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On the Nature of Acidic Centers in the Deep Oxidation of Olefins over $CdMoO_4$: Temperature-Programmed Desorption/Mass Spectrometer Investigation[1]

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INTRODUCTION

In a previous paper some of us reported on the role of surface acidic centers in the deep oxidation of 1-butene over a large series of molybdates including $CdMoO_4$ (*1*). Based on the different yields of carbon oxides and isomers measured at different reaction temperatures as well as in the presence and the absence of steam in the feed, the following reaction mechanism was proposed:

$$\begin{tikzcd}
\text{Brönsted sites} \arrow[r, shift left, "\text{increasing } T"] \arrow[d, shift left, "\text{1-butene}"] & \text{Lewis sites} \arrow[l, shift left, "\text{increasing } H_2O"] \arrow[r, "\text{1-butene} + O_2"] & \text{carbon oxides} \\
\text{2-butenes} \arrow[u, shift left]
\end{tikzcd}$$

The transformation of the Brönsted sites (responsible for low-temperature isomerization) into Lewis sites (responsible for the formation of carbon oxides) is supposed to occur at 300–350°C. In the case where the Brönsted sites are seen as surface hydroxyls the transformation is expected to originate from dehydroxylation of the catalyst surface and the Lewis sites can thus be seen as bridge lattice oxygen atoms or possibly anion vacancies.

In the present study the method of temperature-programmed desorption (TPD) was applied to further investigate the nature of the sites involved in the deep oxidation of the olefins over a poorly selective catalyst such as $CdMoO_4$. The analysis of the products during adsorption and desorption measurements was performed with an on-line mass spectrometer in order to secure high sensitivity in the identification of the species. This was required due to the low surface area of the catalyst ($\simeq 1$ m^2 g^{-1}).

EXPERIMENTAL METHODS

All experiments were carried out in a quartz reactor with He as the carrier gas ($F = 60$ cm^3 min^{-1}). He from the cylinder was passed through a Cu deoxo unit kept at 190°C and through molecular sieves cooled with liquid nitrogen to remove traces of oxygen and water, respectively. The temperature of the catalyst bed was raised at a uniform rate ($\beta = 30°C$ min^{-1}) by the use of a Perkin–Elmer programming controller.

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The temperature was measured by means of an iron–constantan thermocouple placed inside the catalyst bed. A quadrupole mass spectrometer (VG Micromass Q701B) was employed for analysis of the products of adsorption and desorption. The mass spectrometer was placed on line and very close to the reactor exit. Connections from the reactor exit up to the mass spectrometer were heated to prevent condensation of the products.

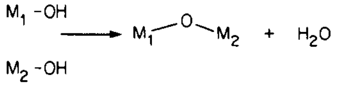
The preparation of $CdMoO_4$ is reported elsewhere (*2*). The catalyst was employed in form of granules (90–120 mesh) and pretreated *in situ* at 200°C in flowing He (F = 60 cm^3 min^{-1}) for 2 h to remove physisorbed water and then cooled under a flow of He down to room temperature. 1-Butene and propylene adsorptions were always carried out at room temperature. After adsorption the carrier gas was allowed to flow over the catalyst for 30 min, and the TPD experiments were then begun. In some cases the temperature of the pretreatment of the catalyst was 500°C but the TPD procedure was always the same.

A few experiments, performed by varying the flow rate of the carrier gas and the particle size of the catalyst, confirmed that either readsorption of the olefins or intraparticle limitations is negligible. Very pure Fluka propylene and Merck Shuschard 1-butene were used.

RESULTS AND DISCUSSION

Preliminary experiments were performed by heating $CdMoO_4$ up to 500°C under a flow of He. No release of oxygen was measured while a small but significant release of water was always detected at 300–350°C.

The absence of oxygen desorption indicates that the thermal treatment at 500°C does not result in the reduction of $CdMoO_4$. This has been confirmed by ESR analysis due to the absence of the signal at $g \simeq 2$ characteristic of Mo(V) sites (*3*) in the sample quenched down to room temperature under He. The release of water at 300–350°C, viz., in the same temperature range within which it is proposed that the transformation of Brönsted sites into Lewis sites occurs (*1*), gives direct evidence that the transformation does indeed consist of the dehydroxylation of the catalyst surface with final release of water. The process can be shown in shorthand form as



$$\begin{matrix} M_1\text{-OH} \\ \\ M_2\text{-OH} \end{matrix} \longrightarrow M_1{-}O{-}M_2 + H_2O$$

so that the Lewis sites can be likely seen as bridge oxygen atoms. The behavior of 1-butene and propylene desorption was then investigated.

The TPD spectra are shown in Fig. 1. Both olefins present a low-temperature desorption peak due to a weakly bound, reversibly adsorbed form (T_m = 100°C for 1-butene; T_m = 145°C for propylene) and a high-temperature desorption peak due to a strongly bound form which desorbs only with decomposition. For both olefins the high-temperature peak begins at 300–350°C, displays a maximum at ~400°C, and represents carbon dioxide, which was observed as the main decomposition product together with traces of water.

The spectra in Fig. 1 clearly indicate that 1-butene and propylene behave quite similarly and that two types of sites are present at the catalyst surface: (a) A-type sites on which reversible adsorption of the olefins occurs; and (b) B-type sites on which irreversible adsorption of the olefins takes place.

Similar spectra have been reported for

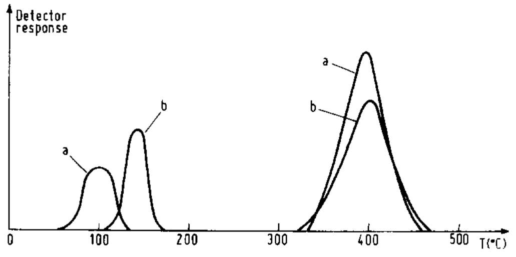


FIG. 1. TPD spectra of 1-butene (a) and propylene (b) on $CdMoO_4$.

TABLE 1

Kinetic Parameters for the Low-Temperature and High-Temperature Desorptions of the Olefins from CdMoO$_4$

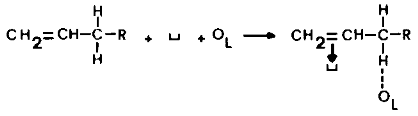
Olefin	Desorption peak		A (s^{-1})	E_d (kcal/mole)
	Temperature	T_m (°C)		
1-Butene	Low	100	7.77×10^{13}	23.0
Propylene	Low	145	8.71×10^{13}	26.0
1-Butene	High	400	14.02×10^{13}	43.1
Propylene	High	400	14.02×10^{13}	43.1

the desorption of propylene from a large series of oxide catalysts (*4–6*). The reversible and irreversible adsorption forms of propylene were shown to be surface species of the allyl type and oxidized surface species of the carbonate carboxylate type, respectively.

Assuming first-order desorption and following the semiempirical approach suggested by Brenner and Hucul (*7*) we calculated the preexponential factor A and the energy of desorption E_d for the two peaks. The values of the kinetic parameters are listed in Table 1.

Retaining the assignment of the reversible adsorption of olefins to surface species of the allyl type, one can speculate that the higher energy of activation for propylene desorption is consistent with the allyl hydrogen interaction with surface oxygen atoms as the rate-determining step for desorption. This conclusion is in line with the observations of Sokolovskii and Bulgakov (*8*) and of Zhdan *et al.* (*9*), who envisaged the nucleophilic attack of lattice oxygen atom on the allyl C–H bond as the basic phenomenon for the activation of the olefins in allylic oxidation. We recall that this mechanism is likely to involve adsorption of the olefins on sites with electron acceptor character so that the A-type sites might be envisaged as anion vacancies or surface defects.

Along these lines the adsorption process on A-type sites (represented by ⊔) can be shown as



$$CH_2{=}CH{-}\overset{H}{\underset{H}{C}}{-}R + \sqcup + O_L \longrightarrow \underset{\sqcup}{\underset{\downarrow}{CH_2{=}}}CH{-}\overset{H}{\underset{\underset{\vdots}{\underset{O_L}{H}}}{C}}{-}R$$

where O$_L$ represents a lattice oxygen atom.

Concerning the adsorption of the olefins on B-type sites we note that the associated desorption starts for both olefins in the same temperature range within which surface dehydroxylation occurs. This strongly suggests that the desorption process occurs because of surface dehydroxylation and, furthermore, that the adsorption of the olefins on the B-type sites is assisted by hydroxyl groups. The adsorption may likely result, due to the participation of hydroxyls, in oxidized surface species of the carbonate carboxylate type as already shown for other oxide systems (*4–6*).

This process can be shown as

B-type site + olefin + M–OH →

irreversibly adsorbed olefin.

In order to point out the role of hydroxyls in the desorption behavior of olefins from CdMoO$_4$ TPD experiments with 1-butene and propylene were performed on the catalyst heated up to 500°C under a flow of He. Because of this treatment the catalyst is not expected to contain surface-reactive hydroxyls; neither is it expected to be reduced.

The TPD spectra are shown in Fig. 2. The desorption peaks due to the reversible

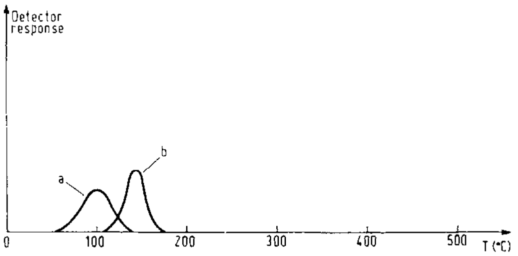


FIG. 2. TPD spectra of 1-butene (a) and propylene (b) on dehydroxylated CdMoO$_4$.

adsorption of the olefins are still present while the irreversible adsorptions no longer occur.

The data indicate that the irreversible adsorptions necessitate the presence of hydroxyls, thus confirming the hydroxyl-assisted character of the adsorption of the olefins on B-type sites. Indeed the adsorption of the olefins on B-type sites does not occur because of the absence of reactive hydroxyls. The possibility that B-type sites could have become reactive once the catalyst surface were dehydroxylated and that the olefins are converted to CO_2 during adsorption at room temperature can safely be rejected. Actually a small fraction of CO_2 was always detected during adsorption of the olefins. However, the amounts measured in these experiments were not larger than those recorded in the previous ones.

Finally TPD experiments with 1-butene and propylene were performed on $CdMoO_4$ heated up to 500°C under a flow of He and further treated at this temperature with oxygen (30 pulses, each one 3 cm^3 in volume).

No desorption was observed either in the case of 1-butene or in the case of propylene. This indicates that the A-type sites have been destroyed during pretreatment of the catalyst. The behavior is consistent with the proposed character of olefin–A-type site interaction in as much as treatment with oxygen at high temperature is likely to cause surface reconstruction and it results in annihilation of anion vacancies and surface defects. In this way the electron acceptor character of the A-type sites is destroyed and the adsorption of the olefins no longer occurs.

CONCLUSIONS

From this study it can be inferred that the presence of water vapor in the calcining atmosphere is responsible for the irreversible adsorption of the olefins on $CdMoO_4$, through the formation of Brönsted surface sites. Recalling that the olefins are primarily adsorbed irreversibly on catalysts for complete oxidation while on catalysts for selective oxidation adsorptions are largely reversible (*5*), it turns out that the presence of water vapor during the calcination step can be detrimental for the selective oxidation of olefins. Based on the similarities outlined in Ref. (*1*) this is expected to occur for a large class of molybdates.

The calcination of the catalysts in a water-free oxidizing atmosphere, while ensuring the absence of surface-reactive hydroxyls, is likely to produce inactive or at least less reactive catalysts (see TPD experiments with the catalyst pretreated with O_2). Therefore the addition of alkaline compounds during the preparation step addresses itself as the more effective way for neutralizing surface-reactive hydroxyls. In this respect it is interesting to note that alkaline elements quite often appear in commercial formulations of catalysts patented for the selective oxidation of olefins (*10*). On the other hand the presence of steam in the feed is supposed to reduce the extent of surface dehydroxylation and indeed it results in higher selectivities (*1*). As a matter of fact this procedure is often accomplished in commercial processes of selective oxidation.

The basic role of water during the calcination step of Mo-based catalysts has been experienced for silica-supported MoO_3 both in the low-temperature isomerization of 1-butene and in the photoreduction behavior on irradiation with uv light (*11*).

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