ASPECTS CONCERNING THE MECHANISM OF THE PARTIAL OXIDATION REACTIONS

A. Szabo [*]**, Adriana Urda and M. Alifanti**

abstract: The study of oxide catalysts by electrical conductivity methods leads to important contributions in the elucidation of the reaction mechanisms taking place on these solids. MoO_3-Fe_2O_3, MoO_3-Bi_2O_3 and V_2O_5-TiO_2 catalysts were prepared with various ratios between the component oxides, and electrical conductivity values in nitrogen, air and hydrogen were determined, showing that they behave as n-type semiconductors. By measuring the electrical conductivity values at constant temperature in three different environments (nitrogen, a reductive atmosphere consisting of a reactant molecule such as methanol, a light alkene or o-xylene, and then in air), it was established that partial oxidation reactions of the reactant molecules take place according to a reduction - oxidation mechanism that implies the action of the lattice oxygen.

key words: mixed oxides, MoO_3-Fe_2O_3, MoO_3-Bi_2O_3, V_2O_5-TiO_2, partial oxidation.

Introduction

An extremely vast literature was devoted to the activity of mixed oxide catalysts [1÷3]. Considering the correlation between activity and phase composition and the modifications that the catalyst suffers during its use, a conclusion was reached that the catalytic process takes place at the boundary between two solid phases [4].

Partial oxidation reactions on oxide catalysts are difficult to understand without knowing the elementary mechanism of oxidation. Papers on this topic conclude that the reactant mixture induces changes in the composition of the catalyst's active phase during reaction, and this composition can be controlled by the reactant mixture.

Different opinions can be found in the literature concerning the mechanism of the partial oxidation reactions on oxide catalysts. There is a consensus about the fact that this is a redox process, but the source of oxygen generates different opinions. Some researchers [5,6] claim that the oxygen that is involved in the catalytic process is the one from the catalyst lattice [7,8], while others claim that the chemisorbed oxygen on the catalyst's surface is important [9]. Eventually, the main feature is the electron transfer between the participants [7,8], depending on the electronic character of both the catalysts and the reactants. As a function of this character, a direction for this electron transfer is imposed. We consider that these aspects could be elucidated by using redox cycles determined by the electrical conductivity method. The aim of this paper is to study MoO_3-Fe_2O_3, MoO_3-Bi_2O_3

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and V_2O_5-TiO_2 catalyst systems by electrical conductivity methods, in order to get insights on the mechanism of oxidation reactions on these solids, seeking experimental evidences about lattice oxygen involvement.

Experimental

The catalysts that were used in the study of the redox cycles were prepared by coprecipitation (Table 1) [6,10÷13] and were tested in the oxidation of methanol to formaldehyde, propene to acrolein and o-xylene to phthalic anhydride.

The catalysts were pelletized as cylinders with a 9 mm diameter and variable thickness. The pelletizing pressure was, in all cases, above 10^7 N m^{-2}, in order to minimize the parasitic resistances.

The cylindrical tablet with known dimensions is placed between two platinum electrodes, introduced in a glass cell. The sample is heated with a filament resistance directly coiled on the cell. The equipment for electrical conductivity measurements was previously described [11].

Table 1. Catalysts prepared by coprecipitation and the reactions in which they were tested

Sample no.	Catalyst composition	Testing reaction	Catalyst type
1	85% MoO_3 15% Fe_2O_3	Methanol oxidation	MoO_3-Fe_2O_3 mixed oxide
2	73% MoO_3 27% Fe_2O_3	Methanol oxidation	
3	64% MoO_3 36% Bi_2O_3	Propene oxidation	MoO_3-Bi_2O_3 mixed oxide
4	76% MoO_3 24% Bi_2O_3	Butenes oxidation	
5	6% V_2O_5 94% TiO_2	o-Xylene oxidation to phthalic anhydride	TiO_2-V_2O_5 mixed oxide
6	20% V_2O_5 80% TiO_2	o-Xylene oxidation to phthalic anhydride	

The electrical resistance for all catalysts was measured in the range of 100-500°C, every 20°C in nitrogen, air and hydrogen, with a heating rate of 2°C·min^{-1}. The electrical conductivity isotherms were determined from resistance measurements for a period of 5 minutes at 300°C, 400°C and 460°C. We used a constant gas flow of 2 l·h^{-1} during all experiments.

The electrical conductivity σ (Ω^{-1} cm^{-1}) was calculated using Ohm's law.

The diagrams of electrical conductivity versus temperature $\sigma = \sigma_0 \exp\left[-(E_\sigma / 2kT)\right]$ were plotted using the least squares fitting of the data.

Electrical conductivity isotherms as a function of time were determined as follows:

- for MoO_3 – Fe_2O_3 catalysts, at 300°C in nitrogen, methanol vapours in nitrogen flow and, finally, air;
- for MoO_3 – Bi_2O_3 catalysts, at 400°C in nitrogen, propene and, finally, air;
- for TiO_2 – V_2O_5 catalysts, at 460°C, in nitrogen, o-xylene vapours in nitrogen flow and, finally, air.

In each neutral, reductive or oxidative environment, the measurement time was chosen so that a plateau for the electrical conductivity values to be obtained.

The measurements were conducted for the catalysts listed in Table 1.

Results and discussion

Oxide catalysts with semiconductor properties form ionic frameworks. The nature of the defects in semiconductor oxides can be varied so it is not always possible to establish their nature.

Defects can be classified upon their character: electron acceptor or donor, or on their chemical nature as deviation from stoichiometry (excess of one constituent or impurities).

In order to study the electronic properties of the catalysts, first the semiconductor type of the catalyst has to be determined. For this purpose, measurements were made by varying the electrical conductivity with temperature and nature of gas environment (nitrogen, air, hydrogen) that was used for the determinations.

If we consider that, regardless of the semiconductor type of the catalyst, oxygen makes an acceptor chemisorption and hydrogen a donor chemisorption, it can be shown that:

– chemisorption on n-type semiconductor	Electrical conductivity	Type of chemisorption
$[n-\text{solid}]+\frac{1}{2}O_2+2\ominus \rightleftharpoons O^{2-}_{chem}$	decreases	depletive chemisorption
$[n-\text{solid}]+\frac{1}{2}H_2 \rightleftharpoons H^{+}_{chem}+\ominus$	increases	cumulative chemisorption
– chemisorption on p-type semiconductor		
$[p-\text{solid}]+\frac{1}{2}O_2 \rightleftharpoons O^{2-}_{chem}+2\oplus$	increases	cumulative chemisorption
$[p-\text{solid}]+\frac{1}{2}H_2+\oplus \rightleftharpoons H^{+}_{chem}$	decreases	depletive chemisorption

where $\ominus$ and $\oplus$ are the free electron and the mobile hole.

Applying the Heckelsberg criterion [14] that is based on these observations, the nature of the semiconductor type for the catalyst can be determined. If the catalyst has electrical conductivity values that are higher in nitrogen than in air, or values that are higher in hydrogen than in nitrogen ($\sigma_{air} < \sigma_{N_2} < \sigma_{H_2}$), it has an n-type semiconductor character. If the electrical conductivity values are higher in air than those in nitrogen are, and the values in hydrogen are lower than those in nitrogen ($\sigma_{H_2} < \sigma_{N_2} < \sigma_{air}$), the catalyst has p-type semiconductor character.

From the diagrams in Figs. 1 and 2 it can be seen that the two TiO_2-V_2O_5 catalysts act as n-type semiconductors, and $\sigma_{air} < \sigma_{N_2} < \sigma_{H_2}$.

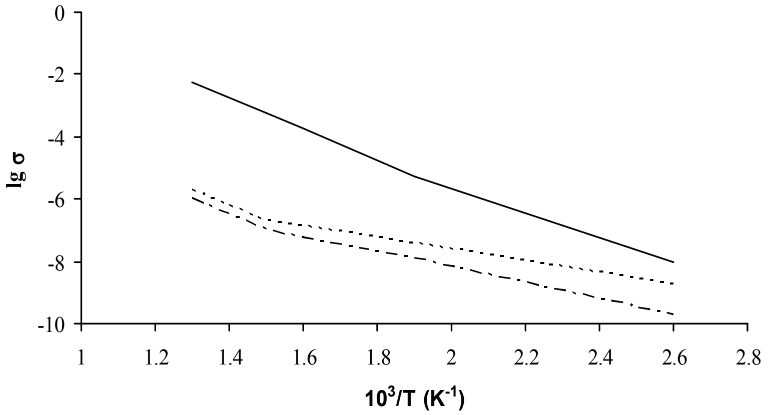

Fig. 1: *Variation of electrical conductivity as a function of temperature for V_2O_5(6%)-TiO_2(94%)catalyst:······· in nitrogen; — · — in air; —— in hydrogen*

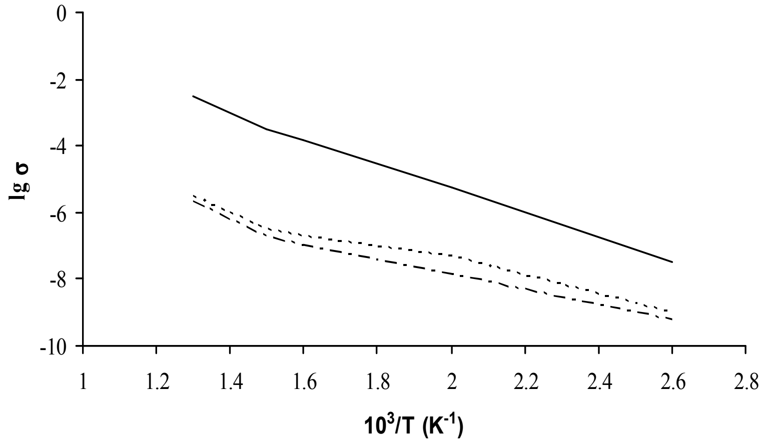

Fig.2: *Variation of electrical conductivity as a function of temperature for V_2O_5(20%)-TiO_2(80%)catalyst:······· in nitrogen; — · —in air; —— in hydrogen*

The results concerning the type of charge carriers for the MoO_3 – Fe_2O_3 and MoO_3 – Bi_2O_3 catalysts were communicated in previous papers, and were based on studying the electrical conductivity differences of the catalysts upon depletive and cumulative chemisorptions for hydrogen and oxygen. It is known that hydrogen is chemisorbed in a donor way and the oxygen in an acceptor way, regardless of the type of adsorptive solid. It was shown for all the catalysts that the charge carriers are electrons, so they show an n-type semiconductor behavior [5,6,9,10,12].

In order to appreciate the way catalysts act, the variation of the electrical conductivity in time was studied at a constant temperature of 300°C for MoO_3 – Fe_2O_3 catalysts, 400°C for the MoO_3 – Bi_2O_3 catalysts and 460°C for the TiO_2 – V_2O_5 catalysts, in the three environments that were already mentioned (neutral, reductive and oxidative). In these measurements, all the catalysts showed the same behavior, the differences consisting only in the value of the electrical conductivity increase (Figs. 3-5).

It can be seen that, after the stabilization of the electrical conductivity in nitrogen (a plateau is obtained), changing the environment with a reductive one leads to a rapid increase for the electrical conductivity values that, after a while, are stabilized again. If the environment is changed again by introducing air, a sudden decrease for the electrical conductivity values is seen, that according to Heckelsberg criterion [14], will be stabilized at lower values than those obtained in nitrogen.

The high values of the electrical conductivity in reductive environment, compared to those obtained in nitrogen and air, can be explained by the fact that upon contact with methanol, propene or o-xylene, the catalyst (n-type semiconductor) is enriched in free electrons. This experimental finding cannot be explained unless we admit that by contacting the reagents with the catalyst a partial oxidation reaction takes place, consuming the lattice oxygen, and when reaction products are desorbed (formaldehyde, acrolein, phthalic anhydride) two electrons are released for each oxygen that was consumed.

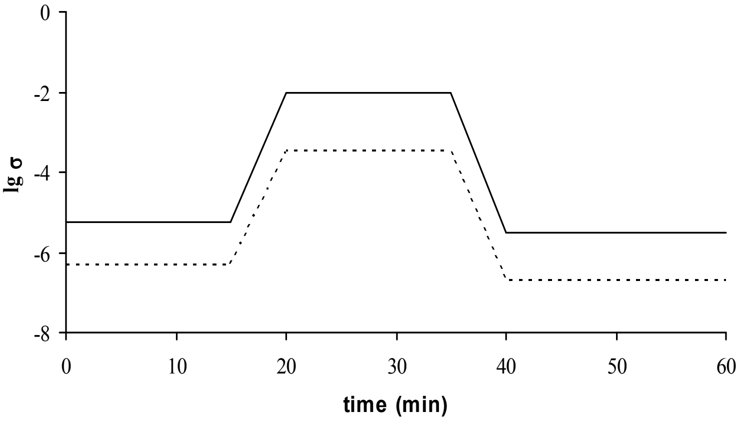

Fig. 3: *Electrical conductivity isotherms at 400oC for the MoO_3(85%)-Fe_2O_3(15%)catalyst (——) and the MoO_3(73%)-Fe_2O_3(27%)catalyst (······)*

As a consequence, the first step for the partial oxidation reaction can be assumed to be the formation of the above-mentioned products at the expense of lattice oxygen from the catalyst, the latter one being reduced:

$$\text{Oxidized catalyst} + \text{Reductive reagent} \longrightarrow \text{Partial oxidation product} + H_2O + \text{Reduced catalyst}$$

After air is introduced, the decrease of the electrical conductivity values can be explained by the consumption of free electrons from the conduction band of the catalyst, induced by the oxygen from air that re-enters in the lattice and re-oxidizes the catalyst:

$$\text{Reduced catalyst} + O_2 \longrightarrow \text{Oxidized catalyst}$$

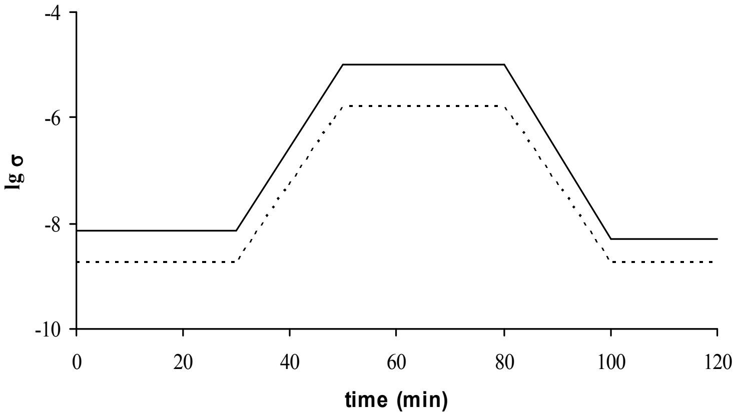

Fig. 4: *Electrical conductivity isotherms at 400oC for the MoO_3(64%)-Bi_2O_3(36%)catalyst (——) and the MoO_3(76%)-Bi_2O_3(24%)catalyst (······)*

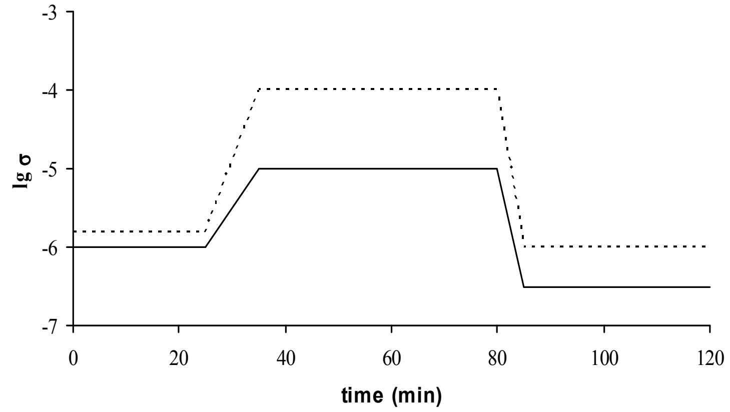

Fig. 5: *Electrical conductivity isotherms at 400oC for the TiO_2(94%)-V_2O_5(6%)catalyst (——) and the TiO_2(80%)-V_2O_5(20%)catalyst (······)*

By repeating these steps, the mechanism for reducing and oxidizing the catalyst remains the same. Since the reaction is performed in the presence of air and reductive reagent, we can assume that the overall reaction consists of the two steps, taking place rapidly and successively.

Therefore, we can consider that these partial oxidation reactions take place according to a reduction - oxidation mechanism that implies the action of the lattice oxygen, and this fact is indicated by the increase in the electrical conductivity values. The larger the increase, the higher is the ability of the catalyst to perform an oxidation reaction. If the electrical conductivity increase is small, this is an indication of a more important implication of chemisorbed oxygen in the oxidation reaction, compared to the lattice oxygen, and this is the case for the $TiO_2 – V_2O_5$ catalyst (see Fig. 4).

Conclusions

Results presented in this paper show that the study of oxide catalysts by electrical conductivity methods could lead to important contributions in the elucidation of the reaction mechanisms taking place on these solids. Also, it was established that in many cases lattice oxygen is involved in these partial oxidation reactions.

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