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The Catalytic Properties of Zeolite X Containing Transition Metal Ions

Part 2—Methane Oxidation

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The oxidation of methane catalyzed by 13X molecular sieves, in which ~20% of the Na^+ had been replaced by transition metal ion, has been investigated in a flow system with reaction temperatures between 253 and 563°C. The oxidation products were solely carbon dioxide and water. The kinetics are best described as first order in methane and zero order in oxygen, and apparent activation energies and pre-exponential factors have been calculated on this basis. An activity series, based on the temperatures necessary to maintain constant catalytic activity, shows a correlation between activity and the normal coordination adopted by the transition metal ions. This is believed to arise from the overall catalytic activity being determined more by the accessibility of the cations to reactants than by their individual intrinsic activities.

INTRODUCTION

Few studies have been made of molecular sieves containing transition metal ions as catalysts for oxidation reactions, and only one kinetic investigation of methane oxidation has been reported (*1*). It was found that 13X molecular sieves in which less than 1% of the sodium ions were exchanged for rhodium, palladium, iridium, and platinum ions were active catalysts for the complete oxidation to carbon dioxide and water. The activation energies showed that the rate-determining step was the same for each catalyst, which was suggested to be the formation of an adsorbed water molecule from a methane fragment and a hydroxyl group attached to the same transition metal ion.

For complete oxidation of methane on bulk oxides of the first transition series (*2*), catalytic activity can be correlated with that for the homomolecular exchange of oxygen (*3*). Further experiments show that this arises from the strength of the bond between the catalyst surface and adsorbed oxygen, in that there is a correlation between this and the activation energy for methane oxidation (*4*). Distinct differences in both the activation energies and the activity series exist between reaction on the bulk oxides (*2*) and on the corresponding oxides supported on high area γ-alumina (*5*).

The present paper describes a study of methane oxidation on 13X molecular sieves in which ~20% of the sodium ions were replaced by transition metal ions. The catalysts were identical to those used in an earlier study of nitrous oxide decomposition (*6*), where the activity series was similar to that obtained on the corresponding bulk oxides.

EXPERIMENTAL

Catalysts

The method of preparation of the catalysts has been fully described, and it has been shown that the transition metal ions are incorporated within the sieve structure without change of valence (*6*). The catalysts are designated by 13X/M(*n*), where

M represents the transition metal ion and *n* the percentage of sodium exchanged. Since the method of preparation also replaces sodium ions with protons, two catalysts containing protons but no transition metal ion, were prepared. The extent of sodium ion exchange in these corresponded with that in the catalysts containing transition metal ion, 22% in all cases other than the catalyst containing palladium, where ion exchange using ammonium chlorpalladite gave a final proton content of 41%. These catalysts are designated by 13X/H(41) and 13X/H(22), respectively. The unexchanged sieve which was only washed with distilled water before use is designated 13X/UE.

Samples of 13X/Cu(19) and 13X/Pd(17) were treated at 510°C with a stream of air saturated with hexamethyldisiloxane at room temperature. Such treatment produces a layer of silica which poisons catalytic activity associated with the surface without affecting the activity within the sieve structure (*6*,*7*), and the samples are designated 13X/Cu(19)*P* and 13X/Pd(17)*P*, respectively.

Apparatus

The oxidation of methane in mixtures of oxygen and nitrogen was followed in a stainless steel flow system operating at atmospheric pressure. In all cases the oxygen content was in excess of that required for complete oxidation of the methane. Gas samples, for analysis by gas chromatography, were regularly taken from the reactant and product streams by an automatic gas-sampling valve. A column of Poropak Q at 25°C, 1.8 m in length and 3.5 mm in diameter, with helium carrier gas flowing at 40 ml min^{-1}, gave a good separation of "air," methane, and oxidation products, which were restricted to carbon dioxide and water. Detection was by means of a Gow–Mac katharometer, bridge network, and chart recorder. The sampling valve was operated by two Crouzet–Valence process timers, such that samples were taken every 5 min until reproducible analyses were achieved at constant reaction conditions.

Catalyst beds were formed by lightly compressing 2 g of catalyst between silica wool pads in a 19-mm bore tubular reactor. A chromel–alumel thermocouple, sheathed in a thin wall stainless steel tube, was embedded in the center of the catalyst bed. Experiments showed that the reactor, thermocouple, and silica wool pads possessed negligible catalytic activity over the temperature range of the experiments. Due to the exothermicity of methane oxidation, limited self-heating occurred with most catalysts during reaction, with a rise of 1°C for an oxidation rate of 3.9×10^{16} molecules g^{-1} sec^{-1}. The recorded temperatures are the highest reached under constant reaction conditions. Prior to oxidation experiments the catalysts were dehydrated *in situ* for 18 hr at 555°C in a stream (10 ml min^{-1}) of high purity nitrogen which had been further dried by passage through a bed of activated 5A molecular sieve.

Gases

A cylinder of ~3% methane in pure nitrogen was used as the source of methane to eliminate risk of explosion, and mass spectrometry showed the mixture to contain 3.81% CH_4, 400 ppm CO_2, traces of other hydrocarbons, and the balance nitrogen. Cylinder helium, nitrogen, and oxygen were of the purest grade available.

RESULTS

The activity for the oxidation of methane was determined as a function of temperature with the 13 catalysts shown in the table, using a gas flow-rate of 60 ml min^{-1} at 25°C (50 ml min^{-1} of 3.81% CH_4 in N_2 plus 10 ml min^{-1} of O_2). Gas chromatographic analysis of normal product streams, or mass spectrometric analysis of products condensed at −195°C for prolonged periods, gave no indication of oxidation products other than carbon dioxide and water. Since the peak height for methane on the chart recorder was directly proportional to the partial pressure of methane in the gas sample, the degree of oxidation x was readily calculated from the methane peak heights given by samples from the reactant and product streams. Stable and reproducible catalytic activities were rapidly achieved, either after the initial dehydration, or after changing the reaction temperature in either direction. An exception to this occurred with the least active catalyst, 13X/Zn(19), which tended to give irreproducible results. X-ray powder diffraction of the catalysts after use showed no evidence of structural breakdown.

Since the same reactant flow rate and mass of catalyst were used in all experiments, the activity for methane oxidation can be constructed from the temperatures necessary to maintain a fixed, but preferably small, degree of oxidation. Temperatures for $x = 0.05$, determined by interpolation from the smooth plots of x against reaction temperature, yield the following activity series:

$$\begin{array}{llllll} \text{13X/Pd(17)} > & \text{13X/Pd(17)}P \gg & \text{13X/Cu(19)} > & \text{13X/Cu(19)}P > & & \\ \text{13X/Cr(19)} > & \text{13X/Ni(19)} > & \text{13X/Fe(19)} \simeq & \text{13X/Mn(19)} > & & \\ \text{13X/Co(18)} = & \text{13X/H(22)} \simeq & \text{13X/H(41)} > & \text{13X/UE} > & \text{13X/Zn(19)}. & \end{array}$$

Selection of any other small x value gives essentially the same series, with only the positions of 13X/Fe(19) and 13X/Mn(19) susceptible to reversal.

The kinetic order of the reaction was determined by a method similar to that proposed by Houghton (*8*). Since in the reaction $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ the number of moles of products equals the number of moles of reactants consumed, the rate constant k_n for a kinetic order n is given by:

$$k_n = \frac{f}{mp^n}\int_0^x \frac{dx}{(1-x)^n},$$

where f is the flow rate of methane, p the partial pressure of methane in the reactant mixture, m the mass of catalyst and x the degree of oxidation. The value of n is that for which the appropriate rate constants give the best straight line in an Arrhenius plot. This method, which is only accurate over an extended range of values of x, is restricted to the most active catalysts 13X/Pd(17), 13X/Pd(17)P, 13X/Cu(19), and 13X/Cu(19)P.

For 13X/Cu(19) and 13X/Cu(19)P, where x did not exceed 0.59, the straightest Arrhenius plots were obtained from rate constants based on $n = 1$ among the values $n = 0.0$, 0.5, 1.0, and 1.5. For 13X/Pd(17) and 13X/Pd(17)P, where x was as high as 0.98, no value of n resulted in linear Arrhenius plots over the complete range of values of x. Arrhenius plots from first order rate constants possessed two distinct linear portions, with the slope at high temperatures being approximately half that at low temperatures and with the break occurring at a value of k_1 corresponding to $x = 0.62$–0.65. We attribute the break in the Arrhenius plots to the onset of diffusion-controlled reaction, which is absent over the range of experimental measurements for 13X/Cu(19), 13X/Cu(19)P, and the other less active catalysts. Arrhenius plots of first-order rate constants for the remaining nine catalysts were found to be linear with the exception of 13X/Zn(19), where irreproducible activity did not permit a meaningful line to be drawn. Arrhenius plots for the four most active catalysts are

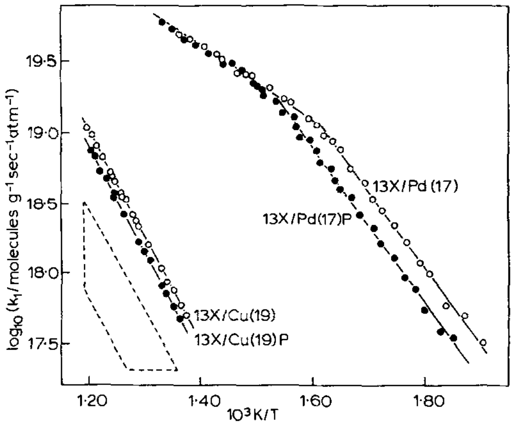

FIG. 1. Arrhenius plots of first-order rate constants for 13X/Cu(19), 13X/Cu(19)P, 13X/Pd(17), and 13X/Pd(17)P. Corresponding plots for the eight less active catalysts lie within the area bounded by ------.

shown in Fig. 1, whereas for the less active catalysts the similarity in their activities precludes individual plots although the range of experimental measurements is outlined. Values of the apparent activation energy E_{app} and the pre-exponential factor k_1^0 are given in Table 1. Hexamethyldisiloxane treatment of 13X/Cu(19) has little effect upon E_{app} and k_1^0 resulting in only a small increase in the temperature necessary to maintain $x = 0.05$. With 13X/Pd(17) the effects are more pronounced at low temperatures, although they are negligible at high temperatures where the reaction is believed to be diffusion-controlled. The results of these poisoning experiments indicate that reaction occurs within the sieve structure as for nitrous oxide decomposition (*6*), although there are some active sites on the external surface of 13X/Pd(17).

Any attempt to determine the individual kinetic orders of the two reactants by variation of their partial pressures in the reactant mixture necessitates the addition of an inert diluent if significant variation is to be achieved. This would result in an increase in the overall flow rate and a corresponding decrease in the residence time of the reactants within the volume of the catalyst bed. It follows that the findings of such experiments are not necessarily relevant to the overall first-order kinetics previously determined, but with 13X/Cu (19) and 13X/Pd(17) such experiments were made at two temperatures with a total flow rate of 210 ml min^{-1}. When the partial pressure of methane was kept constant, calculated first-order rate constants were effectively independent of the partial pressure of oxygen, so that the order with respect to oxygen was zero. When the partial pressure of oxygen was kept constant, calculated first-order rate constants increased slightly with the partial pressure of methane, which can be attributed to a kinetic order which is slightly less than one. It is most probable, therefore, that the overall kinetic order of unity determined from the Arrhenius plots arises solely from the order with respect to methane, and that the kinetics are best described by:

$$-dp_{CH_4}/dt = kp^1_{CH_4}p^0_{O_2}.$$

DISCUSSION

The activity series obtained for the oxidation of methane catalyzed by 13X molecular sieves containing transition metal ions differs from that obtained for the corresponding bulk oxides (*2*) and oxides

TABLE 1
METHANE OXIDATION ON MOLECULAR SIEVES

Catalyst	Experimental temperature range (°C)	Temperature for $x = 0.05$ (°C)	E_{app} (kcal mole^{-1})	$\log_{10} k_1^0$ (k_1^0 in molecules g^{-1} sec^{-1} atm^{-1})
13X/Cr(19)	463–564	503	32.8	27.03
13X/Mn(19)	483–558	513	22.4	24.03
13X/Fe(19)	493–558	512	30.9	26.41
13X/Co(18)	510–556	547	34.2	26.91
13X/Ni(19)	473–557	509	32.7	26.93
13X/Cu(19)	459–565	463	34.2	27.98
13X/Cu(19)*P*	458–558	468	34.0	27.85
13X/Zn(19)	530–563	~560	—[a]	—[a]
13X/Pd(17)	253–505	271	24.9 (11.4)[b]	27.84 (23.10)[b]
13X/Pd(17)*P*	272–480	283	25.4 (11.3)[b]	27.79 (23.05)[b]
13X/H(22)	499–559	547	34.2	26.91
13X/H(41)	504–557	548	34.0	26.85
13X/UE	514–560	552	34.0	26.79

[a] Data too scattered for meaningful values.

[b] High-temperature values.

supported on γ-alumina (*5*). This is to be expected, since the transition metal ions within the sieves are essentially isolated from each other with not more than eight such ions per unit cell if they are evenly distributed. Since the activities, activation energies and pre-exponential factors are closely similar for the three catalysts containing differing proton concentrations [13X/UE, 13X/H(22), and 13X/H(41)], the acidic properties of the catalysts are unimportant in methane oxidation. It follows that the activity series is not determined by protons generated by the hydrolysis of the transition metal ions (*9, 10*).

Although no simple correlation exists between catalytic activity and the electronic structure of the cations, there is a correlation between activity and the normal coordination assumed by the ions. The most active catalysts are sieves containing ions which prefer square planar or distorted octahedral coordination (Pd^{2+}, Cu^{2+}), followed by those containing ions which prefer octahedral coordination (Cr^{3+}, Ni^{2+}, Fe^{3+}, Mn^{2+}), and finally those containing ions which prefer tetrahedral coordination (Co^{2+}, Zn^{2+}) and which have no significant effect upon the activity of the sieves. Anomalies exist with Ni^{2+}, which frequently assumes square-planar coordination in addition to octahedral coordination, and with Co^{2+}, which assumes octahedral coordination in addition to tetrahedral coordination. However, these anomalies do not negate the correlation, since 13X/Ni(19) is the fourth most active catalyst, and 13X/Co(18) is more active than 13X/Zn(19). Since the coordination preferred by the cations will govern their location within the sieve structure, the activity series may be determined more by the accessibility of the ions to the reactants than by their individual intrinsic activities. If this is so, the migration of the cations in the presence of reactants and products (*11–13*) has to be considered, since this may change the concentration of accessible ions during reaction. The observation that the visual appearance of the catalysts after methane oxidation was identical with that of freshly outgassed material (*6*) is insufficient to exclude such an effect, since it is possible that only a small fraction of the ions are in accessible positions even in the most active catalysts. Such a view, which was advanced (*14*) to explain the low activity per transition metal ion in nitrous oxide decomposition (*6*), can be tested by measurements of the specific adsorption of carbon monoxide (*15, 16*). The observation that sieves with and without transition metal ions are equally poor adsorbents for carbon monoxide at 0°C after outgassing at 550°C (*17*) supports the concept of only a small fraction of the cations being effective in catalysis, although the adsorption measurements were not made, and indeed cannot be made, under conditions identical to those existing in catalytic experiments. However, since stable and reproducible activities were rapidly achieved after changes in the reaction conditions, any changes in the concentration of accessible ions are either rapid and reversible, or very slow within the time scale of the experiments. If such changes are rapid, the concentration of "active sites" will be a function of temperature, and will thus contribute to the apparent activation energy for oxidation.

Accepting the nomenclature for cation sites within the sieve structure suggested by Smith, Bennett, and Flanigen (*18*), it is probable that only ions located at site II within the sieve supercage are accessible to methane and therefore contribute to catalysis. Cations within the sodalite units at sites I′ and II′, or within the hexagonal prisms joining sodalite units at site I, are thus inaccessible, although they may constitute a source of active ions if they can migrate to site II. Presumably, ions which assume square planar coordination will be in greater concentration at sites II than those which assume octahedral coordination, which will be greater than those which assume tetrahedral coordination. Clearly the activity series for methane oxidation is not solely determined by the preferred coordination of the transition metal ions, since accessible ions must be capable of catalyzing reactions. In this connection it is relevant that the activity series for nitrous oxide decomposition with identical catalysts is markedly different (*6*), although 13X/Pd(17) and 13X/Cu(19) are the first and third most active catalysts, respectively.

The kinetics presently observed for methane oxidation are closely similar to those obtained by Firth and Holland (*1*) for 13X sieves containing ions from the second and third transition series, both exhibiting an order in methane which is higher than that found for bulk oxides (*2*). Although the apparent activation energies in the present work are higher than those of Firth and Holland (*1*), there is reasonable agreement between catalysts containing palladium (21.5 kcal mole^{-1} (*1*); 24.9 kcal mole^{-1} at low temperatures in the present work). Firth and Holland (*1*) calculated true activation energies for oxidation using theoretical values for the heats of dissociative adsorption of methane onto metal ions and adsorbed oxygen. Since the values obtained were closely similar, they suggested that the rate determining step did not involve bonds to the metal ions, but possibly involved the abstraction of a hydrogen atom from an adsorbed methane fragment. Where possible, we have calculated true activation energies by the same method, but since the values obtained showed a wider numerical spread than the apparent activation energies, we cannot support their thesis concerning the rate-determining step. Similarly, we cannot support the mechanism recently proposed by Cullis, Keene and Trimm (*19*) for methane oxidation on palladium catalysts, since we do not observe the necessary half-order kinetics. A full elucidation of the mechanism of reaction on the present catalysts must await precise measurements of the kinetic order of both reactants over the complete range of experimental temperatures and information on the concentration of accessible cations under the conditions of such experiments.

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