

## CORRELATION BETWEEN TEXTURAL PARAMETERS AND CATALYTIC ACTIVITY IN OXIDATIVE DEHYDROGENATION OF n-BUTENES OVER Bi-Mo-Fe-O CATALYSTS

I. Săndulescu\*, **L. V. Nicolescu**

**abstract:** The mechano-topochemical method for preparation of Bi-Mo-O and Bi-Mo-Fe-O catalysts improved the activity and selectivity in oxidative dehydrogenation of n-butenes, compared with the catalysts prepared by classical methods. Addition of Fe<sub>2</sub>O<sub>3</sub> to the binary catalytic system increases the catalytic performances of Bi-Mo-O oxides. Between the textural characteristics of catalysts and kinetic parameters of oxidative dehydrogenation reaction there are some correlations, which could be taken in consideration for selecting such catalysts.

**keywords:** oxidative dehydrogenation, n-butenes, Bi-Mo-Fe-O catalyst

### Introduction

Oxidative dehydrogenation of n-butenes to butadiene is now an industrial process, which has replaced entirely the classical process of dehydrogenation. This one because the introduction in system of an hydrogen acceptor, which is oxygen, displaces so strongly the reaction equilibrium, that practically the conversion might not be related to equilibrium conditions. Therefore, the butadiene yield increases to about 65-70% and selectivity to 90-95%, per run, at 400-460°C. Since the reaction is highly exothermic, a great deal of conventional fuel is saved [1-3].

The importance of the problem for the industrial practice, the diversity of literature concerning the catalytic systems and preparation methods have conducted to a large number of researches regarding correlations between the nature of active phases, catalyst composition, textural parameters and activity in oxidative dehydrogenation of n-butenes in butadiene [4-7].

In this paper, the activity and selectivity of catalytic systems Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> (Bi/Mo = 0.5:1.0) and Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> (Bi/Mo/Fe = 0.5:1.0:1.2) are compared, and some correlations between textural parameters and the absolute rate of oxidative dehydrogenation over both systems are established.

---

\* University of Bucharest, Faculty of Chemistry, Blvd. Regina Elisabeta 4-12, Bucharest, Romania

## Experimental

Catalysts  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  (Bi/Mo = 0.5:1.0) and  $\text{Bi}_2\text{O}_3\text{-MoO}_3\text{-Fe}_2\text{O}_3$  (Bi/Mo/Fe = 0.5:1.0:1.2) were prepared and characterized [8].

Catalysts were prepared by „mechano-topochemical” method, which consists in a mechanical mixing of components (in solid phase, as crystals-hydrates) with an alkaline component – ammonium carbonate, also in solid state. We used bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ , ammonium paramolibdate  $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}$  and respectively  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

The solid-solid interface reaction took place in a dense fluid medium made up of crystal water according to a topochemical reaction mechanism [9].

Catalytic tests of oxidative dehydrogenation of n-butenes were carried out in a dynamic reactor in fixed bed of catalyst. n-Butenes used were 97.8% purity, with 61.4% 1-butene and 36.4% 2-butenes. The hydrogen acceptor was atmospheric oxygen and the diluent was steam.

The activity and selectivity of both catalysts were determined under the following conditions : temperature 400-520°C ; volumetric flow rate 600h<sup>-1</sup> for n-butenes ; molar ratio n-butene : air : steam = 1 : 3.5 : 7.5.

The textural properties of catalyst were determined.

## Results and discussion

The „mechano-topochemical” method, in this case, allowed us to obtain catalytic systems more active than the same ones prepared by other methods. Therefore, in the case of  $\text{Bi}_2\text{O}_3\text{-MoO}_3\text{-Fe}_2\text{O}_3$  (Bi/Mo/Fe = 0.5:1.0:1.2) catalyst, in table 1 comparative results obtained for the three different methods of preparation are presented.

A - mechano-topochemical method;

B – mixing equivalent quantities of oxide components, in order to obtain the desired atomic ratio, followed by thermal treatment;

C – mixing equivalent quantities of some metallic compounds (bismuth nitrate, iron nitrate, molybdenic acid), followed by thermal treatment.

**Table 1. The influence of preparation method on activity of ternary system Bi/Mo/Fe = 0.5 : 1.0 : 1.2. Reaction temperature 440°C; volumetric flow rate of n-butenes 600 h<sup>-1</sup>; molar ratio n-butenes : air : steam = 1.0 : 3.5 : 7.5.**

Preparation method	n-Butenes conversion (wt %)	Butadiene yield (wt %)	Butadiene selectivity (wt %)
A	49.4	42.6	86.2
B	56.2	49.8	88.4
C	67.2	62.0	92.3

In the following experiments, we used only catalysts prepared by mechano-topochemical method.

By comparing the binary and ternary systems, the introduction of iron shifts the optimum range reaction temperature to smaller values.

In fig. 1, we present comparatively the two catalysts. In the case of binary catalyst, activity increases with increasing temperature up to 480°C, at higher values the butadiene yield being practically constant. The selectivity to butadiene decreases, but until 480°C it is over 90% [9].

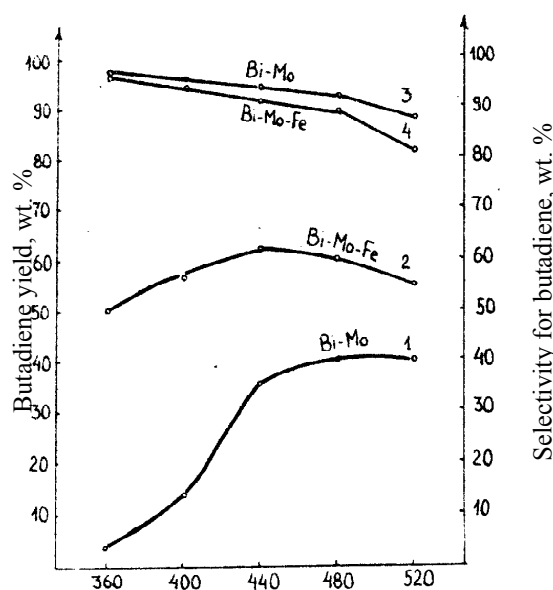


Fig. 1. The activity and selectivity of Bi/Mo and Bi/Mo/Fe catalysts as a function of reaction temperature; 1,2 – yields; 3,4 – selectivities.

For the ternary system, optimum of reaction temperature is 440°C, where the yield to butadiene is over 60%, but above this temperature, it decreases. In the same time, the selectivity to butadiene is over 90% until 480°C. Notice that for the ternary system the best results are obtained between 420 and 440°C.

For establishing the optimum contact time for oxydehydrogenation reaction, the volumetric flow rate of n-butenes varied between 200 and 1200 h<sup>-1</sup>, and a total flow rate between 2400 and 14400 h<sup>-1</sup>. This means that the contact time for n-butenes was from 18 to 3 seconds, and for the whole mixture between 1.5 and 0.25 s.

Figure 2 shows the variation of catalyst performances versus volumetric flow rate of n-butenes, for the ternary catalyst. It can be seen that oxydehydrogenation reaction takes place with increasing reaction rates in the range of 400-900 h<sup>-1</sup>.

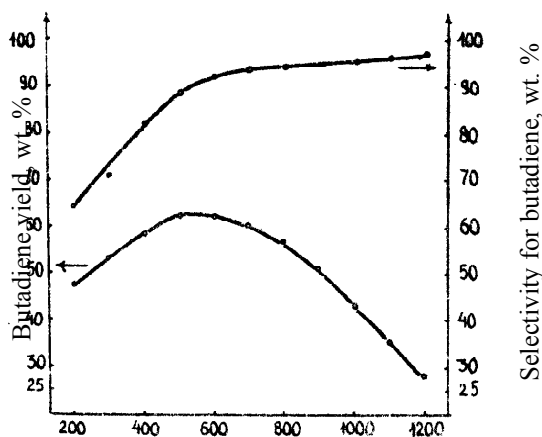


Fig. 2. The Influence of volumetric flow rate on the oxydehydrogenation in the case of ternary catalyst Bi/Mo/Fe = 0.5 : 1.0 : 1.2.

The main textural characteristics for the binary and ternary catalysts are shown in table 2.

Table 2. The main textural characteristics for the binary and ternary catalysts.

Catalytic system	Real density (g/cm <sup>3</sup> )	Apparent density (g/cm <sup>3</sup> )	Surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Macropores volume (cm <sup>3</sup> /g)	R <sub>m</sub> (Å)
Bi/Mo = 0.5 : 1.0	5.81	3.58	2.4	0.13545	0.12155	3400
Bi/Mo/Fe = 0.5 : 1.0 : 1.2	5.40	2.90	3.4	0.1604	0.1474	400 and 25000

Figure 3 shows pores distribution by radius for the binary Bi/Mo = 0.5 : 1.0 and ternary Bi/Mo/Fe = 0.5 : 1.0 : 1.2 systems. Fe<sub>2</sub>O<sub>3</sub> addition changes the distribution of the medium pores and of the macropores. The ternary catalyst Bi/Mo/Fe = 0.5 : 1.0 : 1.2 exhibits a heterogeneous porous structure with medium pores and macropores having radii of 400 and, respectively, 25000 Å.

Now we intend to set out some correlations between activity, expressed as local reaction rate, and the textural parameters of catalysts, such as macroporosity, the pore radius, retention time of the reactant inside the macropores [10].

It is known that in general reaction rate equation, the retention time  $d\tau$  of the reactant flow rate  $V_0$  (cm<sup>3</sup>/s) within the reactor volume  $dV_r$  (reactor cross section infinitely small) is given by:

$$d\tau = \frac{dV_r}{V_0}$$

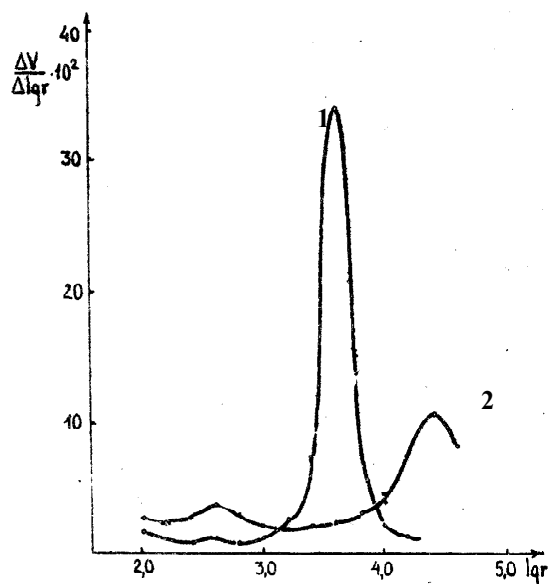


Fig. 3. Pore distribution by the radius; 1 - Bi/Mo = 0.5 : 1.0; 2 - Bi/Mo/Fe = 0.5 : 1.0 : 1.2.

By the substitution of the term that stands for the reaction volume,  $dV_r$ , with the macropores volume  $V_M$ , granting that the reactant flows through them, one obtains:

$$d\tau = \frac{dV_r}{F_{A_0}} = \frac{V_M}{F_{A_0}} = \tau_M$$

$$S_M = \frac{2V_M}{r_M}$$

$$-r_A = F_{A_0} \cdot X_A$$

$$F'_M = -r_A \tau_M; \quad F'_M = \frac{-r_A}{F_{A_0}} V_M$$

where:  $F_A$  – feeding flow rate (mol/g·s);

$X_A$  – moles butenes transformed per second and gram of catalyst;

$\tau_M$  – retention time of the reactants in the macropores;

$S_M$  – internal surface area of the macropores;

$r_M$  – mean radius of macropores;

$F_M$  – moles butenes transformed as a function of retention time inside the macropores

$r_A$  – total reaction rate (moles/g·s).

Figure 4 shows the variation of the apparent reaction rate with the feeding rate for the catalysts  $\text{Bi}_2\text{O}_3\text{-MoO}_3$  (Bi/Mo = 0.5:1.0) and  $\text{Bi}_2\text{O}_3\text{-MoO}_3\text{-Fe}_2\text{O}_3$  (Bi/Mo/Fe = 0.5:1.0:1.2), taking into account the global flow rate of the reactants.

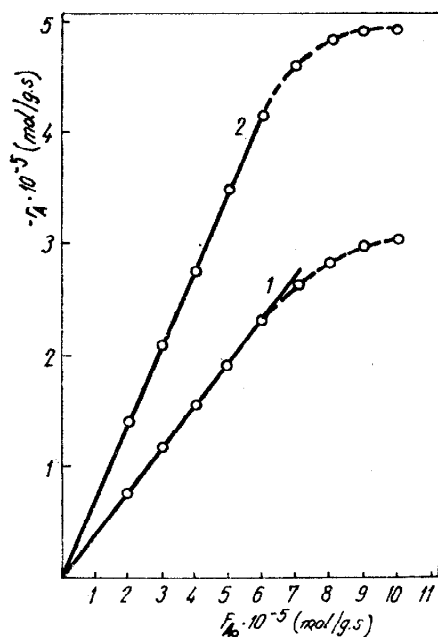


Fig. 4. Variation of the apparent reaction rate with reactant flow at reaction temperature of  $440^\circ\text{C}$ ;

1 - Bi/Mo = 0.5 : 1.0; 2 - Bi/Mo/Fe = 0.5 : 1.0 : 1.2.

We notice a linear dependence between the reaction rate and the reactant flow rate up to a certain value. The linear range corresponds to our experiment conditions. Apparent reaction order calculated from slope, has fractionary values close to zero, which show that the mechanism is more complex when reaction mixtures of 1- and 2-butenes are used.

Figure 5 shows the flow rate of reaction products plotted against the retention time of the reactants inside the macropores, for the same catalysts. In both cases a linear dependence is noticed up to retention time ranging from 1.0 to 1.5 s. These experimental data suggest certain dependences between the kinetic parameters of the reaction and some textural characteristics of the catalysts that could be meaningful when criteria for selecting the catalysts are involved.

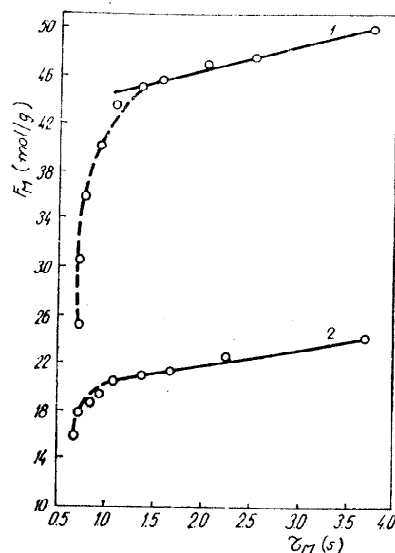


Fig. 5. Variation of the reaction products flow with the retention time of the reactants inside the macropores. Reaction temperature 440°C. 1 - Bi/Mo = 0.5 : 1.0; 2 - Bi/Mo/Fe = 0.5 : 1.0 : 1.2

In conclusion, the new mechano-topochemical method for catalyst preparation highly improves the activity and selectivity against the same catalysts prepared by classical methods. The interface reaction of the solid hydrated particles provides a better interaction among the components of the reaction mixture, thus favoring the formation of active catalyst phases. Addition of  $\text{Fe}_2\text{O}_3$  to the binary catalytic system Bi-Mo-O substantially increases their activity. There are some interdependences between the kinetic parameters of reaction and some textural characteristics of the catalysts, which could be considered as criteria for selecting a particular catalyst.

## REFERENCES

1. Qiu, F. Y., Weng, L. T., Sham E., Ruiz P. and Delmon, B. (1989) *Appl. Catal.*, **51**, 235-253.
2. Nedelcu, Gh. and Nicolescu, I. V. (1990) *Rev. Chim. Bucuresti.*, **41(11-12)**, 881-884.
3. Morselli L., Trifiro, F. and Urban, L. (1982) *J. Catal.*, **75**, 112-121.
4. Yang, B. L., Kung, M. C. and Kung, H. H. (1984) *J. Catal.*, **89**, 172-176.
5. Lambert, J. C. and Germain, J. E. (1982) *Bull. Soc. Chim. France*, **1(1-2)**, 1-33-38.
6. Nedelcu, Gh. and Nicolescu, I. V. (1991) *Rev. Chim. Bucuresti.*, **42(1-3)**, 21-26.
7. Yang, B. L. and Cheng, D. S. (1991) *Appl. Catal.*, **70**, 161-173.
8. Moisin, Ana Maria, Chirtoc, V., Sandulescu, I. And Nicolescu I. V. (1975) *Z. Phys. Chem. (Frankfurt)*, **95**, 159-164.
9. Nicolescu, I. V., Sandulescu, I., Grigoriu, I., Crisan, T., Angelescu, E. and Pascu, S. (1977) Rom. Patent, 62701.
10. Nicolescu, I. V. and Sandulescu, I. (1971) *Anal. Univ. Bucuresti, Chimie*, **20(4)**, 27-31.

11. Sandulescu, I. and Nicolescu, I. V. (1973) *Anal. Univ. Bucuresti, Chimie*, **22(2)**, 555-561.
12. Nicolescu, I. V. and Sandulescu, I. (1979) *Rev. Roum. Chimie*, **26(2)**, 217-228.