

ESR Studies on Zinc Molybdate Catalyst in Relation to Propylene Oxidation

The active sites (in terms of the oxidation state of Mo) responsible for the adsorption and partial oxidation of propylene have been identified through kinetic investigation (1) and on the basis of the observed selectivities (2) Peacock *et al.* (3) have deduced that the adsorption of propylene takes place on Mo⁶⁺ site and the electron released in this step reduces the adjacent molybdenum ions to Mo⁵⁺ which is responsible for the ESR signal observed. On the other hand Sancier *et al.* (4), using ESR to monitor the concentration of Mo⁵⁺ during the oxidation of propylene, obtained a reciprocal relationship between total conversion and the Mo⁵⁺ signal intensity. Che *et al.* (5) have recognized the presence of two types of Mo⁵⁺ species in supported molybdenum catalysts but have not identified the exact nature of these two species. The aims of the present investigation, therefore, are (1) identification of the nature of Mo sites responsible for the adsorption and partial oxidation of propylene, (2) elucidation of the two types of Mo⁵⁺ species normally observed in molybdate catalysts, and (3) finding out the nature of the adsorbed (binding) state of oxygen responsible for direct total oxidation as well as for the reoxidation of the reduced catalyst due to partial oxidation reaction,

through ESR measurements on a typical zinc molybdate catalyst under various treatments.

EXPERIMENTAL

About 0.1 g of the catalyst (prepared by coprecipitation) was used for recording the spectra using a Varian E4 X-Band ESR spectrometer with 100 KHz field modulation and phase sensitive detection. For the calculation of *g* factors DPPH was used as an internal reference.

RESULTS AND DISCUSSION

In Table I a summary of the results obtained in terms of the "g" factors observed and intensities of the various signals obtained after various treatments of the catalyst is given. The intensity of the resonance signals is given by $I = KW^2H$ where *W* is the peak to peak separation, *H* is the peak to peak height, and *k* is a constant. In Fig. 1, the ESR spectrum of the fresh catalyst evacuated at 450°C is given. It is seen that there are in total seven signals due to the presence of two types of Mo⁵⁺ species (A) and (B), as well as due to adsorbed oxygen species tentatively assigned

TABLE I
Summary of ESR Results on ZnMoO₄ Catalyst

Subjected treatments	Observed ESR signals and their probable assignments							Intensity of the various ESR signals						
	<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃	<i>g</i> ₄	<i>g</i> ₅	<i>g</i> ₆	<i>g</i> ₇	<i>I</i> ₁	<i>I</i> ₂	<i>I</i> ₃	<i>I</i> ₄	<i>I</i> ₅	<i>I</i> ₆	<i>I</i> ₇
	Mo ⁵⁺ (A)	free spin	O ⁻	O ₂ ⁻		Mo ⁵⁺ (B)								
1. ZnMoO ₄ catalyst evacuated at 450°C	1.928	1.967	1.998	2.015	2.044	1.896	1.874	102.6	62.4	1.7	0.1	0.2	4.5	0.6
2. ZnMoO ₄ treated with O ₂ at 30°C	1.922	1.961	1.991	2.007	2.034	1.889	1.886	152.8	13.2	4.1	0.1	0.7	5.9	0.8
3. ZnMoO ₄ reduced with C ₃ H ₆ at 300°C for 30 min	1.925	1.969	—	—	2.036	1.892	1.868	410.1	27.7	—	—	0.5	6.1	0.7
4. ZnMoO ₄ reduced with C ₃ H ₆ at 300°C for 3 hr	1.929	1.968	1.997	2.018	2.045	1.896	1.876	116.9	11.3	2.3	0.4	0.4	5.7	1.3
5. ZnMoO ₄ reduced with propylene for 30 min at 300°C and then treated with O ₂ at 30°C	1.936	1.977	2.00	2.010	2.024	1.904	1.868	227.4	15.6	2.9	6.9	12.9	6.0	0.5
6. ZnMoO ₄ treated with propylene at 30°C, propylene is pumped out at the same temperature and the sample is treated with oxygen	1.937	1.977	2.011	2.025	2.054	1.904	1.882	186.6	11.6	8.8	0.4	6.9	5.6	0.4
7. ZnMoO ₄ treated with propylene at 30°C	1.950	1.991	2.020	2.039	2.066	1.917	1.894	102.7	6.8	1.7	0.1	0.4	3.9	0.3
8. ZnMoO ₄ reduced with C ₃ H ₆ at 300°C and treated with O ₂ at 300°C	1.921	1.961	1.995	2.009	2.039	1.891	1.867	109.6	12.7	5.3	0.4	1.5	1.8	0.8

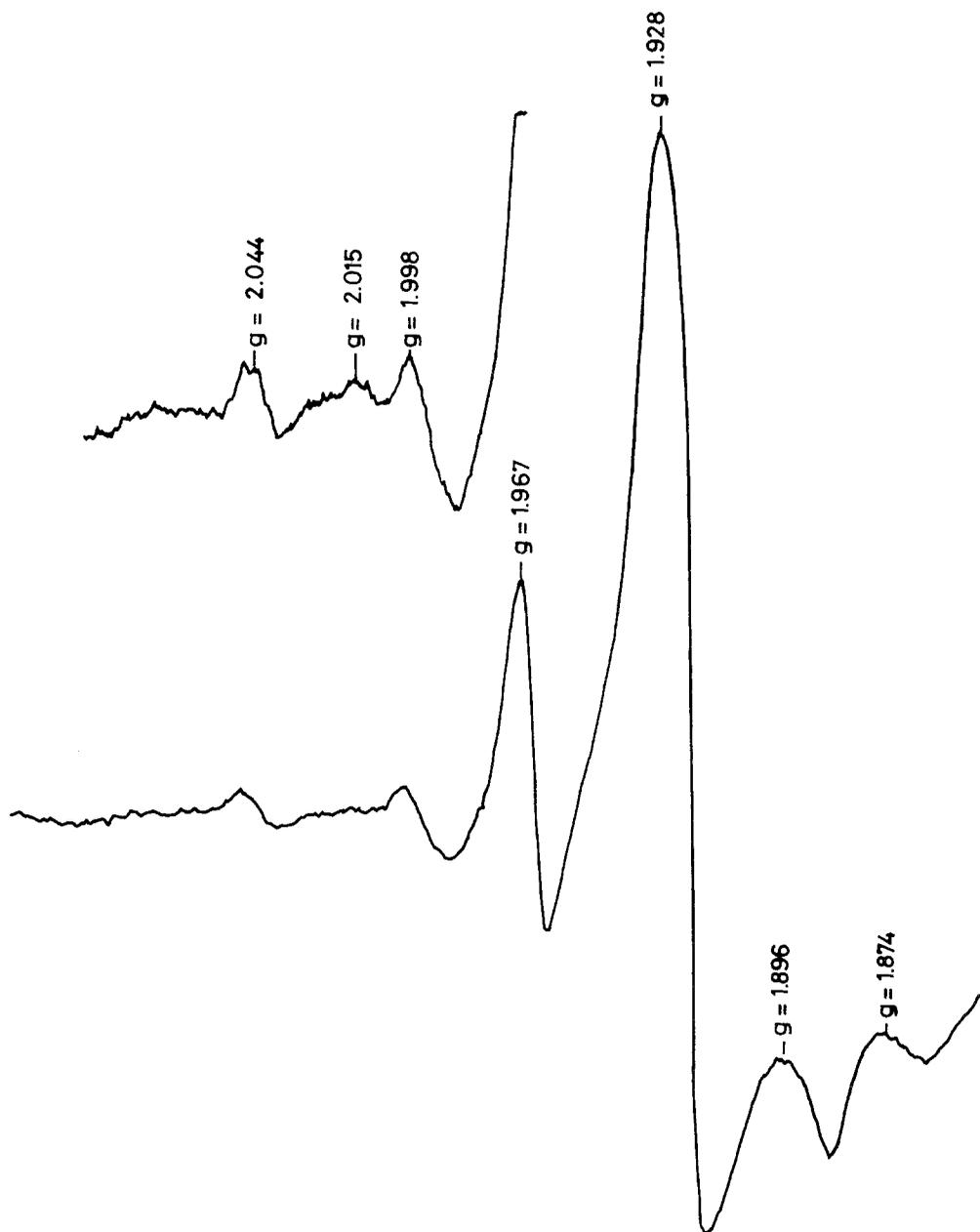


FIG. 1. ESR spectrum of the catalyst evacuated at 450°C.

as O_2^- and O^- in addition to the existence of free spins at $g = 1.967$. The observation that this catalyst is an n -type semiconductor supports this conclusion (7). Treatment of the catalyst with oxygen at room temperature resulted in increased signal intensity due to Mo^{5+} and O^- , while that due to free spins is reduced. Treatment of the catalyst with propylene at 300°C resulted in an enormous increase of the "A" type

of Mo^{5+} species whose intensity is decreased when the treatment is extended for prolonged periods (~3 hr), while that of the "B" type of Mo^{5+} species is increased. This might be taken to indicate that the B species should be associated with Mo^{5+} in the bulk or in a coordination geometry which undergoes reduction with difficulty. The fact that the intensity of Mo^{5+} species associated with $g = 1.930$

(that is, the A type of Mo^{5+} species) decreases with prolonged treatment with propylene indicates that this concentration of surface Mo^{5+} species (A type) is depleted by diffusion of bulk oxygen at this high temperature thus resulting in an enhancement in intensity due to the B type of Mo^{5+} species or due to further reduction to Mo^{4+} state. Keulks (6) has proposed that the bulk oxygen diffuses to the surface, during the oxidation of propylene in the absence of oxygen to account for the isotopic content of the products formed. Present ESR measurements support this conclusion.

In order to understand the nature of reoxidation step, the catalyst was treated with propylene at 300°C for 30 min. a situation favorable for formation of surface Mo^{5+} species and then treated with oxygen at 30°C as well as at 300°C . It was seen that oxygen is mostly adsorbed as O_2^- at 30°C which is transformed to O^- at 300°C , and probably it is this adsorbed oxygen that is responsible for the reoxidation of the reduced catalyst in the catalytic reaction. Though the partial oxidation reaction can proceed by a redox mechanism (intrafacial catalysis), the total oxidation reaction, if it proceeds by a direct reaction route, may not involve the participation of surface oxide ions. When the catalyst contains only strongly adsorbed propylene (since evacuation at the same temperature can be expected to remove weakly held propylene), the treatment with oxygen resulted in the formation of (O^-) adsorbed oxygen species. These results lead to the following conclusions:

1. The adsorption of propylene occurs preferentially on Mo^{6+} sites (since no change in Mo^{5+} signal intensity is observed on treatment of the catalyst with propylene at 30°C).

2. The partial oxidation reaction involves the participation of lattice oxide ions which can result in the further reduction of surface Mo^{5+} to Mo^{4+} or to the diffusion of oxide ions to the surface as is evident

from the increase of Mo^{5+} signal intensity on treatment of C_3H_6 at 300°C . The decrease in Mo^{5+} signal intensity with prolonged treatment with propylene showed that it undergoes further reduction to Mo^{4+} or the oxide ions from the subsurface layers diffuse to the surface to participate in the oxidation reaction. The latter appears to be probable because of the increase of the signal intensity due to bulk Mo^{5+} species (B type).

3. Oxygen is adsorbed as O_2^- and is transformed to O^- in which state it is participating in the total oxidation reaction or in the reoxidation of the catalyst.

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