

temperatures physical adsorption on the support becomes significant and at high temperatures volatile metal carbonyls are formed. There are, however, many hydrogenation reactions which can be conveniently studied at room temperature and the technique described should be directly applicable to such systems. The value of the technique is not, however, limited to hydrogenation reactions and it would appear that with a judicious choice of adsorbate and reaction conditions the technique should be valuable for studying a great variety of different catalytic reactions.

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Catalytic Oxidation over Molecular Sieves Ion-Exchanged with Transition Metal Ions

II. Selective Oxidation of Propylene over Cu(II)-Y in the Presence of Steam

In a previous paper (1), it was reported that Y-molecular sieve ion-exchanged with cupric ions [Cu(II)-Y] had a very high catalytic activity for deep (i.e., total) oxidation of propylene. In addition, some ion-exchanged molecular sieves are reportedly highly active solid acid catalysts for various acid-catalyzed reactions (2). These two characteristics have suggested to us that a molecular sieve might be developed as a bifunctional catalyst which is acidic and oxidative at the same time. Recently, Ohki and Ozaki (3) and Ogasawara *et al.* (4) reported a ketone synthesis using some binary catalysts containing molybdena. This reaction was thought to proceed via

a hydration of olefin followed by an oxidation of alcohol formed. In the present work, selective oxidation of propylene over Cu(II)-Y catalyst has been tried in the presence of steam, and some results are reported.

EXPERIMENTAL METHODS

The Cu(II)-Y molecular sieve used was described in a previous paper (1). The oxidation reaction was studied by an ordinary flow method, with a fixed catalyst bed diluted by carborundum. Composition of the feed and reacted gases were analyzed with gas chromatography using a Porapak Q column (Water Associated Inc.) for car-

TABLE 1
 PROPYLENE OXIDATION ON Cu(II)-Y

Temp ^a (°C)	W ^b (g)	F ^c (ml/min)	Feed gas composition (vol %)				Yield (%)		
			C ₂ H ₆	O ₂	H ₂ O	N ₂	Carbon dioxide	Acrolein	Isopropanol
200	0.9611	135.3	22.5	37.0	34.0	6.5	1.11	0.52	0.58
250	0.3138	221.4	18.1	28.0	45.2	8.7	19.5	6.32	—
280	0.5643	157.0	22.0	36.4	29.3	12.3	23.0	6.67	—
300	0.5761	157.0	22.0	36.4	29.3	12.3	21.9	7.20	—
320	0.6575	232.0	17.3	26.8	47.4	8.5	24.7	6.12	—
310	0.0792	288.0	17.4	17.4	—	65.2	0.83	—	—
310	0.0759	300.0	3.0	50.0	—	47.0	3.9	—	—

^a Reaction temperature.

^b Catalyst weight.

^c Feed rate.

bon dioxide and propylene, and a PEG (Japan Chromato) column for isopropanol and acrolein. Isopropanol and acrolein were further identified by IR and mass-spectrometer analysis of samples trapped after a gas chromatographic analysis.

RESULTS AND DISCUSSION

Results on Cu(II)-Y are summarized in Table 1, where yields were calculated by the following way:

$$\text{Yield for acrolein} = \frac{\text{acrolein formed}}{\text{propylene fed}}$$

$$\text{Yield for isopropanol} = \frac{\text{isopropanol formed}}{\text{propylene fed}}$$

$$\text{Yield for carbon dioxide} = \frac{1/3 \text{ carbon dioxide formed}}{\text{propylene fed}}$$

Although copper supported on silica gel gave reportedly acrolein as an oxidation product (5), it is generally stated that an increase in surface area is accompanied by a decrease in specificity, and that supports with a pore structure are unfavorable for selective oxidation (6). However, although it has a well-developed pore structure, Cu(II)-Y in the presence of steam shows a considerable formation of acrolein, even at a relatively high conversion (Table 1). It is true that the selectivity of this catalyst cannot be commended in comparison to catalysts reported in the literature, but its activity was 10 to 100 times larger (7, 8).

It may be noted that the presence of steam was necessary for the selective oxidation of propylene. The effect of the addition of steam to the feed gas has been extensively studied by Russian researchers (9), who concluded that steam suppressed the deep oxidation only at high content and increased the selectivity of acrolein formation. In the absence of steam, the feed gas must be of a high propylene/oxygen ratio to achieve selective oxidation on Cu(II)-Y. [For a ratio of 7, the selectivity of acrolein was 50% at 4.5% conversion (10)].

The Cu(II)-Y after the reaction was dark brown, but turned light blue when heated in the air. This fact means that the catalyst is still Cu(II)-Y during the reaction. If it had been reduced, black cupric oxide would have been formed on the catalyst on reoxidation. Cuprous oxide has been regarded as an active species for acrolein synthesis (6). It is interesting that the selective oxidation took place to a considerable extent on cupric ion of the molecular sieve in the presence of steam.

Another point to be mentioned is a considerable yield of isopropanol at the lowest reaction temperature (200°C). This formation may be due to the acidity of Cu(II)-Y and suggests the possibility of the acetone formation initially intended. Ozaki *et al.* (3) and Buiten (11) have shown a similar hydration reaction to occur over molybdenum oxide catalysts.

TABLE 2
 PROPYLENE OXIDATION ON Ag(I)-Y AND Ni(II)-Y

Temp ^a (°C)	W ^b (g)	F ^c (ml/min)	Feed gas composition (vol %)				Yield (%)		
			C ₃ H ₆	O ₂	H ₂ O	N ₂	Carbon dioxide	Acrolein	
300	0.5132	228.0	19.0	28.4	43.7	8.9	20.1	2.67	Ag(I)-Y
300	0.9155	221.4	18.1	28.0	45.3	8.7	2.1	—	Ni(II)-Y

^{abc} See Table 1.

Silver and nickel ions were also tried as other transition metal ions. The results are shown in Table 2. Ag(I)-Y formed a small but distinct amount of acrolein although only deep oxidation proceeded on Ni(II)-Y. A volcano-type correlation between catalytic activity for propylene oxidation and the heat of formation of oxide per unit oxygen atom was found for the Y-molecular sieve ion-exchanged with transition metal ions, where platinum and palladium ions were most active (10), in the same manner as indicated for oxide catalysts (12). Based on this correlation, it may be of value to investigate the ions near to cupric ion, namely Pt, Pd, Hg, and Tl. We conclude that improvement of the selectivity with maintenance of high activity can be expected for catalysts based on the Y molecular sieve by the appropriate selection of the feed gas composition and the reaction temperature.

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