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EFFECT OF THE IMPREGNATION STRATEGY IN THE CATALYTIC ACTIVITY OF Pd AND Mo SUPPORTED CATALYSTS

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ABSTRACT

The effect of the impregnation strategy in catalytic activity of Pd and Mo supported on alumina in the oxidative dehydrogenation of propane was studied. Total, metallic superficial areas and total volume of pore behaviour were correlated as a function of the load relationship Mo/Pd and the impregnation strategy. Except for the 3.75 Mo 1.25 PdS catalyst, all the bimetallic catalysts of Pd-Mo present smaller metallic surface area than their corresponding monometallic Pd catalysts. The increment of the specific activities to propene for the bimetallic catalysts in comparison with the monometallic catalysts may indicate modification on the reaction mechanism and the configuration of the surroundings of the active site.

Key words: Pd-Mo catalyst, Impregnation, Oxidative dehydrogenation.

INTRODUCTION

Propane is used as raw material for the production of polypropylene, acrolein, propylene oxide and cumene among other important chemicals products of industrial interest. The oxidative dehydrogenation of propane to propylene (ODHP) has been proposed as a thermodynamically suitable route. ODHP is usually performed between 450-650°C at atmospheric pressure on noble metal supported catalysts (palladium, platinum or chromium)[1]. Some modifiers such molybdenum, tin, arsenic and lead improve selectivity by inhibiting side reactions as hydrocracking and isomerisation[2]. The performances of Pd, Mo and, and Pd-Mo supported on Al_2O_3 catalysts were investigated in the ODHP reaction in order to understand the effect of the Pd-Mo interaction in terms of structural properties and catalytic activity[3]. In the case of bimetallic supported catalyst, several studies have addressed the

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effect of the sequence of impregnation on the catalyst characteristics, without arriving to a clear conclusion[4-6]. $CuCo/SiO_2$ catalysts were significantly affected by the impregnation sequence; the catalyst prepared by co-impregnation method yielded better catalytic performances for the reaction of higher alcohol synthesis[5]. On the contrary, there wasn't clear effect of impregnation sequence on the formation of Pt/Ni bimetallic nanoparticles supported on γ-Al_2O_3 catalysts tested on the selective hydrogenation of acetylene to ethylene[6].

EXPERIMENTAL

Materials and methods

Wet impregnation was used in the production of coimpregnated (C) and sequential (S) catalysts; γ-Al_2O_3 was used as support, impregnated with the appropriate quantity of palladium chloride ($PdCl_2$) and ammonium heptamolybdate ($(NH_4)Mo_7O_{24}.6H_2O$) aqueous solutions to generate the different metallic loads on the support (Table 1 and 2). During impregnation process the support was kept under moderate vacuum and mixed in an ultrasound mixer (Branson B220) for 90 mins; the remaining aqueous solution was evaporated at 120^{o}C; the resulting dried sample was heated in inert atmosphere for 4 hrs at 600 C. A total of 17 catalysts were produced.

Table 1: Procedure and load distributions of bimetallic catalysts

Impregnation strategy	Load distributions		
Coimpregnated	1.25 Pd 3.75 MoC	2.5 Pd 2.5 MoC	3.75 Pd 1.25 MoC
Sequential	1.25 Pd 3.75 MoS	2.5 Pd 2.5 MoS	3.75 Pd 1.25 MoS
Sequential	1.25 Mo 3.75 PdS	2.5 Mo 2.5 PdS	3.75 Mo 1.25 PdS

Table 2: Procedure and load distributions of monometallic catalysts

Impregnation strategy	Load distributions			
Impregnated	1.25 Pd	2.5 Pd	3.75 Pd	5 Pd
Impregnated	1.25 Mo	2.5 Mo	3.75 Mo	5 Mo

All bimetallic catalysts have a total active agents (Pd and/or Mo) load of 5% in weight; the number that precedes the chemical symbol represents the percentage in weight of this metal; the letter S or C at the end designated the impregnation strategy; in sequential impregnation, the order in which the chemical symbols are written represents the sequence in which the metals were impregnated. The catalyst were pretreated in oxidative conditions in dry air with a total flow of 70 mL/min (STP) and with constant increment of the temperature (5°C/min) from room temperature to 450°C and kept at these condition for 120 mins, then the temperature was increased to 600°C at the same rate. The condition of 600°C was maintained for 240 mins; natural cooling allowed. The catalysts were stored in inert atmosphere (He) to avoid degradation. ODHP catalytic activity of the catalysts was evaluated in a packed bed reactor (stainless steel, 6.3 mm i.d.) containing 100 mg of oxidized catalyst sample (particle size between 200-250 microns). The reaction mixture (100 mL/min) contained propane, oxygen and helium as balance gas, flows were controlled using Bronkhorst High-Tech series F-200 and F201 mass flow meters; propylene, carbon monoxide, dioxide and water were determinate by gas chromatography. Propane conversion (X) and propylene selectivity (S) were evaluated at three temperatures (400, 450 and 500°C). Preliminary experiments indicated the absence of mass transfer restrictions for the reaction conditions.

RESULTS AND DISCUSSION

Total superficial area (TSA) was determined using the BET method; values of the total volume of porosity (VTP) were obtained using the Gurvitsch's method. Fig. 1 shows the behavior of the total surface area as a function of the Mo content; molybdenum content increases from left to right in the X axis for bimetallics Pd-Mo and monometallic Mo catalysts. Palladium content increases from right to left in the X axis for bimetallics Pd-Mo and monometallic Pd catalysts. All bimetallic catalysts have a total active agents load of 5% in weight (i.e. the tendency line of PdMoC catalyst at the 1.25% Mo value represents the 3.75 Pd1. 25 MoC catalyst and the tendency line of Pd at the 1.25% Mo value represents the 3.75 Pd).

Fig. 1 shows that TSA of monometallic catalysts are inversely proportional with the load; however, the bimetallic catalysts show different behavior from the monometallics. The impregnation strategies PdMoS and MoPdS generate catalysts with intermediate values of TSA lower than monometallic Pd. However, the PdMoC strategy presents big fluctuations of the TSA values. Behaviors like those presented by the TSA are related with changes in the mechanisms of the precursors adsorption on the support. Fig. 2 shows the behavior of TPV values as a function of Mo and Pd content and it presents similar behavior as the TSA, which strengthens the hypothesis of variation of the mechanisms of the precursor adsorption as a function of the load and the preparation strategy.

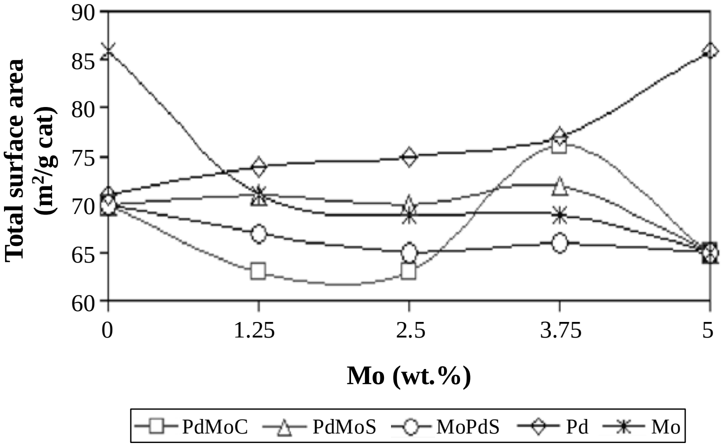


Fig. 1: Total surface area as a function of the Mo content (wt.%)

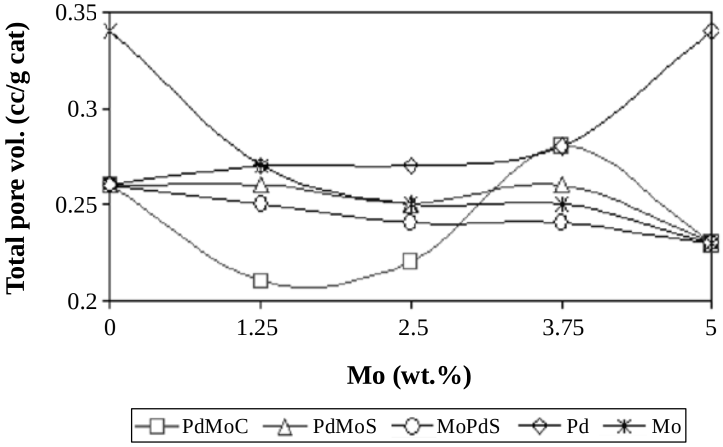


Fig. 2: Total pore volume as a function of the Mo content (wt.%)

Results of metal surface area (MSA) are presented in Fig. 3 as a function of Mo and Pd content. In the calculations of MSA, the number of metal atoms per square meter of Pd was taken as 1.27 x 10^{19} and assuming H/Pd ratio of 2:1. Hydrogen adsorption on molybdenum has been reported as neglectable at temperatures lower than 100^oC[7]. The MSA values of monometallic Pd catalyst are directly proportional and almost lineal with the Pd load; the bimetallic catalysts present MSA values smaller than their respective monometallic Pd catalyst, except for the 3.75 Mo 1.25 PdS catalyst.

The slopes in Fig. 3 represent the rate of change of the active area of the metallic Pd as the load of Mo is increased, it can be observed for MoPdS and PdMoC strategies that this slope is negative for values between 1.25 and 2.5% Mo; from this Mo content it has an abrupt change to values almost similar to zero or slightly positive up to 3.75% Mo. Similar behavior happens for the strategy PdMoS but the change of the slope to values almost similar to zero or slightly positive occurs closer to values of 1.25% Mo; tendency which is well correlated with that obtained in the loss of total surface area, in which changes in the mechanisms of adsorption reveal changes in the values of total surface areas. These changes of mechanisms are accountable under the consideration that during the process of impregnation, different competitive adsorption mechanisms are presented as a function of the relationship between the amounts of Mo and Pd in the impregnating solutions and also of the impregnation strategy. It is well known that the molybdenum adsorbs on alumina as MoOx species (X depends on the conditions of oxidation during pretreatment)[8-10].

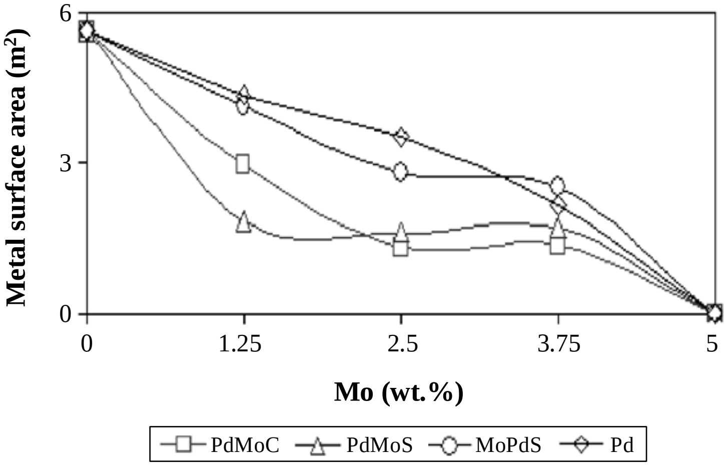


Fig. 3: Metal surface area as a function of the Mo content (wt.%)

In the catalysts prepared by MoPdS strategy in which Pd adsorbs on a support, which already contains species MoOx impregnated, the mechanisms of adsorption that could explain the behavior of the MSA with regard to the percentage of Mo are: 1) occupation of the pore walls available for metal precursors, by the formerly impregnated MoOx species which reduce the MSA, via the formation of large Pd crystallites on top or surroundings of the MoOx species previously impregnated[8]; this mechanism is in agreement to the low values of TPV obtained for these catalysts, 2) textural promotion of the Pd by MoOx species, which act as diluents and that allow the formation of small and better distributed Pd crystallites[9]. These results are in agreement with the values of dispersion obtained for catalysts with Mo contents above 2.5 and up to 3.75%. It can also be deduced that in the MoPdS impregnation strategy, the mechanism of pore occupation by species MoOx prevails for values between 1.25% and 2.5% Mo; while the mechanism of textural promotion begins to be significant for values between 2.5% and 3.75% Mo.

For catalysts prepared by PdMoS impregnation strategy, in which the Mo adsorbs on a support that already has Pd crystallites, the mechanisms of adsorption that could explain the behavior of the MSA with regard to the percentage of Mo are: (1) Covering of the crystallites of Pd, previously impregnated, with species MoOx that are placed on top them[8]; (2) Textural promotion of the Pd by MoOx species, which act as diluent and that allow the formation of small and better distributed Pd crystallites[9]. Accordingly, PdMoS impregnation strategy in Fig. 3, at 1.25% Mo the mechanism of impregnation that prevails is the covering of Pd crystallites by MoOx species; the transition region of a mechanism to the other is presented at values higher than 1.25% and up to 3.75%, Mo where the mechanism of textural promotion prevails over the covering mechanism.

Fig. 4 shows the small contribution of monometallic Mo catalyst to the conversion of propane (less than 1%); the conversion is proportional to percentage of Pd. The bimetallic catalysts that contain 1.25% Mo present similar conversion values or smaller than their corresponding monometallic Pd catalyst. 2.5% Mo catalyst presents conversion values closer to the monometallic Pd catalyst, except the MoPdS catalyst which almost duplicates the conversion values of the catalysts prepared by the other strategies and its corresponding monometallic Pd catalyst. At 3.75% Mo content; all the preparation strategies have higher conversions than its corresponding monometallic Pd catalyst: 6.3 times for PdMoC strategy, 4.7 times for PdMoS strategy and 4 times for MoPdS strategy. The selectivity toward propene of the catalysts at 300°C is neglectable for mono and bimetallic catalysts.

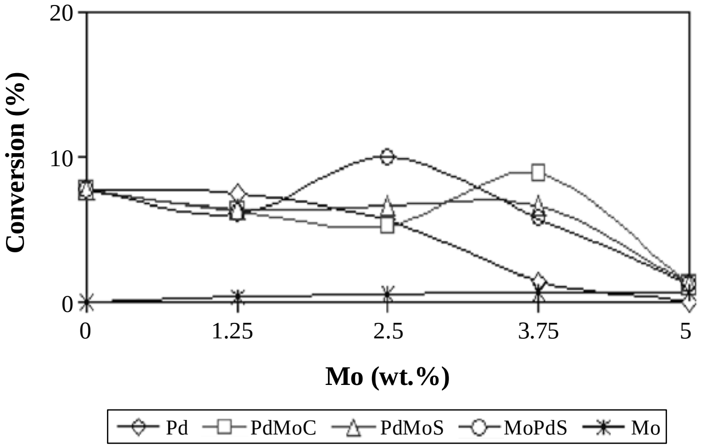


Fig. 4: Propane conversion at 300°C as a function of the Mo content (wt.%)

Fig. 5 shows the small contribution of monometallic Mo catalyst in the conversion of propane at 400°C (less than 1%); contrary to the proportional conversion behavior to the percentage of Pd, that presented the monometallic Pd catalyst at 300°C, its activity for 400°C is affected by marked fluctuations as a function of the content of Mo. The strategies of impregnation PdMoC and PdMoS present their maximum at 1.25% Mo and similar values for the Pd monometalic catalyst with 1.25 and 2.5% Pd; the strategy of impregnation MoPdS presents its maximum at 2.5% Mo. It can be highlighted that the maximum values of each one of the strategy surpasses their corresponding conversion value of the monometallic Pd catalyst in the following factors: 6.38 times for PdMoC, 3.7 times for PdMoS and 2.58 times for MoPdS.

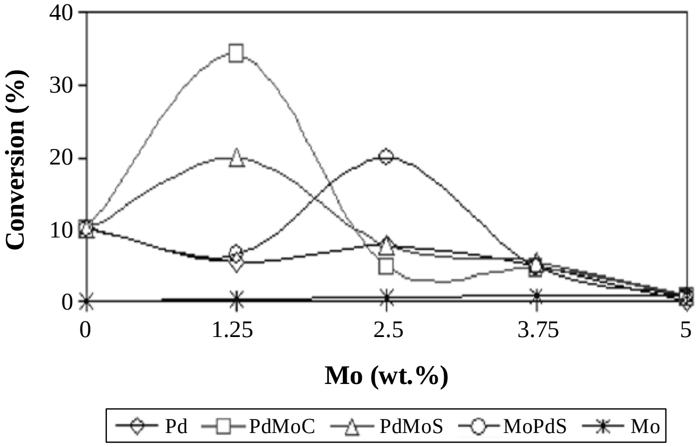


Fig. 5: Propane conversion at 400°C as a function of the Mo content (wt.%)

Selectivity results at 400°C (Fig. 6) shows that PdMoS and PdMoC present an almost identical behavior with a maximum of selectivity at 3.75% Mo (closer to the value of the monometallic Pd catalyst) and minima at 1.25% Mo (under the monometallic Pd catalyst); on the other hand, the strategy MoPdS presents its maximum of selectivity at 1.25% Mo (16.1% of selectivity).

The specific activity to propene is shown in Fig. 7. It can be observed that in terms of generation of molecules of propene for square meter of active site, the behaviors of the impregnation strategies vary notably regarding the selectivity.

Catalysts prepared by MoPdS strategy present specific activity values smaller than the specific activity values of the monometallic Pd and decrease their specific activity values as the Mo content increases; even so, the 1.25 Mo 3.75 PdS catalyst presents higher specific activity than the 5 Pd. The catalysts prepared by PdMoC strategy increases the specific activity with the percentage of Mo (from 0 to 3.75), and their maximum specific activity value is at 3.75% Mo, which is higher than the specific activity of its corresponding monometallic Pd catalyst. The catalysts prepared by PdMoS strategy show specific activity values closer to the monometallic Pd catalyst, and this strategy surpasses lightly the specific activity values of the monometallic Pd catalyst at 1.25% and 3.75% of Mo.

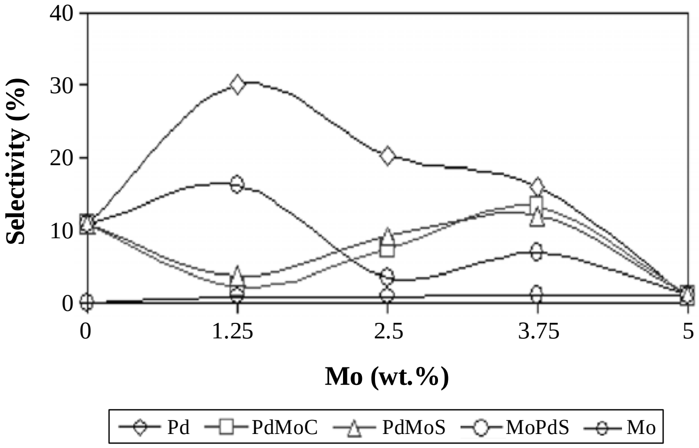


Fig. 6: Propene selectivity at 400°C as a function of the Mo content (wt.%)

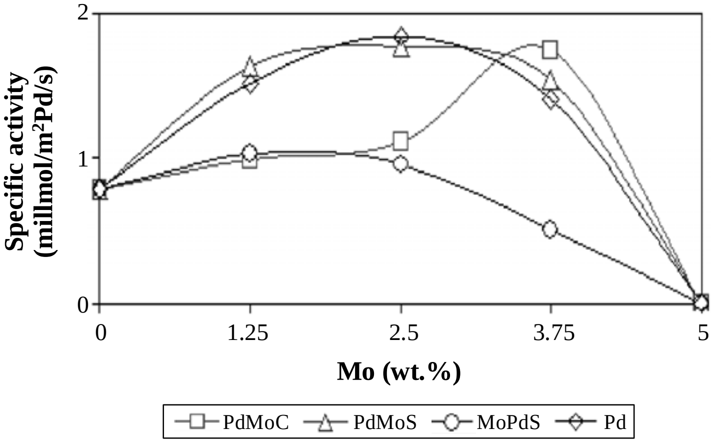


Fig. 7: Specific activity at 400°C as a function of the Mo content (wt.%)

The behavior of the conversion at 500°C (Fig. 8) differs from the behaviors obtained for 300 and 400°C. All the impregnation strategies follow the same behavior of the monometallic Pd catalyst; only the PdMoS and MoPdS strategies present conversion values slightly bigger than its respective monometallic Pd catalyst at 1.25% Mo; the others conversion values are closer to the conversion of the monometallic Pd catalyst.

Fig. 9 describes the propene selectivity behavior at 500°C; selectivity increases as the percentage of Mo increases up to values close to 3.75% Mo. At this point and in 2.5% Mo the bimetallic catalysts present better selectivity than its corresponding monometallic Pd, being this the only composition where the monometallic Pd catalyst has lower selectivity than the bimetallic catalysts.

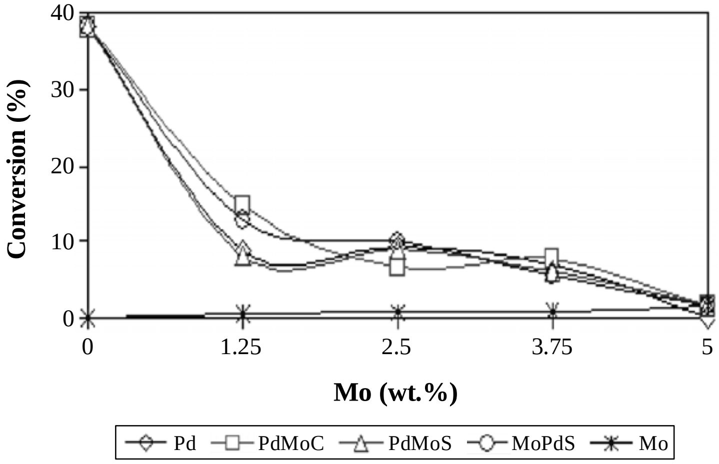


Fig. 8: Propane conversion at 500°C as a function of the Mo content (wt.%)

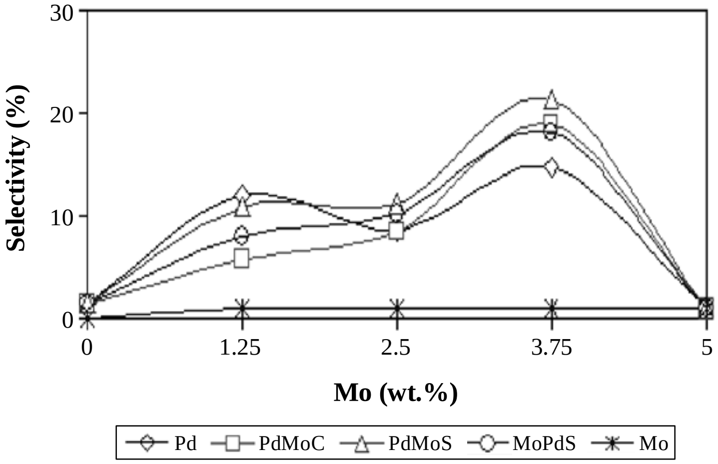
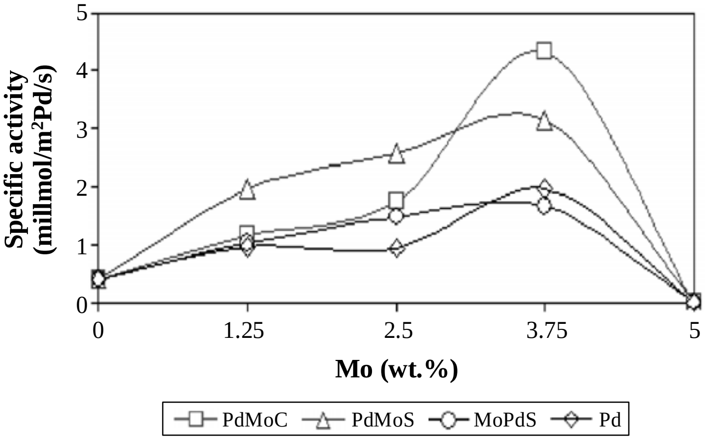


Fig. 9: Propene selectivity at 500°C as a function of the Mo content (wt.%)

Fig. 10 shows the specific activity as a function of the % Mo, at the temperature of 500°C, in which most of the catalysts present a better specific activity than its corresponding monometallic Pd catalyst.



Fig, 10: Specific activity at 500°C as a function of the Mo content (wt.%)

CONCLUSION

The behavior of the total, metallic superficial areas and total volume of pore is correlated as a function of the load relationship Mo/Pd and the impregnation strategy. Except for the 3.75Mo 1.25PdS catalyst, all the bimetallic catalysts of Pd-Mo present smaller MSA than their corresponding monometallic Pd catalysts; this could be ascribed to promotion of the Mo on the Pd and the impregnation strategies covered in this study. The increment of the specific activities to propene for the bimetallic catalysts in comparison with the monometallic catalysts may indicate modification on the reaction mechanism and the configuration of the surroundings of the active site.

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