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NOTES

The Role of Surface Oxygen in Reactions of Propylene at Mg(0001) Surfaces

In this note we explore some aspects of the role of oxygen in the selective oxidation of propylene. There is interest in whether the selectivity can be associated with the electrophilic $O^-(a)$ or $O_2^-(a)$ or the nucleophilic $O^{2-}(a)$ species, which is the kind of question that has been discussed by, for example, Haber (*1*), Grasselli *et al.* (*2*), and Volta *et al.* (*3*) in their studies of propylene oxidation over bulk oxides.

Over the last decade it has been established, as emphasized by Dowden (*4*) recently, that the dehydrogenation activity of a metal surface can be enhanced substantially by the presence of chemisorbed oxygen. In coadsorption studies of dioxygen and ammonia at Mg(0001) surfaces it was shown (*5*) that a transient oxygen species, which we designated as $O^-(s)$, was responsible for activation and H-abstraction leading to surface amide formation. The lifetime of the $O^-(s)$ species was estimated (*6*) to be about 10^{-8} s, forming either the stable surface oxide $O^{2-}(a)$ or interacting with (weakly) adsorbed ammonia generating OH(a) and $NH_2(a)$ species. In this paper we explore the selectivity of C–H bond activation in propylene to surface oxygen at a Mg(0001) surface, monitoring the surface by X-ray photoelectron spectroscopy (XPS) and the gas phase mass-spectrometrically. An indication that propylene activation by chemisorbed oxygen occurred at a copper surface at low temperature has been reported earlier (*7*).

The photoelectron spectrometer and data processing procedures used have already been described (*8*), as has also the cleaning of the Mg(0001) single crystal.

It was first established (Fig. 1) that the atomically clean Mg(0001) surface adsorbed propylene only weakly; desorption was virtually complete at 110 K, suggesting a heat of adsorption of no more than 30 kJ $mole^{-1}$. The C(1*s*) binding energy of physically adsorbed propylene, $C_3H_6(a)$, is at 286 eV. Having shown that the atomically clean Mg(0001) surface exhibits no chemisorption activity at 295 K we studied preoxidized surfaces. The preoxidized surface generated by exposing Mg(0001) to dioxygen at 295 K was similarly unreactive to propylene. In other words the oxide overlayer, $O^{2-}(a)$, is inactive for propylene activation at 295 K.

If, however, a physisorbed propylene adlayer at 77 K is exposed to oxygen at a pressure of 10^{-6} Torr and the surface warmed to 295 K, there is little change in the total C(1*s*) intensity up to 160 K and a substantial C(1*s*) intensity is still present at 295 K. The C(1*s*) profile, however, has two main components, the major one at 286 eV and also a smaller one at 291.5 eV which develops in intensity as the temperature is increased to 295 K (Fig. 2). There is also an increase in intensity toward lower binding energy (~283 eV); this is obvious in the raw spectra at 250 and 295 K. The corresponding O(1*s*) profile exhibits a peak at 531 eV with a high binding energy component at 533.5 eV which becomes more obvious as the temperature increases (Fig. 2). The spectra were curve-fitted as described elsewhere (*8*) and the atom concentrations of the surface species calculated. The two O(1*s*) components (531 and 533 eV) are assigned to $O^{2-}(a)$ and $CO_3(a)$ species, respectively, and the two C(1*s*) peaks at 285 and 292 eV to chemisorbed hydrocarbon and carbonate species, respectively.

There are obvious similarities between

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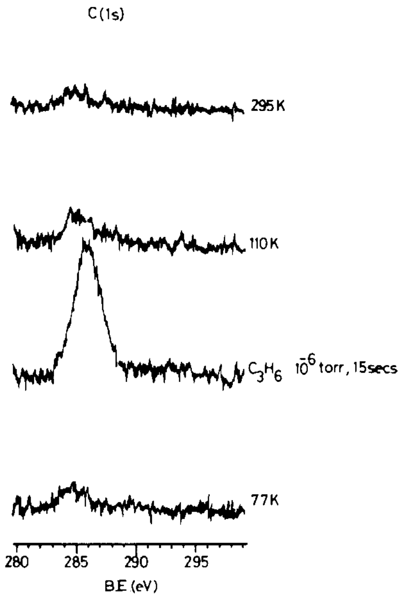


FIG. 1. C(1*s*) X-ray photoelectron spectra for adsorption of propylene at a Mg(0001) surface at 77 K followed by warming to 295 K. The $C_3H_6(g)$ exposure was 15 s at a pressure of 10^{-6} Torr.

the present results and our recent studies (*5*, *8*) of the activation of N–H bonds in ammonia by surface oxygen. Both propylene and ammonia are "not adsorbed" at either a Mg(0001) surface or at an oxide overlayer present at the Mg(0001) surface at 295 K. The heat of adsorption of both molecules is below 40 kJ mole^{-1} and the surface coverage (at 295 K) is very low, i.e. undetectable. Nevertheless when dioxygen–propylene mixtures are exposed to Mg(0001) surfaces at 295 K a C(1*s*) peak develops first at a binding energy of about 285 eV and with further exposure a second major C(1*s*) peak develops at 291.5 eV (Fig. 3). The corresponding O(1*s*) spectra have components at 531 and 533.5 eV (cf. Fig. 2). The intensities of the two C(1*s*) peaks (292 and 285 eV) observed during oxygen activation of the hydrocarbon do not increase in parallel and must therefore be assigned to two different carbon-containing surface species (Figs. 2 and 4). Mg(1*s*) spectra were also monitored and during exposure to the propylene–dioxygen mixture there is a gradual shift from the clean metal (Mg^{0}) value of 1303 eV to the "oxide" (Mg^{2+}) value at 1304 eV. Difference spectra enabled the onset of Mg^{2+} formation to be detected and its concentration to be monitored during the catalytic reaction (Fig. 3).

Mass-spectrometric analysis of the gas phase during the reaction at 295 K indicated the presence of two major peaks, one at mass 78 and the other in the 54–56 mass range (Fig. 5). There is a very small peak at mass 92. Clearly gaseous C$_6$ and C$_4$ species are being formed; the former is benzene, confirmation being obtained from its crack-

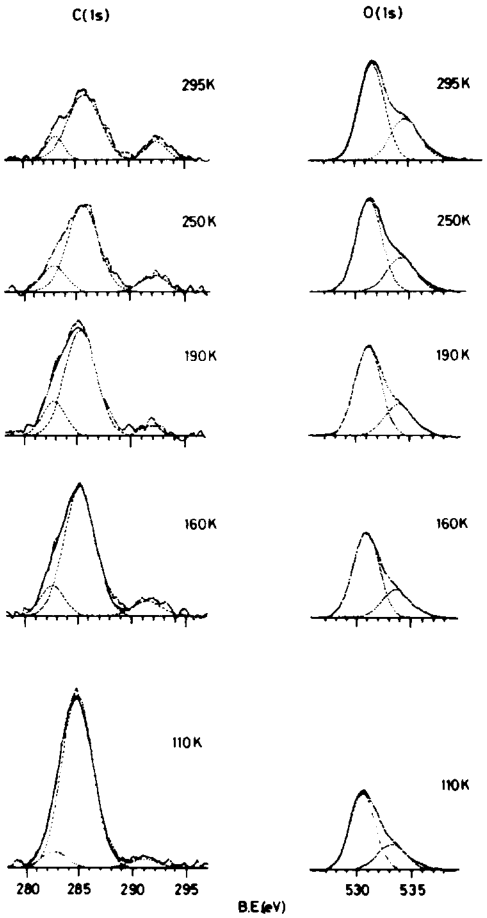


FIG. 2. Curve-fitted O(1*s*) and C(1*s*) spectra when C_3H_6 adsorbed at 77 K (see Fig. 1) was warmed to 295 K in the presence of dioxygen at a pressure of about 10^{-6} Torr.

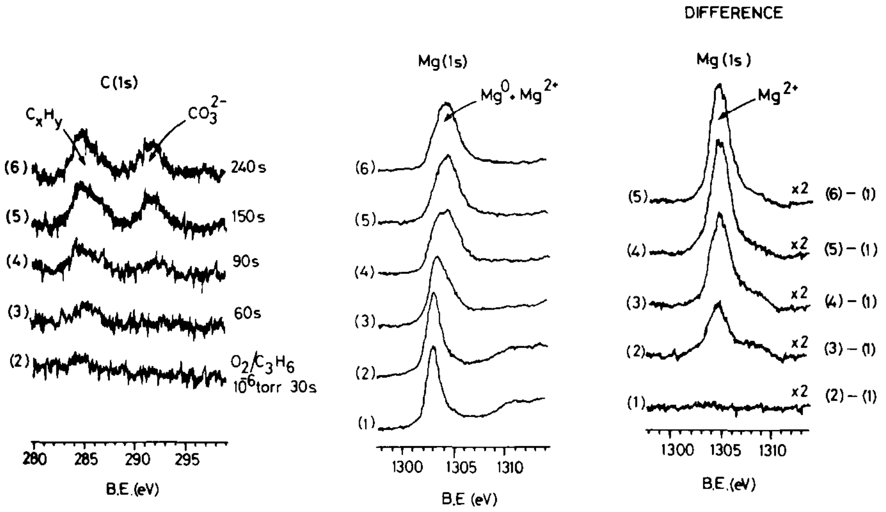


FIG. 3. C(1*s*), Mg(1*s*), and Mg(1*s*) difference spectra during the exposure of a Mg(0001) surface to a dioxygen–propylene mixture (1 : 1) at a pressure of ~1 × 10^{-6} Torr and 295 K.

ing pattern (Fig. 5). The species at mass 92 is likely to be toluene. Although the exact nature of the species responsible for peaks in the mass range 54–56 is not known, the use of ^{18}O showed that they do not contain oxygen.

The role of the surface oxygen transient is therefore mainly to effect H-abstraction,

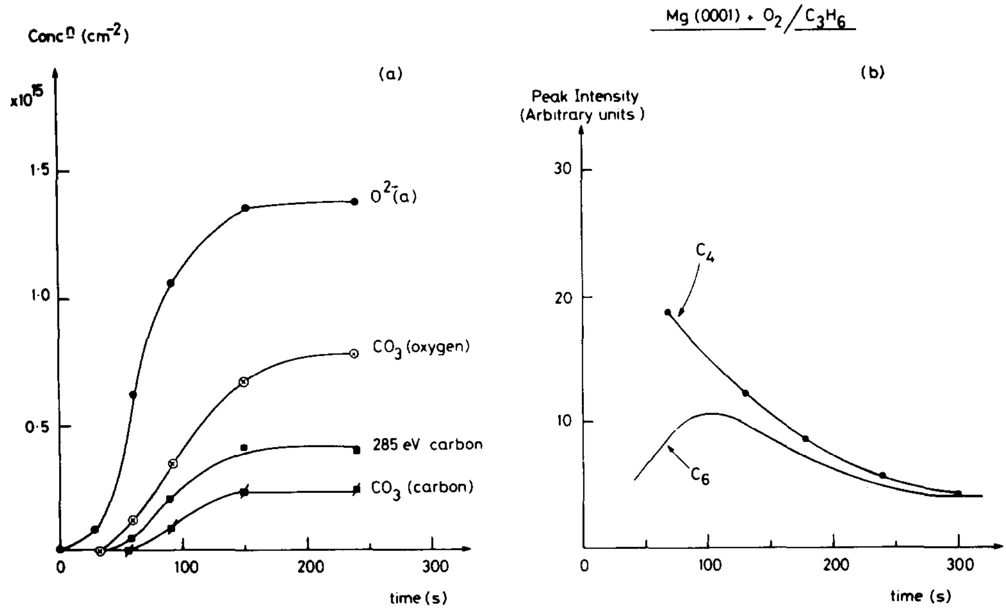


FIG. 4. (a) Calculated surface concentrations of the O^{2-}(a), CO_3(a), and C_xH_y(a) species from the C(1*s*) and O(1*s*) spectra. (b) Mass-spectrometric analysis of the gas phase showing peaks in the range 54–56 (C_4) and also at 78 (C_6) during exposure of a clean Mg(0001) surface to a propylene–dioxygen (1 : 1) mixture at 295 K.

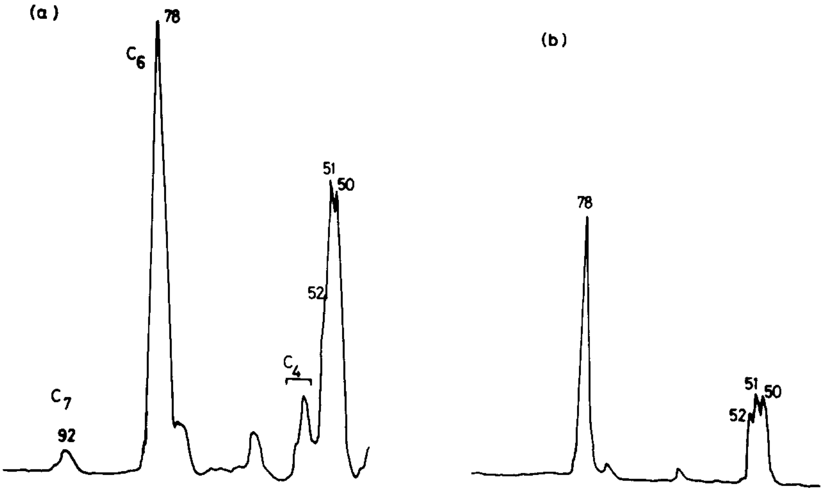
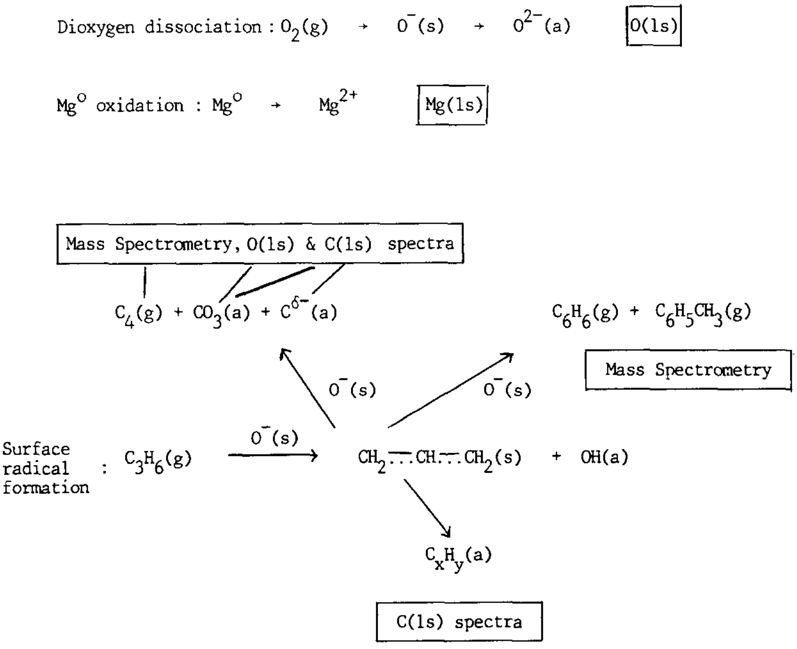


FIG. 5. (a) Mass-spectrum analysis of the gas phase during interaction (t = 100 s, Fig. 4) of a propylene–dioxygen mixture with an atomically clean Mg(0001) surface at 295 K. (b) Cracking pattern observed with authentic C_6H_6(g) in the absence of Mg(0001) crystal. The recorder speed is slower (×10) than in (a) with consequent improved resolution.

a very facile process, leading to dimerization and the formation of gaseous C_6 species. The oxygen is also active in C–C bond cleavage as indicated by the formation of surface carbonate. Both the metal (Mg^0) and the oxide (Mg^{2+}) overlayer are unreactive under the present conditions. As with the activation of N–H bonds in ammonia (*5, 6*), at a Mg(0001) surface we suggest that the electrophilic surface oxygen transient O^-(s) is the active species. Although we have no direct spectroscopic evidence for O^-(s) in these studies the species can be stabilized as O^-(a) with an increase in the concentration of surface oxide O^{2-}(a); under these circumstances it can be observed as a high binding energy shoulder to the O(1*s*) profile.

It is clear from a comparison of the time dependence of the gas phase composition and the surface composition analysis (Fig. 4) that the formation of C_4 and C_6 species only occurs during the initial stages of the interaction. For exposures greater than 100 s, surface oxidation, i.e., O^{2-}(a) and Mg^{2+}(a) formation, is virtually complete and this coincides with the maximum concentration of benzene formed. If we take into consideration the pumping characteristics of the system, and that the study is a dynamic one, then we can assume that C_4 and C_6 formation has become small at this stage (Fig. 4b). It is also at this stage, i.e., for an exposure time greater than about 80 s, that carbonate and "carbon" formation begin to dominate the surface reaction as reflected by C(1*s*) peaks at about 292 and 285 eV, respectively. Although we have shown (*9*) that small amounts of surface carbonate formation can occur at a *clean* Mg(0001) surface during oxidation with dioxygen (from traces of CO_2 present), this is never significant for an oxidized surface. The present substantial surface carbonate formation, $\sim 0.2 \times 10^{15}$ molecules cm^{-2} at 295 K, we attribute to C–C bond cleavage resulting in the total oxidation of the surface hydrocarbon species. The major C(1*s*) component at 285 eV we attribute to hydrocarbon fragments such as a chemisorbed allylic-type species and, prior to chemisorption, likely the essential precursor to benzene formation. A much smaller component at 282.5 eV, which becomes clearer as the temperature increases (Fig. 2), is a carbidic-type species. We have included this in our analysis (Fig. 4a) of the total C(1*s*) peak at low binding energy (282.5- plus 285-eV components). Our results suggest that as the Mg^{2+} concentration develops at the surface, so the likelihood of the allylic species being chemisorbed at the surface increases and therefore its dimerization to give benzene decreases. Surface concentrations of the individual species were calculated, using procedures already described, as a function of exposure to the propylene–oxygen mixture (Fig. 4a). The oxygen : carbon atom ratio in the O(1*s*) and C(1*s*) photoelectron peaks which we have assigned to the carbonate species is seen to be close to 3 : 1, providing further evidence for their identification.

The reaction scheme below summarizes both the photoelectron and mass-spectrometric data. We use the symbol(s) to designate a transient radical-type surface species. The mass-spectra provide evidence for the desorption of C_4 and C_6 hydrocarbons while X-ray photoelectron spectroscopy has provided evidence for the strongly chemisorbed species O^{2-}(a), CO_3(a), and C_xH_y(a) and also the transformation of Mg^0 to Mg^{2+}. Although there are some strong similarities between these conclusions and the discussions relating to selective oxidation at bulk oxide surfaces at high temperatures (*1*, *2*) the present data emphasize how the observed chemical specificity is related to changes in surface composition and the oxidation state of the metal at low temperatures. The formation of C_4 and C_6 species is to be associated with that stage of the oxidation of the atomically clean Mg(0001) surface when the transient O^-(s) species are prevalent. When the surface transforms to an MgO-overlayer, as indicated by both the Mg(1*s*) shifted component and the presence of O^{2-}(a) species in the O(1*s*) spectra, the activity of the surface for H-abstraction leading to oxidative dimerization, and for carbon–carbon bond cleavage, ceases. The observations therefore not only provide indirect experimental evidence for a surface oxygen species intermediate between dioxygen and the dissociated oxygen asso-



SCHEME 1

ciated with the oxide overlayer, but also emphasises the need to distinguish between studies involving preadsorption and the dynamic or time-dependent coadsorption approach.

When nitrous oxide is used as the oxidant there is no evidence for the formation of benzene, and for propylene-rich mixtures little surface carbonate formation is observed: the main reaction appears to be the formation of $C_xH_y(a)$ species. For N_2O-rich mixtures surface carbonate forms. The particular alternative reaction pathways in the scheme above which dominate depend on the $O^-(s)$ concentration and the relative rates of the generation of $C_xH_y(a)$, surface carbonate formation and desorption of C_6 and C_4 hydrocarbons.

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