THEORETICAL CONSIDERATIONS ON THE OXIDATION OF PROPYLENE ON TRANSITION METAL MOLYBDATES

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Molecular orbital calculations of charge distributions for the π -allyl complex with transition metal ions in molybdates show that the activated π -allyl species is formed by transfer of charge density to the metal ion. The relative charge distributions on the three carbon atoms of the adsorbed allyl species govern the course of oxidation reaction.

Расчеты МО распределения заряда для π-аллильного комплекса с ионами переходных металлов в молибдатах показали, что активированные π-аллильные частицы образуются путем переноса плотности заряда на металлический ион. Относительное распределение заряда на трех атомах углерода адсорбированных аллильных частиц руководит ходом реакции окисления.

The partial oxidation of propylene on molybdate catalysts is usually considered to proceed by charge transfer to the catalyst /1/. The allyl species thus formed undergoes transformations through a surface complex to yield partial/complete oxidation products. The mechanistic pathway of the surface reaction leading to partial oxidation, complete combustion or dimerization can be rationalized on the basis of the extent of activation of the olefin, i.e. on the basis of the net positive charge concentrated on each of the three carbon atoms. Calculations by the SCCC-MO (Self-Consistent in Charge and Configuration Molecular Orbital) method of the allyl complexes of Co, Ni, Fe, and Mg by Haber et al. /2/ show that when the positive charge

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is concentrated on the terminal carbon atoms of the allyl group, then the system is capable of promoting the oxidation of propylene. However, they have not attempted to rationalize, on the basis of charge distribution at the respective centers, the preference for partial or complete oxidation. Therefore, in the present investigation an attempt is made to distinguish between the possibilities of occurrence of complete/ partial oxidation on the basis of charge distribution at the reaction centers obtained through SCCC-MO computations of π -allyl complexes of divalent ions of Mn, Co, Ni as well as of ferric ion in typical molybdates in two configurations, namely (1) for the π -allyl group bonded to the metal ion in a symmetric fashion, and (2) for a slided geometry wherein the allyl group is bonded to the metal ion through one of its double bonds, by SCCC-MO method. The procedure described in the literature /3/ for calculating the charge distribution and electronic configuration has been adopted with Mulliken's population analysis with the resonance integrals being approximated according to the Wolfsberg-Helmholz formula with F = 1.75. The results of these calculations are summarized in Table 1.

Since low-spin complexes had lower orbital energies in all cases studied, it is assumed that the formation of these species is more probable on the surface and, therefore, data relevant to this configuration alone are considered for discussion. In all the cases, the average number of π -electrons in the allyl group is always less than 2, indicating that an appreciable charge density is shifted towards the metal ions, resulting in the positively charged allyl group appearing as the sixth ligand of the octahedral complex considered. This transfer of charge density provides the necessary bonding of the allyl group to the surface as well as the required activation.

The extent of charge transfer and the resultant charge distribution appear to control the course of oxidation. The values given in Table 1 show that in the slided configuration the terminal carbon atom possesses a greater positive charge, which will facilitate nucleophilic attack of the lattice oxide ions (oxide ion linked to the nearest cation) and yield an oxygenated surface complex, which may ultimately

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							traí Total charge	0.416	0, 106	0.280	0.247
etric configuration	Charge on carbon atoms (in e units)	Total charge	0,377 0.053	0. 215	0,196		Cen <i>a</i> -contribution	0.462	0.173	0.329	0.296
		Central <i>m</i> -electronic contribution	0,431	0.278	0, 252		nal II Total charge	0.676	0.461	0, 618	0, 488
		T otal charge	0, 592 0, 403	0, 523	0.467		Termi <i>n</i> -contribution	0, 804	0.631	0.747	0.614
	Terminal π -electronic contribution		0.718	0.650	0, 590		nal I Total charge	0.457	0.139	0.352	0,404
	rerage number electrons on allyl		1.132	1,422	1, 568		Termi <i>π</i> -contribution	0, 578	0,301	0.475	0, 529
a) Symm	Metal		Fe ³⁺ Mn ²⁺	Co ²⁺	Ni ²⁺	lded configuration	Average number of electrons on allyl	1, 154	1, 893	1.447	1, 559
						b) Sli	etal	3+	n ²⁺	₃ 2+	2+

Metal

 Fe^{3+} Mn²⁺ Co²⁺ Ni²⁺

Results of theoretical calculations Table 1

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desorb as acrolein. This is true only when the fractional positive charge on other carbon atoms is small in magnitude. When the terminal carbon atoms in the slided configuration possess almost the same amount of positive charge and the charge on the middle carbon atom is also high (> 0.2), then no preferential nucleophilic attack of oxide ions takes place and complete oxidation results.

Table 2

Rate constants at 330 °C (mol min⁻¹ m⁻²) for the oxidation of propylene

	MnMoO ₄	CoMoO ₄	N i MoO_4	$\operatorname{Fe}_{2}^{(MoO_{4})}$
For total reaction	16, 2 5	221.8	214, 0	8 18, 5
For acrolein formation	11, 11	48. 5	55 . 6	120, 5
For carbon dioxide formation	5 .4	170.7	16 5, 4	690, 1
Selectivity to acrolein	68, 3	21, 9	26,0	14, 5

on molydbates

It can, therefore, be concluded that the average number of π -electrons on the allyl group seems to be the critical parameter controlling the partial, total or no oxidation activity. Further computations with all possible relaxed configurations of the π -allyl group on the surface may be useful for developing a unified framework to predict the oxidation activity of a given system.

The kinetic parameters (Table 2), the observed selectivity order namely $MnMoO_4 > NiMoO_4 > CoMoO_4$ and the predominant complete oxidation activity of ferric molybdate generally conform to the expectations based on these computations. However, quantitative correlations are not possible at this stage because of the idealized conditions assumed for theoretical calculations.

REFERENCES

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- 1. S. G. Gagarin, A. P. Gorshkow, L. Ya. Margolis: Kinet. Catal., 12, 1269 (1967).
- 2. J. Haber, M. Sochacka, B. Grzybowska, A. Golebiewski: J. Mol. Catal., <u>1</u>, 35 (1976).
- 3. P. T. Manoharan, H. B. Gray: Inorg. Chem., 3, 1113 (1964); 5, 823 (1966).