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The Effects of Precious Metal Promoters on the Reduction of Vanadium Pentoxide by Hydrocarbons

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The reduction of V_2O_5 by hydrocarbons (ethylene, propylene, ethane, propane) proceeds at lower temperatures in the presence of Pd, Pt, Ru or Ag. Pd is the most effective in promoting reactivity.

For V_2O_5–Pd with ethylene, a dimerization to butenes was the principal reaction at 100°C, a partial oxidation to acetaldehyde predominated at 150°C, and a more complete oxidation to CO, CO_2 and water at temperatures above 200°C. No dimerization and no significant yield of acetaldehyde or other oxygen containing hydrocarbons was observed with the other additives. The oxidation of the hydrocarbons by the precious metal–V_2O_5 combinations is believed to proceed by a migration of oxygen through the V_2O_5 lattice to react with hydrocarbon or hydrocarbon residues adsorbed at sites on or near the precious metal additives.

INTRODUCTION

It is now well established that certain metal oxides are reduced more readily by hydrogen when precious metals are present (*1*). This effect has been attributed to "hydrogen spillover"; that is, to the dissociative adsorption of hydrogen on the metallic component of the mixture, followed by a migration of the hydrogen to the oxide component and a reduction of that phase. The process has been studied in sufficient detail to permit a reasonably detailed mechanism for the process (*2*).

It has recently been reported that the reduction of V_2O_5 with ethylene (at 250°C) or with *o*-xylene (at 320°C) proceeds more rapidly when palladium is present (*3*). Thus, cooperative effects like those observed with hydrogen may also occur with hydrocarbons. The results reported here were obtained to investigate this possibility in more detail.

EXPERIMENTAL METHODS

The samples investigated are listed in Table 1. The samples containing vanadium were prepared by digesting solutions of ammonium metavanadate and salts of the appropriate metal, followed by evaporation to dryness. The metal levels were 2% by weight. The Pd–alumina sample was prepared by impregnating a porous α-alumina support (SAHT-99, Carborundum Co.) from solution to a level of 3.5% Pd. All materials were heated in flowing air to 400°C at 2°C/min, and held at temperature for 12 hr.

TGA was used to survey the relative reactivity of the various solids. The gases (Union Carbide Corp., Linde Division) were 5% in the reactants, and the balance, nitrogen. More detailed information on the reactions occurring during the very early stages of reduction with ethylene was obtained with a pulsed reactor. For these measurements, a reactor consisting of a 10 mm o.d., 8 mm i.d. Pyrex U-tube 250 mm in length was inserted into the carrier gas stream ahead of the sample port of an Aerograph Model A-700 chromatograph. A typical reactor charge was 4 to 5 g of catalyst sized to 10/20 mesh. Two milli-

TABLE 1
SUMMARY OF CATALYSTS INVESTIGATED

Sample	Starting materials	Surface area (m^2/g)	Phases detected by X-ray diffraction
V_2O_5	$NH_4VO_3{}^a$	4.5	V_2O_5, $V_2O_4{}^c$
V_2O_5-Pd	NH_4VO_3, $PdCl_2{}^b$, HCl	5.7	V_2O_5, $V_2O_4{}^c$, Pd, PdO
V_2O_5-Ru	NH_4VO_3, $RuCl_34H_2O^b$, acetic acid	10.0	V_2O_5
V_2O_5-Pt	NH_4VO_3, $PtCl_2{}^b$, HCl	6.4	V_2O_5, $V_2O_4{}^c$, Pt
V_2O_5-Ag	NH_4VO_3, $AgNO_3{}^a$	10.6	V_2O_5, $V_2O_4{}^c$, $AgVO_X{}^d$
Al_2O_3-Pd	α-Al_2O_3, $Pd(NH_3)_4(NO_3)_2$	4.0	α-Al_2O_3, Pd, PdO

[a] Fisher Scientific Co.
[b] Englehard Industries.
[c] Trace amounts.
[d] An unidentified phase presumed to be a silver vanadate.

liter pulses of ethylene were introduced into the carrier gas stream (He, 30 psig, 50 cc/min) ahead of the reactor. Unreacted ethylene and products (except CO) were collected in a liquid nitrogen trap which consisted of a 0.125 in. copper U-tube located behind the reactor. Product identifications were based on retention times observed for known substances that were introduced through a sample port located ahead of the cold trap. The identification of the reaction products was confirmed by mass spectrometry.

RESULTS

TGA Measurements

As shown in Fig. 1, the reactivity of V_2O_5 toward ethylene was enhanced (i.e., reduction proceeded at lower temperatures) in the presence of all of the metals. However, the sample doped with palladium was significantly more reactive than those doped with the other metals, while the reactivity of the samples containing ruthenium, platinum, and silver were comparable. An enhanced reactivity was also observed with other hydrocarbons (Figs. 2, 3 and 4). For a given hydrocarbon, the doped V_2O_5 samples were more reactive than the undoped material in all cases, and also in all cases, the V_2O_5-Pd specimens were more reactive than the samples doped with silver. The orders of reactivities were as follows:

Undoped V_2O_5
$C_3H_6 > C_2H_4 > C_3H_8 > C_2H_6$,

V_2O_5 with Ag
$C_3H_6 > C_2H_4 > C_3H_8 > C_2H_6$,

V_2O_5 with Pd
$C_2H_4 > C_3H_6 > C_2H_6 > C_3H_8$.

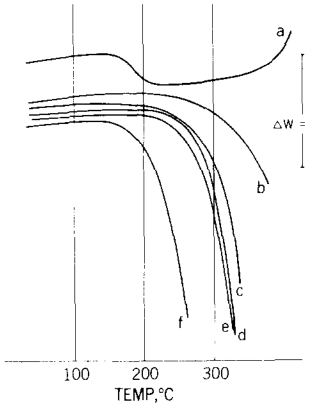

FIG. 1. TGA curves for the samples of Table 1 when heated with 5% ethylene: (a) Pd-Al_2O_3, (b) V_2O_5, (c) V_2O_5-Ru, (d) V_2O_5-Pt, (e) V_2O_5-Ag, and (f) V_2O_5-Pd. The curves have been displaced along the weight axis for clearer presentation. The data were obtained with a Mettler thermoanalyzer at a heating rate of 4°C/min. The distance along the ordinate corresponding to a 1% change in sample weight is indicated.

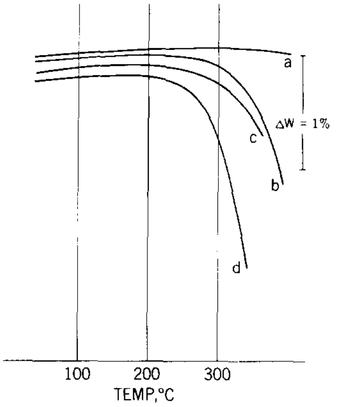

FIG. 2. TGA curves for V_2O_5 heated in: (a) 5% ethane, (b) 5% propane, (c) 5% ethylene, and (d) 5% propylene.

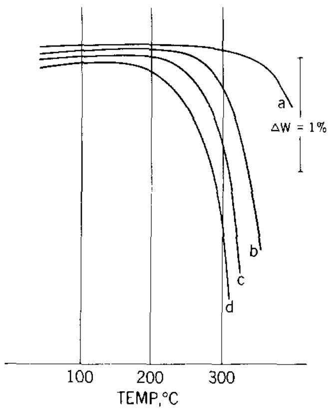

FIG. 4. TGA curves for V_2O_5–Ag heated in: (a) 5% ethane, (b) 5% propane, (c) 5% ethylene, and (d) 5% propylene.

With Pd–alumina, which was chosen to be representative of behavior with an inert support, there was a small loss in weight in the 150–200°C interval due to the reduction of PdO to the metal. Weight then increased with increasing temperature, becoming particularly pronounced above 350°C. The weight increase is consistent with previous observations that hydrogen-deficient residues form from ethylene adsorbed on Pd–alumina (*4*). With V_2O_5–Pd, there was a continuous loss in weight, with no discontinuity for the reduction of PdO apparent.

The total weight changes shown in Fig. 1 represent approximately one-fourth the loss that would occur for the conversion of all of the V_2O_5 present to V_2O_4. Thus, the weight changes observed correspond to much more than a surface depletion. Consistent with this, a sample of V_2O_5–Pd held in 5% ethylene at 300°C for several hours, lost weight equivalent to a final composition of approx $VO_{1.9}$. The X-ray diffraction pattern for this material was similar to one that has been reported for a phase of composition, $VO_2 \cdot 0.04\ H_2O$ (*5*).

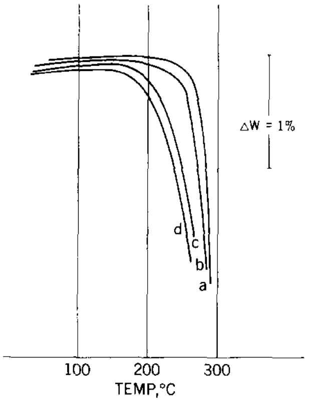

FIG. 3. TGA curves for V_2O_5–Pd heated in: (a) 5% propane, (b) 5% ethane, (c) 5% propylene, and (d) 5% ethylene.

Pulsed Reactor Results

The behavior for V_2O_5–Pd was quite different from that for V_2O_5 with the other metals. For the latter group, little ethylene adsorption ($< 10^{-6}$ moles/g) or reaction occurred at temperatures less than about 150°C. Above this temperature, significant amounts of CO, CO_2, and H_2O were obtained, with the ratio of CO to CO_2 increasing with increasing temperature. Traces of partial oxidation and/or polymerization products (i.e., products with chromatographic residence times greater than those for CO_2, ethylene or water) were observed in some cases, but the amounts were too small for convenient analysis or identification. Essentially the same behavior was observed with undoped V_2O_5.

A considerably more complex chemistry

was observed with V_2O_5–Pd. At room temperature, ethylene was adsorbed in amounts corresponding to approx 1×10^{-5} moles/g. At least a portion of this was adsorbed reversibly, that is, there was a gradual desorption of ethylene to the carrier gas stream after the sample was treated with a pulse of ethylene. With increasing temperature, an increasing portion of the ethylene was adsorbed irreversibly, as indicated by a gradual evolution of carbon dioxide and water to the carrier gas and a decrease in the evolution of ethylene. There was also an increase in products found to be a mixture of *cis*- and *trans*-2-butene and either 1-butene or isobutylene. The third component was presumed to be the former on the basis of the relative yields of the three products, specifically, the amounts produced were in good agreement with reported equilibrium concentrations for the isomerization of the 1- and 2-butenes (*6*).

Acetaldehyde and carbon dioxide were identified in the product streams at about 100°C. Acetaldehyde and carbon dioxide production increased and butene yields decreased as temperatures were increased from 100 to 175°C, at which temperature only traces of the butenes were detected. Above 150°C small, but readily detectable amounts of propylene were also observed.

The pulsed reactor experiments were run under conditions of low conversion. Typically, less than 5% of an ethylene pulse was converted to other products. The low conversion conditions were chosen because the longer retention time products such as acetaldehyde and the butenes were further oxidized by the catalyst, and were only seen when an excess of ethylene was present. Thus, quantitative determinations of product yields would have had little meaning, and they were not attempted. On a semiquantitative basis, most of the ethylene that was converted formed products other than CO, CO_2, and water at temperatures below about 175°C, while above 200°C, these were the predominant products.

DISCUSSION

It does not seem attractive to attribute the effects reported here to processes like those that have been proposed for hydrogen spillover. A direct analogy would require a dissociative adsorption of the reactants on the metal additives, followed by a migration of all of the decomposition products over and into the supporting phase to react with lattice oxygens. A complete decomposition to hydrogen plus carbon atoms is without precedent, and seems particularly unlikely. A decomposition to hydrogen plus hydrogen-deficient residues would provide hydrogen that could migrate, and would be in keeping with previous interpretations of hydrocarbon–metal interactions (*4*). However, it is doubtful whether these residues could migrate into or onto the oxide, and it is difficult to reconcile the extent of the observed weight losses with any significant buildup of residues. Thus, a migration of oxygen through the bulk oxide to react with hydrocarbons held at specific sites seems to be indicated. These sites, presumably are at or near the metal additives.

Palladium additions were particularly effective in promoting reduction, and the V_2O_5–Pd combination was unique in its ability to absorb ethylene and to yield polymerization (butenes) and partial oxidation (acetaldehyde) products. A V_2O_5–Pd based system has previously been shown to be effective for the heterogeneous catalytic oxidation of ethylene to acetaldehyde (*8*). In that study, similarities were found between the reactions occurring at the gas–solid interface and the mechanism that has been established for homogeneous Wacker chemistry (*9*). Specifically, the oxidation appeared to proceed via a coordination of both an olefin and a hydroxyl to Pd(II), followed by the formation of the carbonyl compound and the reduction of the V_2O_5 substrate adjacent to the palladium center.

There are also similarities between the butene formation over V_2O_5–Pd and the dimerization of ethylene over nickel oxide on silica (*10*), (or NiO on SiO_2–Al_2O_3). With the latter systems both components of the catalyst are needed, and the order of reactivity is

$$C_2H_4 > C_3H_6 > C_4H_8$$

instead of the inverse order normal for acid catalyzed reactions. Butenes were isomerized over V_2O_5, but no butenes were formed over Pd–Al_2O_3. Some dimerization of propylene occurred over V_2O_5–Pd, but yields were much smaller than with ethylene.

The dimerization over NiO–silica has been attributed to a cooperative effect between a nickel and an acid site that involves the formation of an adsorbed ethyl species (*10*). An insertion of an ethylene molecule into the adsorption bond, followed by an elimination of hydrogen then completes the reaction. The V_2O_5–Pd system may involve a similar chemistry with dimerization occurring at the lower temperatures where the lattice oxygen has limited mobility, oxygen insertion at intermediate temperatures where oxygen migration begins to occur, and complete oxidation at the higher temperaure where the lattice oxygens are mobile.

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