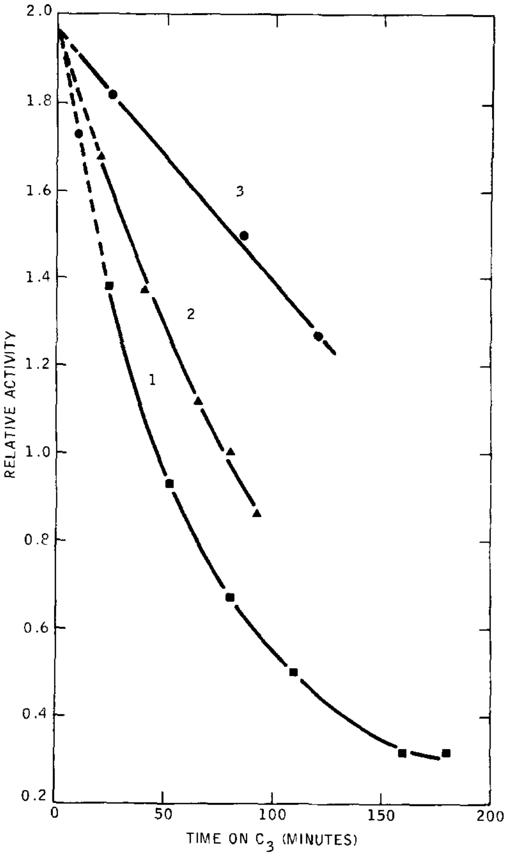

FIG. 2. Conversion to C_3^{2-} (relative to blended feed conversion) vs time on C_3 (after switching from blended feed), with supported chromia at 1200°F using (1) C_3 feed, no H_2; (2) alternating pulses, $\tau_{C_3} = \tau_{H_2} = 5$ sec; (3) $\tau_{C_3} = \tau_{H_2} = 1$ sec.

Figure 2 clearly shows that the ability of a hydrogen pulse to remove precursors formed during the propane pulse strongly depends upon switching frequency. Comparison of slopes indicates that the relative initial rates of deactivation for $\tau = 1$, $\tau = 5$, and $\tau_{H_2} = 0$ (continuous, pure C_3) are, respectively, 1:3:5. Assuming a linear relationship between residue formation and activity loss, this may be interpreted to mean that 80% of precursor formed during 1 sec of development can be removed by the intercession of a 1-sec hydrogen pulse. If 5 sec for precursor development is allowed, removal with a subsequent 5-sec hydrogen pulse is reduced to 40%. It thus appears that, for this catalyst and conditions, the time required for formation of critically large (nonregenerable) precursor oligomers is of the order of 1 sec.

REFERENCE

1. ROHRER, J. C., AND SINFELT, J. H., *J. Phys. Chem.* **66,** 1193 (1962).