

## Binding state of propylene in relation to partial oxidation reaction

B VISWANATHAN, C V BHUVANA and M V C SASTRI  
Department of Chemistry, Indian Institute of Technology, Madras 600 036

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**Abstract.** The binding state of propylene responsible for partial oxidation reaction on cobalt molybdate catalyst has been identified to be the adsorbed state that is desorbable at the temperature of oxidation through TPD measurements. In addition, at low temperatures there is another weak reversible form of adsorption. The adsorbed state of the olefin responsible for complete oxidation and at times for partial oxidation could not be identified by TPD studies under some experimental conditions like high heating rates because of the simultaneous occurrence of the catalytic reaction through the participation of the lattice oxide ions.

**Keywords.** Propylene oxidation; molybdate catalyst; cobalt molybdate; temperature programmed desorption.

### 1. Introduction

Preferential adsorption and activation of propylene on oxide surfaces lead to the formation of selective oxidation products by the participation of lattice oxide ions (intrafacial catalysis) while surfaces capable of activating oxygen favour complete combustion reaction (Mamoru Ai 1977). On multifunctional catalyst surfaces total oxidation products are formed either by a consecutive or by a direct reaction route (Giordano *et al* 1977). From a series of adsorption measurements of olefins on typical bismuth molybdate catalysts and the analysis of the results through simple Langmuir isotherms it has been established (Matsuura and Schuit 1971, 1972) that there are two different types of surface sites leading to either

- (i) slow, strong, irreversible single site adsorption of the olefin with high heat of adsorption and low  $V_m$  value where  $V_m$  is the volume at saturation, or
- (ii) fast, weak, reversible dual site adsorption of the olefin with low heat of adsorption and greater  $V_m$  value.

Except for this indirect detection of the binding states of propylene on molybdate catalysts, attempts have not been made to elucidate the different forms of adsorption of propylene by desorption methods which are especially suitable for this purpose (Madey and Yates 1977). Secondly, the nature of the adsorbed state of the olefin leading to the partial oxidation reaction has not yet been established. The purpose of the present investigation is, therefore, to identify the nature of the binding state of propylene on a typical molybdate catalyst (namely  $\text{CoMoO}_4$ ) through Temperature Programmed Desorption (TPD) technique.

## 2. Experimental

Cobalt molybdate employed as the adsorbant was prepared by the method of coprecipitation (Smith 1962) and has been characterised by standard methods.

TPD curves, recorded in an unit similar to that described by Rasser (1977), have been obtained after adsorption at 30, 100, and 150°C using different heating rates of 2 to 10° per minute and nitrogen as the carrier gas. The desorbed phase was directly analysed by on-line gas chromatography.

## 3. Results and discussion

Typical TPD spectra obtained after adsorption at 100°C at different heating rates are shown in figure 1. Similar desorption spectra were obtained after adsorption at 30°C as well as at 150°C. The choice of the temperatures of adsorption was based on the consideration that there should be no catalytic oxidation activity at or near the temperatures of adsorption as these systems promote oxidation reaction even in the

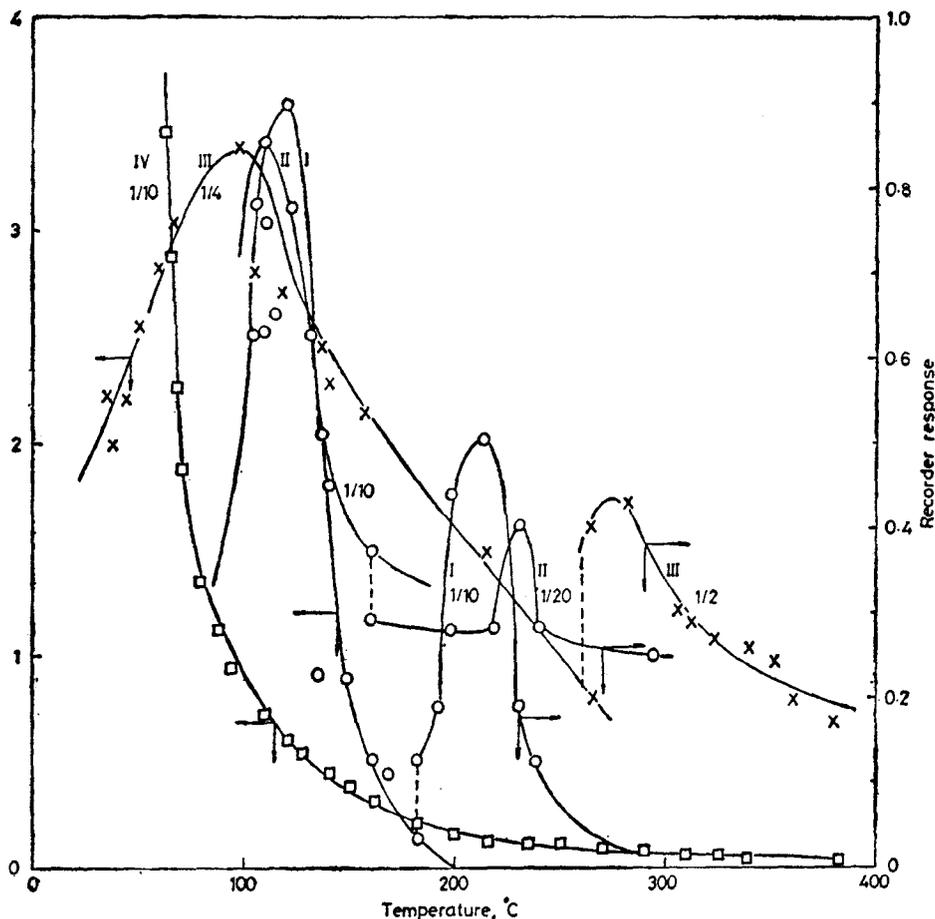


Figure 1. Propylene TPD spectra from cobalt molybdate-adsorption at 100°C.

Table 1. Summary of TPD results for the adsorption of propylene on cobalt molybdate.

Temperature of adsorption	Heating rate, (°C/min)	Peak 1 $T_M$ °C	Peak 2 $T_M$ °C
100	1.6	120	210
100	2.5	110	230
100	5	100	270
100	9	80	no peak
160	2.2	150	230

absence of gas phase oxygen through the participation of lattice oxide ions. The TPD spectra obtained after adsorption at 30, 100, 150°C showed that there are at least two binding states of propylene irrespective of the temperature of adsorption, in the range 30-150°C discernable by TPD and they are (i) weak reversible adsorption of propylene which is completely desorbed at the temperature of adsorption itself. (ii) Another reversible adsorption of propylene desorbable only above 200°C and the desorption temperature depends on the heating rate as well as on the temperature of adsorption. This deduction is based on the data presented in table 1.

If propylene is activated at the surface in two different modes one responsible for the partial oxidation reaction and the other for the total oxidation, (Ethirajulu *et al* 1977) then the former can be expected to desorb at a slightly higher temperature as the adsorbed symmetric allylic species ( $\pi$  or  $\sigma$  bonded) can interact with hydrogens present on the surface acidic sites or the hydroxyl groups formed by initial hydrogen abstraction and yield propylene in the gas phase. On the other hand, propylene adsorbed in the mode responsible for complete oxidation cannot desorb as such because of the high temperatures required at which the hydrocarbon can undergo reaction. This process is facilitated because of the considerable weakening of the C-C bonds as well as of the participation of lattice oxide ions in the reaction. On this basis, it can be concluded that the peak observed around 200°C can correspond to propylene adsorbed in the mode responsible for partial oxidation.

In this mode the propylene molecule might be bonded to the surface cations as a symmetric  $\pi$  allylic species or as a  $\sigma$  bonded species through the oxide ions. In this form, the molecule has not lost its identity and can desorb as acrolein with the participation of the lattice oxide ions. It is also probable that it can desorb as propylene by recombination with the hydrogen atoms abstracted in the initial stages of adsorption. If, on the other hand, the propylene molecule is adsorbed with considerable weakening and probably breaking of the C-C bond, then the molecule could only give rise to complete oxidation products and cannot yield back propylene in the gas phase. Therefore, it was not possible to identify the nature of the adsorbed state of propylene responsible for complete oxidation through TPD measurements.

The fact that the peak around 200° shifts to higher temperatures as the heating rate is increased and is not observable at still higher heating rates indicates that the desorption is an activated slow process and at higher heating rates the temperatures attained before any discernable desorption takes place, are high enough to promote the oxidation reaction itself and therefore only the products of the reaction were desorbed and detected. The observations that the activation energy for desorption is  $\sim 46$  kJ mol<sup>-1</sup> while for the reaction it is of the order of  $\sim 34$  kJ mol<sup>-1</sup> support this con-

clusion. This is in agreement with the absence of the second peak above 200°C at a heating rate of 9°C/min.

The following points emerge out of this investigation.

- (i) Propylene that is desorbed at the temperature of oxidation itself is alone responsible for partial oxidation reaction.
- (ii) The rate of desorption is (mostly) slower than the rate of oxidation.
- (iii) The simultaneous occurrence of the oxidation reaction often affects the elucidation of the nature of adsorption of propylene through TPD under certain experimental conditions (e.g. high heating rates).

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