JOURNAL OF CATALYSIS 18, 343–360 (1970)

NOTES

Catalytic Oxidation of Propylene on Mixed Metal Oxides*

Recent experimental studies on the catalytic oxidation of propylene demonstrated the high specificity of cuprous oxide for the formation of acrolein (*1*). To learn more about the role of the valence state of the copper ion in the catalyic oxidation process, a series of experiments was carried out on mixed oxide catalysts composed of the oxides of copper and chromium. Such mixed oxides are of special interest since it has been shown (*2*) that the partial pressure of oxygen is significantly enhanced in equilibrium with the mixed oxide in accordance with

$$2CuO + Cr_2O_3 \rightleftarrows Cu_2Cr_2O_4 + \tfrac{1}{2}O_2(g). \quad (1)$$

Cu(I) in the mixed crystal ($Cu_2Cr_2O_4$) is stable in the presence of much higher concentrations of oxygen as compared to the equilibrium:

$$2CuO \rightleftarrows Cu_2O + \tfrac{1}{2}O_2(g). \quad (2)$$

Extrapolation of the data in Ref. (*2*) indicates that at 700°K the equilibrium partial pressure of O_2 over $Cu_2Cr_2O_4$ amounts to 3×10^{-2} Torr, while for Cu_2O it is 1×10^{-6} Torr. In addition to the mixed oxide $Cu_2Cr_2O_4$, in which copper is present in the +1 valence state, the spinel structure $CuCr_2O_4$ is known to contain copper in the +2 valence state (*3, 4*). General enhancement has been reported (*5*) in the catalytic properties of cupric oxide by the addition of chromic oxide for complete oxidation of hydrocarbon, but a systematic study of the properties of mixed oxides involving copper and chromium cations has been limited to the oxidation of CO (*6*) and decomposition of N_2O (*7*). The results suggested significant differences between the catalytic properties of cuprous chromite and cupric chromite. The present study was limited to quantitative measurements of the catalytic properties of $Cu_2Cr_2O_4$ (Cu(I)) and $CuCr_2O_4$(Cu(II)) in the oxidation of propylene in an attempt to relate the selectivity of the catalyst to the valence state of the copper ion.

EXPERIMENTAL DETAILS

The mixed oxide catalysts were prepared by the procedure described in Ref. (*3*). A mixture of 1 mole of CuO and 2 moles of Cr_2O_3 was placed in an aluminum boat and heated in air at 1140°K for 21 hr and in oxygen at 1270°K for an additional period of 6 hr. The resulting material was examined by X-ray analysis (*3*) and found to contain > 90 mole % of $CuCr_2O_4$. For the preparation of cuprous chromite an equimolar mixture of $CuCr_2O_4$ and Cr_2O_3 were heated in air at 1475°K for 16 hr. Analysis by X-ray diffraction demonstrated conversion of the material to $Cu_2Cr_2O_4$ to the extent of more than 90 mole %. The catalysts were ground in an agate mortar and screened, with the particle-size range from 43 to 61 μ. The surface area of the catalysts was evaluated by the BET procedure (Kr-sorption). The results showed a surface area of 0.269 m^2/g of $Cu_2Cr_2O_4$ and 0.412 m^2/g of $CuCr_2O_4$.

The experiments were carried out in a continuous flow reactor composed of a Pyrex cylinder (10-cm^3 volume) containing a fritted glass disk for the support of the powdered catalyst sample (0.1 g). The

---

* This study was carried out under the sponsorship of several industrial companies whose support is gratefully acknowledged.

flow rate of reactants entering the reactor was metered with calibrated flow meters. The gas stream was composed of propylene, oxygen, and helium, which was employed as an inert carrier gas. The partial pressures of the various gases were adjusted to yield the following relative composition: $O_2:C_3H_6:He = 1:8:10$. The system was operated at a pressure slightly above 1 atm. The total flow rate of gas was 325 ml/min. A cylindrical furnace surrounding the reactor was used to maintain the reactor temperature at 623°K. The gases* employed were of the following purities: $O_2 > 99.999$, $He > 99.99$, and $C_3H_6 > 99$ vol %.

At suitable time intervals the product distribution in the efflux from the reactor was examined by withdrawing samples for analysis by gas–liquid chromatography. Separate columns were employed in the analytical procedure: propylene and carbon dioxide were separated at 298°K on a column containing BMEA-sebacate; acrolein, acetaldehyde, and propylene oxide were separated at 350°K on a column containing Ucon.

RESULTS AND DISCUSSION

The differences in the product spectrum resulting from the catalytic oxidation are shown in Table 1. The total specific conversion of propylene to products is higher in the case of $Cu_2Cr_2O_4$ than $CuCr_2O_4$. In addition, the distribution of products points to a marked enhancement in acrolein formation for the catalyst containing Cu(I) (Table 2). Thus the ratio of CO_2/C_3H_4O is 2 in the case of $Cu_2Cr_2O_4$ while it amounts to 8 in the case of $CuCr_2O_4$. In the absence of any catalyst an entirely different product distribution is obtained under the same experimental conditions of residence time and reactor temperature (Table 2). Presumably the gas-phase reaction yields acetaldehyde and propylene oxide as the major products while the catalyzed reaction favors acrolein and carbon dioxide. In the absence of catalyst the total conversion of propylene was much smaller than observed in the presence of catalyst.

TABLE 1
PRODUCT DISTRIBUTION FROM CATALYTIC OXIDATION OF PROPYLENE

Catalyst	Conversion[a] (vol %)	Product (μmoles/m²)			
		Acetaldehyde	Propylene oxide	Acrolein	Carbon monoxide and dioxide
$Cu_2Cr_2O_4$	13	1.5	0.45	11.5	22.9
$CuCr_2O_4$	9	0.6	0.7	2.4	19.4

[a] Based on propylene.

TABLE 2
RELATIVE PRODUCT DISTRIBUTION

Catalyst	Product			
	Acetaldehyde	Propylene oxide	Acrolein	Carbon monoxide and dioxide
$Cu_2Cr_2O_4$	4	2	32	62
$CuCr_2O_4$	3	3	11	83
None[a]	51	34	6	9

[a] Conversion: 1 vol %.

The results lend further evidence to the role of the cation valence state in the selective oxidation of propylene over copper oxide. It appears that stabilization of Cu(I) in the presence of oxygen by the formation of the mixed oxide $Cu_2Cr_2O_4$ definitely favors acrolein formation as compared with Cu(II) in $CuCr_2O_4$, consistent with the observations made on cuprous and cupric oxide (*1*). It is unlikely that the chrome ion is responsible for this selectivity in catalyst activity since Cr_2O_3 has been found to be a relatively poor catalyst next to copper oxide (*6, 7*). If the formation of carbon monoxide and dioxide over copper oxide is the result of sequential oxidation, with acrolein as a stable intermediate, as suggested in Ref. (*8*), we are led to the conclusion that some catalyst property associated with Cu(I) is responsible for interfering with complete oxidation of the propylene, a property which is lost in the case of CuO.

---

* The Matheson Chemical Company.

In a comparison of the catalytic activities of various metal oxides, the bonding of the allyl radical in terms of a π-complex with the metal cation appears to be a property common to all the catalysts which are active in oxidative dehydrogenation (*9*). Thus we may conclude that the existence of the allyl radical is an essential feature in the oxidation of propylene. However, the extent of oxidation or the selectivity of the catalyst is more likely controlled by the different species of oxygen present on the surface and in the lattice. This aspect of the problem has received attention in recent papers by other investigators (*10, 11*). The crude model for relating oxidation specificity to the metal–oxygen bond strength in the lattice has been refined by us in terms of different sorbed oxygen species, charged and neutral. It is the distribution of the various oxygen species that governs the specificity of the catalytic reaction (*1*).

REFERENCES

1. Wood, B. J., Wise, H., and Yolles, R., *J. Catal.* **15**, 355 (1969).
2. Schenck, R., and Kurzen, F., *Z. Anorg. Allg. Chem.* **235**, 97 (1937).
3. Schulz, I. W., Ebert, T., and Scheve, J., *Z. Anorg. Allg. Chem.* **346**, 66 (1966).
4. Keeley, W. M., and Mathes, W. B., *J. Chem. Eng. Data* **11**, 582 (1966).
5. Schenck, R., and Kurzen, F., *Z. Anorg. Allg. Chem.* **220**, 97–106 (1934).
6. Rienacker, G., *Z. Anorg. Allg. Chem.* **258**, 280 (1949).
7. Scheve, J., and Schulz, I. W., *Int. Congr. Catal., 4th, Moscow, 1968,* Prepr. 84.
8. Isaev, O. V., Margolis, L. Y., and Sazanova, I. S., *Dokl. Akad. Nauk SSSR* **129**, 141 (1959).
9. Adams, C. R., *Proc. Int. Congr. Catal., 3rd, 1964* **1**, 240 (1965).
10. Sachtler, W. M. H., and DeBoer, N. A., *Proc. Int. Congr. Catal., 3rd, 1964* **1**, 252 (1965).
11. Boreskov, G. K., *Discuss. Faraday Soc.* **41**, 263 (1966).

S. Henry Inami
Henry Wise

Solid State Catalyst Laboratory,
Stanford Research Institute,
Menlo Park, California 94025

Received December 10, 1969

Mass Transfer Effects in the Olefin Disproportionation Reaction

Preliminary propylene disproportionation studies on a WO_3–silica catalyst have shown increased catalyst efficiency with increased flow rate. This clearly indicates a mass transfer or interphase diffusional effect, although calculations made on the basis of generalized equations for diffusion predict no limitation in reaction rates by mass transfer (*1*). Such calculations use the external, catalyst surface area to estimate the area over which diffusion occurs. However, with few exceptions, only a very limited fraction of the total catalyst surface is active, and there is reason to question any *a priori* calculation which rules out interphase diffusion limitations on the basis of external surface area.

Runs were made using a split bed quartz reactor in which the propylene flow could be reversed. Gas samples were withdrawn after full or ½-bed contact with the catalyst. This split bed, reversible flow reactor allowed two catalyst specimens to be compared simultaneously under identical reaction conditions. Hence, direct comparisons were made between two different weights of catalyst as well as between two different particle sizes.

The disproportionation of propylene on cobalt molybdate–alumina catalyst at 150°C is shown in Fig. 1 where conversion is plotted against catalyst weight/flow rate (W/F) for two different weights of catalyst. The fact that the data from the two