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The Influence of Ligands on the Disproportionation of Olefins Catalyzed by Tungsten Oxide on Silica

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The influence of ligands on the disproportionation of olefins catalyzed by tungsten oxide on silica is discussed on the basis of concepts derived from molecular orbital theory. The effects of the ligand π-orbitals on the energy levels of the metal atom and on its catalytic activity are examined in detail. The predictions arising from these considerations are shown to be in accord with existing experimental data and with the results of experiments performed to test the theoretical model.

INTRODUCTION

In the field of coordination metal catalysis the study of the influence of ligand modifications on catalytic activity constitutes a dominant portion of the empirical research. Yet, little effort has been made to rationalize these ligand effects on the basis of theories with predictive value. This is in part due to the fact that any theory aimed at the interpretation of reactivity and selectivity patterns must of necessity deal with the role played by the metal atom in the electronic rearrangements responsible for the observed reactions. About this role generally very little is known.

We have proposed recently (*1*) that olefin disproportionation (*2*) catalyzed by tungsten oxide on silica proceeds through promotion of electrons from molecular orbitals comprising metal *d*-orbitals and olefin π-orbitals to levels comprising metal *d*-orbitals and olefin antibonding π-orbitals. So, the principal role of the metal atom is that of facilitating the transfer of electrons from bonding to antibonding π-orbitals of the reactant olefin molecules by reducing the energy difference between them through their interaction with the metal *d*-orbitals. According to this view, in order for the catalyzed reaction to occur, ΔE, the energy difference between the two orbitals involved in the postulated transition, must not exceed a maximum critical value that is a function of temperature. This model suggests that the course of the disproportionation reaction can be influenced in a predictable way by appropriate modifications of the energy level distribution on the metal atom and, consequently, of ΔE.

The magnitude of ΔE is a function of several variables including the olefin, the transition metal, the ligands, and their steric arrangement; since the latter is dictated mainly by the surface configurations of the support, ΔE is also a function of the support. The purpose of this communication is to consider only the effects that, according to our model, ligand modifications produce on the disproportionation activity of tungsten oxide supported on silica, and to provide experimental verification of the theoretical arguments.

CLASSIFICATION OF LIGANDS

In heterogeneous catalysts it seems desirable to distinguish between two classes of ligands, referred to here as *primary* and *ancillary* ligands.

The first are permanent ligands whose nature and steric arrangement are determined by the methods of preparation and of pretreatment of the catalyst. They impart to the catalyst its characteristic properties and its electronic structure. For example, in tungsten oxide supported on silica, the primary ligands are oxide ions and, because at least some of these are part of the silica framework, the silica support. Any change in these ligands, e.g., the replacement of an oxygen atom with a halogen, or the replacement of silica with alumina, constitutes a permanent alteration of the fundamental characteristics of the catalyst.

Ancillary ligands are those which coordinate to an active site when more vacancies are present than required to accommodate the molecules undergoing the reaction. They may modify the electronic structure of the catalyst and thus affect its activity, but their influence is temporary and is a function of their concentration. In reactions of olefins, the reactant olefins or one of the reaction products may play the role of ancillary ligands; in the latter case the reaction may exhibit a pronounced induction period as a consequence of the concentration dependence of the ancillary ligand effects.

In tungsten oxide on silica, as well as in other supported metal oxides which catalyze olefin disproportionation, the arrangement of the primary and of the ancillary ligands can be visualized as in Fig. 1. This idealized configuration is derived from current ideas about the local environments of these metal oxides on support. Transition metal ions supported on silica have been pictured (*3*) as sitting above the center of the exposed face of an SiO_2 tetrahedron with the site of tetrahedral coordination, or the three sites for octahedral coordination, above the metal either occupied by an anion or vacant. Spectroscopic evidence, analogous to that obtained for molybdenum oxide on alumina (*4*), suggests that tungsten oxide on silica possesses a tetrahedral structure. Therefore we picture the active sites initially either as metal ions tetrahedrally coordinated to four oxide ions, some of which are part of the silica surface, or as metal ions coordinated to three oxide ions with the fourth tetrahedral position vacant. In the latter case, coordination to the metal of two ancillary ligands and of a reactant olefin molecule results in the formation of an octahedral complex, as shown in Fig. 1a. If all four tetrahedral positions are occupied by an oxide ion the metal may accommodate only one ancillary ligand.

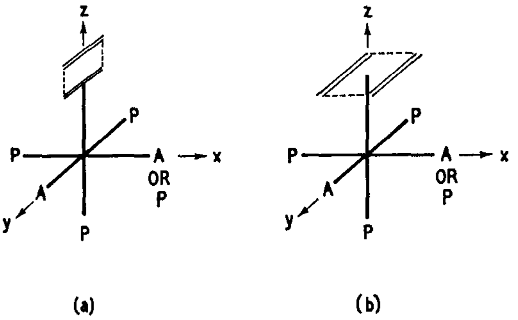

Fig. 1. Idealized configurations of an olefin disproportionation site on a supported metal oxide catalyst. (a) With only one olefin coordinated to the metal; (b) with both olefins coordinated to the metal; P = primary ligand; A = ancillary ligand.

Effects of Ligands on ΔE

There is abundant evidence (*5–7*) for a "four-center mechanism" in olefin disproportionation, but it is not at all clear how the olefin molecules are arranged with respect to the metal atom. Two possible configurations (*8*, *9*) are shown in Fig. 1a, and b. In one (Fig. 1b) both olefins are coordinated to the metal atom, in the other (Fig. 1a) only one molecule is coordinated to the metal; however, the second olefin molecule may be attached to another metal atom (*8*).

It is readily established, by simple symmetry considerations, that the olefin π-orbitals combine with the metal *d*-orbitals as shown in Fig. 2. Of these metal *d*-orbitals only one, d_{x^2}, is involved in σ-bonding with the ligands. The others are involved in π-bonding.

ΔE can be adjusted by modification of either Ψ_A or Ψ_B (see Fig. 2). However, Ψ_B contains a much smaller metal *d*-orbital contribution than Ψ_A, so it is much less sensitive than Ψ_A to changes in the energy levels of the central atom and, consequently, to the electronic effects of the

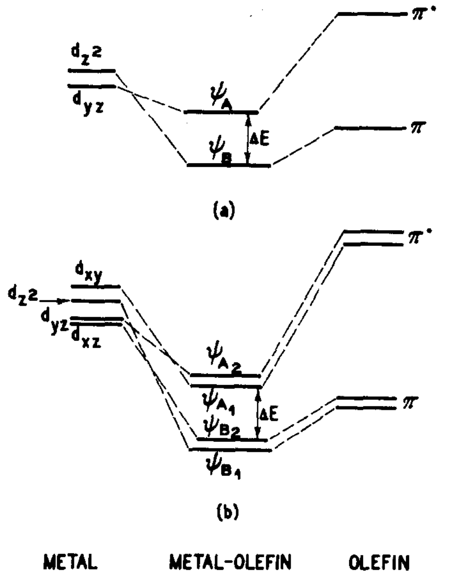

FIG. 2. Bonding molecular orbitals arising from the combination of metal d-orbitals and olefin π-orbitals. (a) According to Fig. 1a; (b) according to Fig. 1b.

ligands. For this reason the changes in ΔE affected by the ligands are best rationalized in terms of the changes in Ψ_A. It should be noted that this statement is generally valid and applies to symmetries other than octahedral.

The direction and magnitude of the changes in ΔE produced by a ligand depends, of course, on the nature of the ligand. Ligands that possess empty π-orbitals, as for example phosphines and arsines, or empty antibonding π-orbitals, as for example olefins, tend to depress the energy of the metal d-orbitals with which they combine, while the opposite effect occurs with ligands that have filled π-orbitals, as for example oxygen or fluorine. This occurs because in the first case the π-orbitals are less stable than the d-orbitals and consequently depress the d-orbital energy through π-bonding effects, while in the second case the π-orbitals are more stable than the metal d-orbitals and raise the energy of the latter through π-antibonding effects.

It should be noted that the designation π refers to the symmetry with respect to the ligand–metal bond, and not with respect to bonds within the ligand. For example, olefins possess both bonding π-orbitals and antibonding π-orbitals, but only the latter form π type orbitals with the metal *(10)*. Referring specifically to our model, it is readily established that, when an olefin coordinates to the metal at the ancillary positions shown in Fig. 1, only the olefin antibonding π-orbitals combine with metal d-orbitals that participate in Ψ_A. The bonding π-orbitals of the ancillary olefin combine with the metal $d_{x^2-y^2}$ which is not involved in bonding with the olefins undergoing disproportionation (see Fig. 2).

These considerations indicate how ΔE can be adjusted by an appropriate choice of ancillary ligands or by suitable modifications of the primary ligands. Ancillary ligands containing empty π-orbitals depress Ψ_A and decrease ΔE, while those containing filled π-orbitals produce the opposite effect. Similarly, replacement of a primary ligand that has stable π-orbitals with one that has unstable π-orbitals decreases ΔE, but replacement with another ligand possessing stable π-orbitals may either increase or decrease ΔE depending on the relative π-antibonding effects of the two ligands.

COMPARISON WITH EXPERIMENT

To increase the activity for olefin disproportionation of tungsten oxide on silica it is necessary to increase the number of active sites rather than to improve the reactivity of the sites already operational *(1)*. According to our model, sites can be activated by reducing ΔE to a value below the maximum critical value stipulated by the reaction temperature.

Ancillary ligands. The arguments developed in the preceding section predict that this can be accomplished, in one way, by the introduction of ancillary ligands possessing empty π-orbitals. This prediction has found experimental confirmation. As we have reported previously *(1)*, small amounts of polyenes, added to the propylene feed, enhance markedly the disproportionation of propylene catalyzed by tungsten oxide on silica. Similar improvements by tributyl phosphine have been reported for the disproportionation of pentenes (*11*). On the other hand, ancillary ligands possessing stable π-orbitals should produce the opposite effects, i.e., they should increase ΔE and reduce the number of active sites. Accordingly, compounds such as alcohols, H_2O, H_2S, and others with stable π-orbitals have been found to retard the disproportionation reaction. Of course, the inhibiting effects of these compounds cannot be attributed solely to their role as ancillary ligands; probably in most cases they have a much stronger affinity for the metal atom than the olefin and they impede coordination of the olefin with the active site.

Primary ligands. The arguments presented in the preceding section also indicate that ΔE can be reduced by replacing the oxide ions in the tungsten oxide on silica with ligands possessing filled π-orbitals that produce weaker π-antibonding effects than the oxide ions. Molecular spectroscopic evidence (*12*, *13*) indicates that in transition metal compounds with the metal atom in a high oxidation state, oxide ligands exhibit stronger π-antibonding effects than halides. Therefore replacement of oxide ligands with chloride ligands should result in the reduction of ΔE and should produce a catalyst which is active at lower temperatures.

To test this viewpoint we have made a comparative study, as a function of temperature, of the disproportionation of 1-butene catalyzed by tungsten chloride on silica and by tungsten oxide on silica.

The tungsten chloride catalyst was prepared by impregnation of silica, which had been predried at 500°C under N_2, with a benzene solution of WCl_6. The impregnation and the subsequent removal of the solvent were carried out in an argon atmosphere under strict anaerobic anhydrous condition. The amount of WCl_6 added corresponded to 6.7% of the catalyst weight. Butene-1 was passed over this catalyst in a tubular glass reactor at a rate of 1700 vol of gas/vol of catalyst/hr, while the temperature was gradually raised from 50 to 250°C. The catalyst was then treated with air at 400°C for 1 hr, to form the tungsten oxide, and the disproportionation test was repeated at the same space rate from 120 to 440°C. The results are shown in Fig. 3. In agreement with expectation, the tungsten oxide catalyst required higher temperatures (~200°C) to produce the same conversions obtained with the chloride.

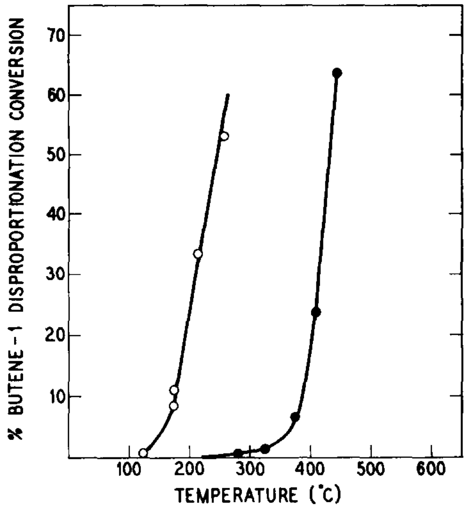

FIG. 3. Temperature dependence of the disproportionation of 1-butene catalyzed by: (○) tungsten chloride on silica; (●) tungsten oxide on silica.

Additional verification of the theoretical arguments is provided by a study of the effect on propylene disproportionation of replacing oxide with chloride. In a flow-through experiment, steady state propylene conversion at 500°C, atmospheric pressure and 900 vol of gas/vol catalyst/hr, over a commercial tungsten oxide on silica catalyst, was 10%. The propylene flow was interrupted and HCl was passed over the catalyst at 500°C for 20 min. When, after sweeping the catalyst with N_2, propylene was readmitted over the catalyst under the same conditions as before, conversion was 45%. Regeneration of the catalyst with air, reduced the conversion to its previous value, while retreatment of the catalyst with HCl again raised the conversion to near-equilibrium values. This repeatability indicates that the increase in activity after HCl treatment was not due to redistribution of the tungsten oxide on the silica surface, or removal of excess tungsten oxide by formation of volatile oxychlorides, but to modification of the active sites. Similar results have been observed with other chlorinating agents such as alkyl chlorides (*14*).

CONCLUSIONS

The agreement between prediction and experiment for both ancillary and primary ligands lends support, if not credence, to the theoretical arguments introduced here. Perhaps more importantly, it points out their value as a heuristic stimulus in the study of olefin disproportionation catalyzed by supported metal oxides.

In a broader sense, the discussion and the examples presented here indicate the usefulness of applying concepts derived from molecular orbital theory and molecular spectroscopy to problems of catalysis, not only for the interpretation, but also for the prediction of reactivity patterns, which often are of great practical value.

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