

The Catalytic Properties of Zeolite X Containing Transition Metal Ions

III. Propylene Oxidation

S. J. GENTRY, R. RUDHAM, AND M. K. SANDERS

*Chemistry Department, University of Nottingham,
Nottingham, NG7 2RD, England*

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The catalytic activity of X zeolites for the oxidation of 4.5% propylene in air in a flow system was enhanced by the exchange of ~20% of the sodium ions for transition metal ions. The major oxidation products were CO₂ and H₂O; small quantities of acrolein, acetaldehyde, and formaldehyde were also detected. An activity series at 630 K showed that activity depended upon the acidity of the zeolite and the nature of the transition metal ion.

The reaction was subsequently studied, using 2.3% propylene in air, on 22 catalysts in which controlled variations in the acidity and the extent of replacement of Na⁺ by Cu²⁺ had been made. First-order kinetics with respect to propylene were obeyed, and over the temperature range of the experiments, 434-623 K, the products were confined to CO₂ and H₂O. The dependence of the activity at 500 K upon copper ion content and Brønsted acidity emphasizes the importance of the combination of these two factors in determining catalytic activity.

INTRODUCTION

The oxidation of propylene on copper-exchanged Y zeolites has been studied by Mochida *et al.* (1-3). The major products were carbon dioxide and water, with minor yields of formaldehyde and traces of acrolein and acetaldehyde (1). The addition of steam was found to increase the selectivity for acrolein formation, although it reduced the overall activity (2). Limited hydration of the propylene to isopropanol also occurred at low reaction temperatures, and this was attributed to the acidity of the catalyst (2). A comparison of the results obtained on a series of ion-exchanged Y zeolites showed that the overall activity, and the order of reaction with respect to propylene, varied considerably with the exchange ion (3). A correlation was found between the activity and the ability of the ion to form a dative π -bond, the so called Y factor (4). It was suggested that as the Y factor increased the propylene was more

strongly adsorbed, resulting in the observed decrease in reaction order.

The only known investigation of propylene oxidation on X zeolites (5) showed that the replacement of sodium or calcium by iron increased the overall activity, and that the reaction was first order in propylene. The present contribution reports an investigation of propylene oxidation on X zeolites containing transition metal ions. The results indicate the importance of the acidity of the catalysts, and the effects of variations in the acidity and extent of replacement of sodium by copper have been investigated in detail.

EXPERIMENTAL

Catalysts

Preliminary experiments were made with samples of the identical catalysts used to study N₂O decomposition (6) and CH₄ oxidation (7). These had previously been

prepared from 13X molecular sieve (Lot 2892700) by a technique which ensured that the ions were incorporated in the sieve structure without change of valence (6). The majority of the experiments were confined to X zeolites in which the acidity and cupric ion content were varied, and these were prepared by the same technique from 13X molecular sieve (Lot 0003940). Variations in the acidity were made either by controlled treatment at $\text{pH} > 6$ with dilute HCl, or by exchange with NH_4^+ and subsequent deammoniation at 623 K. To obtain acidities less than that necessarily introduced by pH reduction prior to Cu^{2+} exchange (6), the zeolites were subsequently back exchanged with concentrated aqueous NaCl, washed, dried, and exchanged with the appropriate quantity of NH_4^+ . Specific spot tests of filtrates showed that (i) no aluminum had been extracted from the zeolites during acidification and ion exchange (ii) no Cu^{2+} was extracted during back exchange and reacidification. X-ray diffraction showed no evidence of structural breakdown during either catalyst preparation or propylene oxidation.

To express the compositions of the present catalysts, we have modified the nomenclature previously used (6, 7). The catalysts are designated X/M(*a*)H(*b*)- NH_4 (*c*), where *a*, *b*, and *c* are the percentages of Na^+ exchanged for transition metal ion M, protons, and ammonium ions, respectively. Where no exchange has been made the appropriate exchange ion is deleted.

Apparatus

The oxidation of propylene in air was followed in a stainless-steel flow system operating at atmospheric pressure. In experiments using zeolites containing a range of transition metal ions the reaction vessel and analysis system were identical to those used in CH_4 oxidation (7), although the chromatographic column was maintained at a higher temperature (363 K). This analysis was insufficiently sensitive to detect trace amounts of partial oxidation products, and in a number of experiments it was replaced by a Pye-Unicam Series

104 Flame Ionisation Gas Chromatograph. A 1.5-m column of polyethylene glycol adipate at 323 K, using a nitrogen carrier gas flow of 40 ml min^{-1} , gave a good separation of propylene and the small yields of formaldehyde, acetaldehyde, and acrolein.

In subsequent experiments with zeolites of varying acidity and Cu^{2+} content, the stainless-steel reactor was replaced by a glass reactor of smaller volume, a new reactor being used for each catalyst studied. Catalyst beds were formed by supporting 1 g of zeolite on a No. 2 porosity glass sinter fused across the body of the reactor, and a thin glass well permitted temperatures at the center of the bed to be measured using a chromel-alumel thermocouple. A Servomex SV234 gas-sampling valve was used, such that samples were taken alternately from the reactant and product streams at 3-min intervals until reproducible analyses were achieved under constant reaction conditions.

Experiments showed that both the stainless-steel and glass reactors possessed negligible catalytic activity over the temperature range of the experiments.

Gases

The propylene used was Air Products CP grade, and the nitrogen used in catalyst pretreatment was Air Products high-purity grade. Air for oxidation studies was obtained from a Charles Allen Capex 2 compressor after passage through a gas-mask canister. No impurities in the propylene, nitrogen, and air could be detected by gas chromatography.

RESULTS

Preliminary experiments were made using the same 2-g samples that had previously been used for CH_4 oxidation (7). To remove any residues that might affect the activity, the catalysts were pretreated at 773 K in flowing air for 20 min and then in flowing nitrogen for the same time. The reactant mixture consisted of a 200 ml min^{-1} flow of 4.5% propylene in air. The major oxidation products were CO_2 and H_2O ; formaldehyde, acetaldehyde, and

acrolein were also detected, but at no reaction temperature did the combined yields of partial oxidation products correspond to more than 3% of the propylene oxidized. Since the peak height for propylene on the chart recorder, using the katharometer detector, was directly proportional to the partial pressure of propylene in the gas sample, the degree of oxidation x was readily calculated from the peak heights given by samples from the reactant and product streams. Catalytic activities were reproducible over rising and falling temperature sequences, and an activity series based on the activity at a fixed temperature can be obtained using interpolated values from plots of x against reaction temperature. The activity series obtained at 630 K is given in Table 1. Selection of any other temperature at which x for every catalyst can be determined accurately gives essentially the same series, with only the relative positions of X/Zn(19)H(22), X/Ni(19)H(22), and X/Mn(19)H(22) susceptible to change. It is evident that all the transition metal ions increase the activity of X zeolite to levels above that of X/H(22). The incorporation of Pd²⁺ and Cu²⁺ yields highly active catalysts, which is in agreement with the findings of Mochida *et al.* (3) for propylene oxidation on Y zeolite. Unlike the activity series obtained for the identical catalysts in N₂O decomposition (6) and CH₄ oxidation (7), the activities of X/H(22) and X/H(22)NH₄(19) are dissimilar, indicating the possible importance of the acidity of the zeolites in the present reaction.

The oxidation of propylene was then studied on 22 catalysts in which controlled variations in the acidity and extent of replacement of Na⁺ by Cu²⁺ had been made.

Prior to catalytic measurements, 1-g samples of the zeolites were dehydrated and deammoniated by heating at 623 K in a 10 ml min⁻¹ flow of pure nitrogen for 16 hr. The normal reactant stream consisted of a 50 ml min⁻¹ flow of 2.33% propylene in air. This reactant mixture was chosen so that the reaction could be studied at temperatures not exceeding 623 K, using a single cylinder of propylene for all experiments. Over the temperature range of the experiments, 434–623 K, the reaction products were confined to H₂O and CO₂. Since the response of the flame ionization detector was not linearly dependent on the partial pressure of propylene in the gas sample, degrees of oxidation x were computed from a polynomial equation, which had been obtained from an experimental calibration using the method of least squares.

The effect of temperature on the activity of each catalyst was determined over the range $x = 0.02$ – 0.40 , measurements being made at an average of 12 temperatures in random sequence. After the first measurement with any one catalyst, stable and reproducible activities were rapidly achieved on changing the reaction temperature in either direction. The kinetic order with respect to propylene n was determined for five representative catalysts (catalysts 6, 10, 11, 15, and 21 in Table 2) at temperatures where x remained small. For small values of x at a constant total flow rate, the slope of a plot of $\log x$ against $\log p$ is equal to $n - 1$, where p is the partial pressure of propylene in the reactant mixture. Measurements made in this way at values of p between 6×10^{-3} and 6×10^{-2} atm gave a mean value of n for the five catalysts of 1.1. The kinetic order

TABLE 1
THE ACTIVITY SERIES FOR PROPYLENE OXIDATION^a

X/Pd(17)H(22)NH ₄ (19)—0.89 > X/Cu(19)H(22)—0.34 >
X/Co(18)H(22)—0.22 > X/Zn(19)H(22)—0.18 >
X/Ni(19)H(22)—0.17 > X/Mn(19)H(22)—0.16 >
X/Cr(19)H(22)—0.13 = X/H(22)NH ₄ (19)—0.13 >
X/Fe(19)H(22)—0.10 > X/H(22)—0.04

^a Based on the degree of oxidation at 630 K, which is given for each catalyst.

TABLE 2
ARRHENIUS PARAMETERS AND RATE CONSTANTS AT 500 K

No.	Catalyst Composition	E_{app} (kJ mole ⁻¹)	$\log_{10}k_1^0$	$\log_{10}k_1$ at 500 K
			(k_1^0 in molecules g ⁻¹ sec ⁻¹ atm ⁻¹)	(k_1 in molecules g ⁻¹ sec ⁻¹ atm ⁻¹)
1	X/unexchanged	77	24.58	16.53
2	X/Cu(2)H(20)	68	25.13	18.03
3	X/Cu(5)H(20)	87	27.11	18.02
4	X/Cu(10)H(20)	80	26.76	18.40
5	X/Cu(15)H(20)	78	26.65	18.50
6	X/Cu(20)H(20)	76	26.55	18.62
7	X/Cu(30)H(20)	94	28.93	19.11
8	X/Cu(41)H(20)	97	29.32	19.18
9	X/Cu(50)H(20)	114	31.27	19.37
10	X/H(20)	71	24.98	17.57
11	X/Cu(20)	76	26.24	18.30
12	X/Cu(20)NH ₄ (6.4)	83	27.15	18.48
13	X/Cu(20)NH ₄ (9.4)	78	26.72	18.57
14	X/Cu(20)NH ₄ (13.4)	82	27.34	18.77
15	X/Cu(20)NH ₄ (23.4)	88	28.02	18.83
16	X/Cu(20)H(30)	77	26.97	18.93
17	X/Cu(20)H(45)	98	29.29	19.05
18	X/NH ₄ (8.6)	63	24.11	17.53
19	X/NH ₄ (13.6)	57	23.60	17.64
20	X/NH ₄ (20.3)	61	24.22	17.85
21	X/NH ₄ (23.4)	57	23.82	17.87
22	X/NH ₄ (28.4)	63	24.39	17.81

can thus be taken as unity, and the first-order rate constants are given by

$$k_1 = \frac{f}{mp} \left[(1 + 0.5y) \ln \left(\frac{1}{1-x} \right) - 0.5yx \right]$$

(molecules g⁻¹ sec⁻¹ atm⁻¹),

where f is the feed rate of propylene in molecules sec⁻¹, m the mass of catalyst, and y the fraction of the reactant mixture, which is propylene. Linear plots of $\log k_1$ against $1/T$ were obtained for all catalysts, showing that the Arrhenius equation $k_1 = k_1^0 \exp(-E_{app}/RT)$ adequately describes the effect of temperature on catalytic activity. Values of the apparent activation energy E_{app} , logarithmic values of the pre-exponential factor k_1^0 , and k_1 at 500 K are given in Table 2.

Since the data recorded in Table 2 show that the catalytic activity is increased by increasing the acidity of the zeolites, the effect of introducing pyridine vapor into the reactant mixture was investigated. Three catalysts were pretreated at 623 K

as above and the catalytic activity determined at a convenient temperature. A small side tube containing pyridine at 295 K was then attached to the flow system, and after 2 hr the activities were determined at the same temperatures. The results given in Table 3 show that pyridine is an effective poison.

DISCUSSION

The results presented in Table 2 may be considered as three series of experiments on the effect of the degree of exchange of

TABLE 3
THE EFFECTS OF TREATMENT WITH PYRIDINE

Catalyst	Tem- pera- ture (K)	Degree of oxidation	
		Before pyridine	After pyridine
X/Cu(20)	495	0.087	0.034
X/Cu(20)NH ₄ (23.4)	462	0.047	0.000
X/NH ₄ (28.4)	526	0.067	0.000

sodium on the activity of X zeolite for the complete oxidation of propylene to carbon dioxide and water.

Series 1. Catalysts 2–10 represented by $X/Cu(n)H(20)$, studied to determine the effect of cupric ion concentration on the activity of zeolite of constant acidity.

Series 2. Catalysts 6, 11–17 represented by $X/Cu(20)H(n)$ or $X/Cu(20)NH_4(n)$, studied to determine the effect of acidity on the activity of zeolite of constant cupric ion concentration.

Series 3. Catalysts 1, 18–22 represented by $X/NH_4(n)$, studied to determine the effect of acidity on the activity of zeolite free from cupric ions. The influence of varying concentration in these series of experiments is shown in Fig. 1, where k_1 at 500 K is plotted against the percentage exchange of sodium ions by the species in question. The much greater slopes of the plots for series 1 and 2 compared with that for series 3 show that for significant

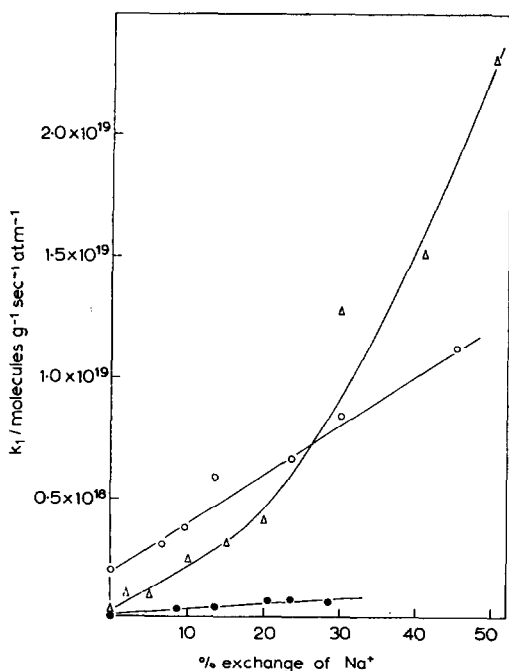


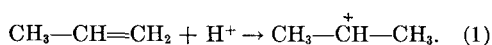
Fig. 1. The first-order rate constant at 500 K as a function of the extent of sodium ion exchange: (Δ) series 1 catalysts, $X/Cu(n)H(20)$; (\circ) series 2 catalysts, $X/Cu(20)H(n)$ or $X/Cu(20)NH_4(n)$; (\bullet) series 3 catalysts, $X/NH_4(n)$.

enhancement of catalytic activity both acidity and cupric ions are necessary. These results thus confirm the indications given by the activity series drawn from our preliminary experiments.

Ammonium ions in zeolites have been shown to decompose at temperatures above 523 K, liberating ammonia and leaving a proton in association with lattice oxygen (8, 9). The hydrogen–oxygen bond remains polarized and the group behaves as a Brønsted acid. Infrared studies have shown that significant dehydroxylation begins above 773 K with Y zeolites (10, 11) and at considerably lower temperatures with X zeolites (9, 12, 13). Pyridine is strongly adsorbed on Brønsted acid sites in zeolites to form pyridinium ions (10–13). The pretreatment temperature presently employed was selected to minimize dehydroxylation, while ensuring that all the ammonium ions had been decomposed. The catalysts studied, with the possible exception of unexchanged X zeolite, thus contain Brønsted acid sites, and the poisoning effect of pyridine is evidence for their involvement in the oxidation of propylene. Pyridine may also act as a poison for $X/Cu(20)$ and $X/Cu(20)NH_4(23.4)$ by interacting with cupric ions in the zeolite supercages (14, 15). It is suggested that propylene is adsorbed at Brønsted acid sites as a secondary carbonium ion and is subsequently attacked by oxygen, which is activated by copper ions in close proximity. The initial activity of catalysts in series 3 is most probably due to the presence of cationic impurities capable of activating oxygen. Their low concentration is reflected in the insensitivity of the activity to subsequent increases in acidity. The relatively high activity of $X/Cu(20)$ compared with that of $X/NH_4(20.3)$ is unexpected if a dual-site mechanism is operative and the back-exchange technique wholly eliminates protons. However, it has been proposed (16) that polyvalent cations may be hydrolyzed, producing a proton and a hydroxyl group bound to the cation. Thus if a fraction of the cupric ions are hydrolyzed, protons will be generated and dual sites established. The high activity of $X/Cu(20)$ -

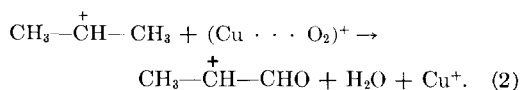
NH₄(13.4) compared with that of X/Cu-(20)H(20) shows that protons introduced by ammonium ion decomposition are more active than those introduced by acid washing. We attribute this to different distributions of the protons between accessible and inaccessible sites, since the activity for isopropanol dehydration on deammoniated X zeolites was consistently greater than that on X zeolites where nominally equivalent acidities had been introduced by acid washing (17).

The failure to observe the partial oxidation products found in the preliminary experiments results from greater contact times in the subsequent experiments. Nevertheless, such products must be closely related to intermediates in complete oxidation, and any mechanism proposed should account for both their formation and subsequent oxidation. Valuable information on the mechanism of propylene oxidation on bulk oxides results from the study of the reactions of partial oxidation products (18), and similar studies are necessary before a full mechanism can be proposed for complete oxidation on zeolites. Since propylene cannot enter the sodalite units, the present results suggest that it is initially adsorbed as a secondary carbonium ion at a Brønsted acid site in the supercage:



The Brønsted acid sites are acidic OH groups originating from proton and ammonium ion exchange, protons generated in the hydrolysis of Cu²⁺ (16), or possibly protons generated in the reduction of Cu²⁺ to Cu⁺ by propylene (15, 19). Since series 2 catalysts are more active than series 3 catalysts, carbonium ion attack by oxygen activated by neighboring Cu⁺ ions is more likely than direct attack by molecular oxygen, the necessary Cu⁺ ions being generated by the reduction of Cu²⁺ in II or II' sites by propylene or, once reaction was under way, by its partial oxidation products. Since the preferred location of Cu²⁺ in X and Y zeolites is at I and I' sites (14, 15), it is probable that only a relatively small

proportion of the total Cu²⁺ content is active in catalysis. The oxidation of the carbonium ion produced in Eq. (1) might lead to a second carbonium ion, water, and release of the Cu⁺ ion:



The subsequent loss of a proton would regenerate the Brønsted acid site and yield acrolein, the least heavily oxidized product in the preliminary experiments:



Further oxidation products, ultimately leading to CO₂ and H₂O, would result from the oxidation of acrolein or the oxidative fission of carbon-carbon bonds in either of the carbonium ions formed in Eqs. (1) and (2).

The mechanism suggested above is necessarily speculative and differs from that proposed by Mochida *et al.* (3) for propylene oxidation on Y zeolites containing transition metal ions. Nevertheless, it takes into account the observed dependence of activity upon both acidity and copper ion content in such a way that the "active centers" are regenerated following the initial reaction steps. The implicit assumption that partial oxidation products are more reactive than propylene itself requires experimental investigation before further advances can be made.

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