Catalytic Oxidation of Propylene over Cu(II)–Y Molecular Sieve

Molecular sieves have been recognized as important catalysts for acid-catalyzed reactions such as cracking, isomerization, and dehydration (*1*). Some investigations on the nature of molecular sieves ion-exchanged with transition metal ions have been reported (*2*). The oxidation of hydrocarbons over such sieves, however, has scarcely been attempted (*3*). Agudo *et al.* (*4*) reported the oxidation of hexane isomers over NaX, CaX, and MnX. Because the reactants were paraffinic hydrocarbons, the nonheterogenous processes were predominant and the character of the transition metal ion appeared obscurely.

It may be interesting to investigate the role in oxidation reactions of the isolated ion produced on the molecular sieve surface by ion-exchange, and to compare it with the same ion on ordinary oxide catalysts. In the present work, the oxidation of propylene over a Y molecular sieve exchanged with copper(II) ions was studied and was compared with the oxidation over a CuO–silica gel catalyst.

Very recently, Rouchand *et al.* (*5*) reported the oxidation of hydrocarbons on a molecular sieve ion exchanged by transition metal ions.

EXPERIMENTAL METHODS

The sodium ions of a Y molecular sieve (Linde) were exchanged with aqueous cuprammonium ions (Cu–Y). The color of the ion-exchanged sieve was deep blue. The Cu–Y was dried at 100° and calcined at 400° for 7 hr in the atmosphere. The calcined catalyst was light blue and its BET surface area was 400 m^2/g. X-Ray diffraction showed that the Cu–Y sieve kept the same high crystallinity as the original Y sieve. The Cu–S catalyst was prepared by impregnating silica gel (Wako) with cupric nitrate solution, and was calcined at 400° for 7 hr. X-Ray diffraction showed that the copper in the Cu–S catalyst was in the form of cupric oxide. This catalyst which contained nearly the same amount of cupric ions on silica gel was dark green.

The oxidation reaction was studied by the ordinary flow method, with a fixed catalyst bed diluted by carborumdum (Nakarai). The thermowell was located in the middle of the catalyst bed. The reactant gas consisted of 2% propylene, 50% oxygen and 48% nitrogen. Carbon dioxide, propylene, and oxygen were analyzed with gas chromatography using a Porapak Q column (Waters Associated Inc.) of 2 m at 70° for the former two and the molecular sieve 13X (Linde) of 2 m at room temperature for the latter. Formaldehyde was analyzed by iodide titration against samples trapped at the tail of the reactor.

The catalytic activity kept constant for 20 hr after the initial increase for 8 hr, and then decreased slowly.

RESULTS AND DISCUSSION

Carbon dioxide and water were the main products. Formaldehyde was found to about 10% of the carbon dioxide in both cases of Cu–Y and Cu–S, independent on the conversion. Acrolein and acetaldehyde were detected by the spot test in the reaction above 350°, however, they occurred in minor quantities. An example of the reactions at 350° is shown in Table 1, where the conversions were calculated in three ways; one from the decrease of the reactant propylene (Line I), one from the decrease of oxygen (Line II), and one from the yields of carbon dioxide and formaldehyde converted to a propylene basis (Lines III plus IV). These conversions thus calculated coincide with one another, so that the material balance was maintained. When Norton α-alumina was used as a diluent, however, the carbon balance was not maintained which may be caused by the strong

TABLE 1
MATERIAL BALANCE AND REACTION PRODUCT

At 350°	(%)
Decrease of propylene	12.1
oxygen[a]	12.5
Formed carbon dioxide[b]	9.5
formaldehyde[b]	2.4

[a] Decrease of oxygen converted to a propylene basis of a complete oxidation.

[b] An inlet-propylene basis.

adsorption of unreacted propylene on alumina. Aguda *et al.* (*4*) reported also that the carbon balance did not maintain in their oxidation of hexane, and a carbon deposit was found. In our case the Cu–Y catalyst kept light blue after the reaction.

Catalytic activities of Cu–Y and Cu–S for carbon dioxide formation were compared, and Arrhenius Plots and activation energies are shown in Fig. 1 and Table 2, respectively. Because the reaction rate was accelerated when the conversion exceeded 15%, the catalytic activities of Cu–Y at higher temperatures were relatively overestimated, so that the calculated activation energy may be larger to some extent. The catalytic activity of Cu–Y for propylene oxidation was very large and its activation energy was so small that the high activity at low reaction temperatures could be expected. Amounts of cupric ions and surface areas of both catalysts were nearly equal, so the difference in catalytic activity by an order of magnitude may be due to the difference in the function of cupric ions. To clear this situation, preliminary LFER approach about reactant (*7*) was adopted. The catalytic activities for ethylene oxidation are compared in Table 2. The catalytic activities of supported cupric oxide were similar for either ethylene and propylene as reported by Nobe and Accomazzo (*6*), however, over the Cu–Y catalyst the catalytic activity for propylene was much higher than that for ethylene by an order of magnitude. Comparisons between reactivities of ethylene and propylene in oxidation on various catalysts were briefly summarized from the literature; Belousov and Rubanik (*8*) reported by competitive reactions that propylene was more reactive by a factor of 1.5 than ethylene on a silver catalyst. This tendency was more emphasized on a nickel oxide catalyst (*9*). On the other hand, ethylene was more reactive than propylene on a metallic platinum catalyst (*10*) and also on a palladium chloride catalyst in aqueous solution (*11*). The notable difference between Cu–Y and Cu–S in catalytic activity may be due to the difference of the states of cupric ions on the catalysts. Cupric ions on the Y molecular sieve are isolated and are not part of an oxide even after the reaction of the oxidative atmos-

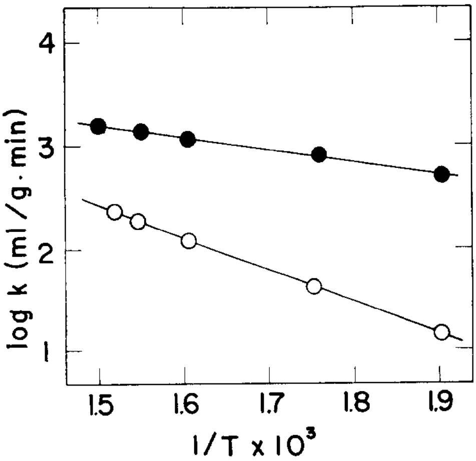

FIG. 1. Arrhenius plots of propylene oxidation into carbon dioxide over Cu–Y and Cu–S catalysts: ●, Cu–Y; ○, Cu–S.

TABLE 2
OXIDATION REACTIVITIES OF ETHYLENE AND PROPYLENE OVER Cu–Y AND Cu–S
(olefin, 2%; oxygen, 48%; nitrogen, 50%)

	Propylene	Ethylene
Cu–Y		
Rate of 350°[a]	1.37×10^3	1.39×10^2
Activation energy[b]	4.2	18.0
Cu–S		
Rate at 350°[a]	1.28×10^2	1.45×10^2
Activation energy[b]	15.5	17.5

[a] (ml/g.min).

[b] (kcal/mole).

phere as indicated by its light blue color, but they are the part of an oxide on silica gel as distinctly shown by X-Ray diffraction. More precise investigations in the kinetics and mechanism of the oxidation over the Cu–Y and for other olefins are in progress.

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Interaction of Oxygen and Butene with Gold*

In previous studies (*1*) of the catalytic activity of polycrystalline gold for the isomerization of 1-butene, the degree of isomerization was found to increase in the presence of hydrogen, while the addition of oxygen completely suppressed isomerization. To obtain a better understanding of the inherent catalytic properties of a nontransition metal, such as gold, for nonskeletal isomerization, a series of measurements was carried out on the interaction of O_2 and 1-butene on gold foil ribbons in an ultrahigh vacuum (UHV) apparatus.

The apparatus used in these studies consisted of two chambers separated by a remote-control shutter and evacuated by separate ion-getter pumps (*2*). Such an arrangement allowed pretreatment of the catalyst in a separate chamber, preceding the admission of various reactants. The gold catalyst,† a polycrystalline foil ribbon (0.002 in. thick, 11 cm^2 in geometric area, C.P. grade), was supported in one of the chambers of the UHV system by two electrodes through which an electric current could be passed for heating the ribbon.

Before a sorption experiment the ribbon was cleaned by flash desorption (1075°K for 2 min) and then allowed to cool to the reaction temperature for 3 min, at a background pressure of 5×10^{-9} torr. The rate

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† The gold foil was obtained from Wildberg Bros., San Francisco, Calif. It contained 0.065 wt % carbon.