Reaction Network for Selective Oxidation of Propene on a (Mo-Pr-Bi)O/SiO$_2$ Catalyst

J. M. López Nieto, J. M. D. Tascón,† and G. Kremenić*
Instituto de Catálisis y Petroleoquímica, C. S. I. C., Serrano 119, 28006 Madrid, Spain
†Instituto Nacional del Carbón y sus Derivados, C. S. I. C., Apartado 73, 33080 Oviedo, Spain
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Oxidation of propene on a $Mo_4Pr_{0.5}Bi_{0.5}O_x/SiO_2$ catalyst was studied in order to establish the reaction network. In the temperature range 598—653 K the primary reaction products were propenal (main product), acetone, acetaldehyde, and carbon dioxide. Other products (mainly aldehydes and acids) could be classified as secondary reaction products. From studies of oxidation of the primary unstable products and the kinetics of formation of minor primary products it is concluded that both, acetaldehyde and carbon dioxide, are formed through parallel and consecutive reactions. Acetone formation is strongly influenced by reaction temperature, probably due to changes in the active centers of the catalyst.

Catalytic oxidation of olefins gives rise to a large number of products, and only a close control of catalyst characteristics and/or operation conditions may selectively favor a given type of reaction: allylic oxidation, oxyhydration, or scission reactions.[1,2]

A limited amount of published work has dealt with establishment of the overall reaction network in olefin selective oxidation processes. For allylic oxidation of propene only propenal and carbon oxides formation pathways have generally been taken into account.[3–5] However, many other products are usually originated in this process through parallel and/or consecutive reactions. For different catalytic systems, various authors[6–8] have proposed that propenal forms directly form propene while acetaldehyde and carbon oxides are formed through both, parallel and consecutive reactions; the origin of acetaldehyde and carbon oxides is not clear. Margolis[9] proposed that acetaldehyde forms directly by oxidation of the double bond, while Keulks et al.[10] suggested that acetaldehyde comes almost exclusively from propenal oxidation. In the case of CO$_2$, the situation is much more complicated since, depending on the catalyst used, parallel-consecutive pathways by propene and propenal oxidation,[11] as well as only consecutive reactions from propenal[9,10] have been proposed.

In a previous work, the kinetics of propene and isobutene oxidation at 653 K were studied on a (Mo-Pr-Bi)O/SiO$_2$ catalyst. It was deduced that similar mechanisms operate for both reactants,[12] and that propenal is formed from propene through a redox mechanism.[13] The aim of the present work is to establish the reaction network for propene oxidation on the same catalyst, from analysis of: i) Products distribution; ii) oxidation of primary reaction products; iii) influence of operation conditions on formation of minor primary products; and iv) kinetics of formation of minor primary products.

Experimental

Catalyst Preparation and Characterization. The catalyst was prepared by sequential impregnation of BASF D-11-11 silica particles. Impregnations were carried out respectively with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$ (Merck, p.a.) and with an acid solution of $Bi(NO_3)_3$ (Koch Light) and $Pr(NO_3)_3\cdot 5\ H_2O$ (Fluka, a.g.). The final calcination was carried out at 823 K for 16 h.[13]

The atomic ratio in the oxide catalyst was Mo:Pr:Bi=4:0.5:0.5, with a concentration of MoO$_3$ of 20 wt%. The BET surface area was 55.6 m^2 g^{-1} the pore volume being 1.31 cm^3 g^{-1} and the mean pore radius 40 nm. X-Ray diffraction showed the presence of three crystalline phases: MoO$_3$, α-Bi$_2$O$_3$, and Bi$_2$MoO$_6$. By means of Analytical Electron Microscopy the presence of highly dispersed praseodimium on the catalyst surface was observed.

Methods. The flow system and calculations used for catalytic activity and selectivity determination have been described previously.[14] Catalyst samples with a particle size of 0.042—0.059 cm, in amounts from 0.2 to 0.8 g, were diluted with carborundum (0.059 cm particle size) in order to keep a constant catalytic bed volume (5.6 cm^3). Blank tests were carried out with a reaction mixture of molar composition $C_3H_6:O_2:He:H_2O=20:30:30:20$. In the absence of catalyst, total conversion at 673 K was lower than 0.3% (molar). No diffusion effects on reaction rate were found at 653 K for propene flows greater than 1.1×10^{-2} mol h^{-1} and catalyst particle sizes lower than 0.141 cm. Prior to each experiment, the catalyst was placed in the reactor and heated to 573 K in a helium stream. Then, the reaction mixture was introduced while heating until reaching the reaction temperature. The system was left to reach stead-state conditions for 1.5 h before analyzing the reaction products. Duplicated experiments showed the constancy of catalytic activity with time.

Results

Nature and Stability of Products. In Fig. 1 the influence of contact time, W/F (g cat. h mol^{-1} C$_3$H$_6$) on total propene conversion at different temperatures (593—653 K) for a mixture containing a molar ratio $C_3H_6:O_2:He:H_2O=20:30:30:20$ is shown. From yields to the different products selectivity curves, as proposed by Corma et al.,[15,16] were obtained. The plots corresponding to a temperature of 653 K are given in Fig. 2 (qualitatively similar results were obtained at the other temperatures studied).

We detected a number of products in propene oxidation on our catalyst. They originate either from partial oxidation, partial degradation or total oxidation reactions. From the shape of selectivity curves one can establish the nature and stability of the different products.[15] It can be deduced from plots in Fig. 2 that propenal, acetone, and acetaldehyde are primary products, while acrylic acid, acetic acid, formic acid, and ethylene are secondary products. In the case of CO and CO_2 it is not possible from Fig. 2 to differentiate clearly if they are either primary or secondary products.

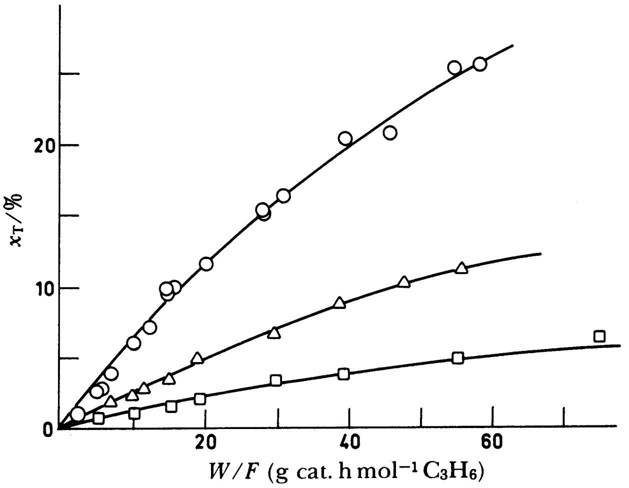

Fig. 1. Effect of contact time, W/F, on total conversion at 593 K (○), 623 K (△), and 653 K (□). Molar composition of the reaction mixture: 20% propene, 30% oxygen, 30% helium, and 20% water.

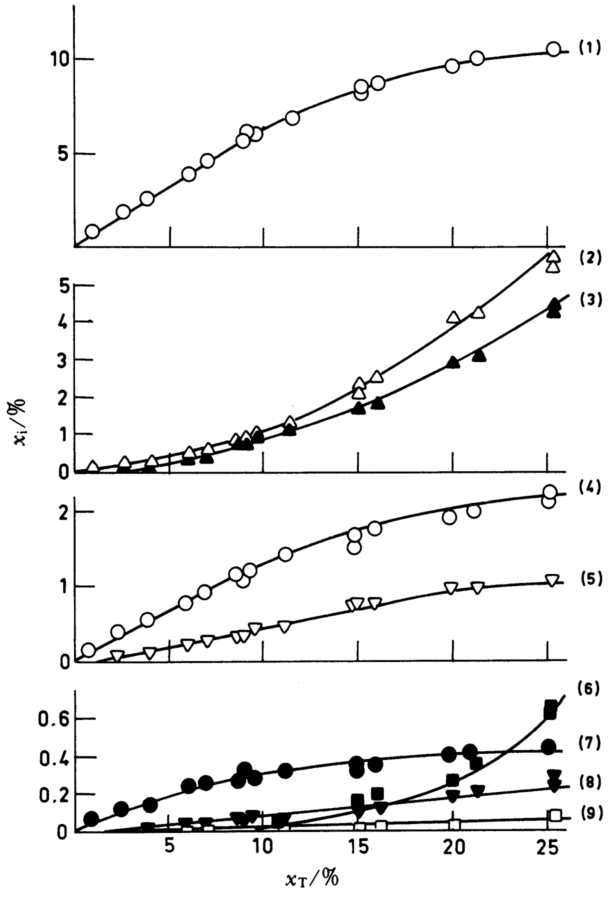

Fig. 2. Variation of yields to the different reaction products of propene oxidation with total conversion at 653 K. Same reaction conditions as for Fig. 1. (1), propenal; (2), CO_2; (3), CO; (4), acetaldehyde; (5), acetic acid; (6), acrylic acid; (7), acetone; (8), formic acid; (9), ethylene.

From plots of selectivity to each product (S_i) vs. total conversion (Fig. 3) it can be observed that selectivities decrease with increasing total conversion in the case of propenal, acetone, and acetaldehyde, thus clearly showing that these products are unstable. In the case of CO and CO_2 it is deduced that, while CO_2 is a primary+secondary product (with a selectivity of 6% at $x_T \rightarrow 0$), CO is merely a secondary product (selectivity at $x_T \rightarrow 0$ equal to zero or very small). On the other hand, at lower temperatures and/or for propene-poor reaction mixtures, the presence of CO was not detected at total conversions lower than 5%.

In the case of acetic acid, formic acid, and ethylene, selectivities initially increase with total conversion and afterwards remain constant or diminish. This shows

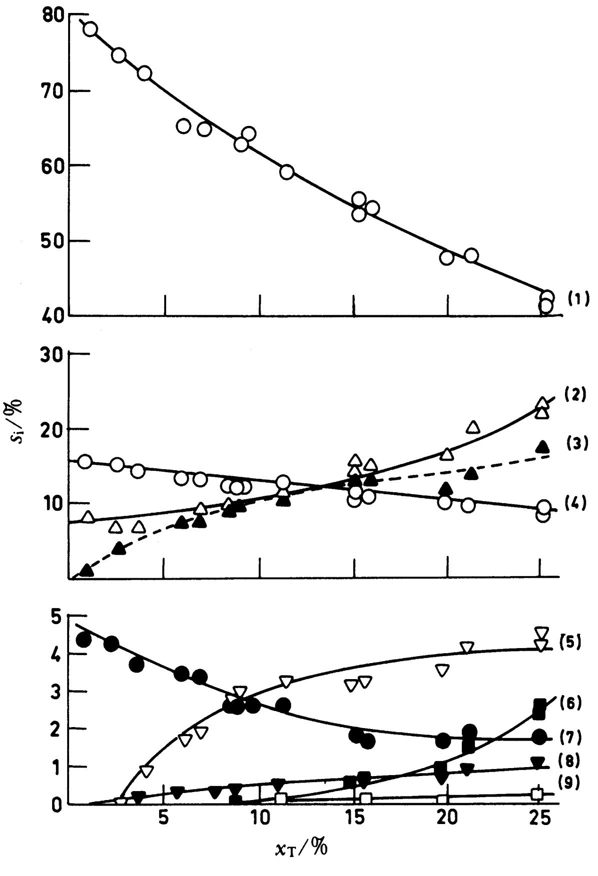

Fig. 3. Variation of selectivities to the different reaction products of propene oxidation with total conversion at 653 K. Same reaction conditions and symbols as for Fig. 2.

the stable character of these products. The very low yield of acrylic acid make it difficult to evaluate the stability of this product, especially at high temperatures and/or high conversions.

Oxidation of Primary Products. Experiments to study oxidation of unstable primary products were carried out in reaction conditions similar to those used for propene oxidation, i.e. at 653 K and molar ratio reactant: O_2 : He : H_2O=20 : 30 : 30 : 20.

In propenal and acetaldehyde oxidations it was observed that homogeneous reaction takes place in a large extent, it being thus impossible to carry out a quantitative study on the nature and type of reaction products. However, the remarkable differences between homogeneous and catalytic reaction permit to make a qualitative study. The results obtained for both, propenal and acetaldehyde, are shown in Table 1.

Propenal: In homogeneous oxidation of propenal, CO appears as the main reaction product. The other products (in a decreasing selectivity order) are CO_2, acetic acid, ethylene, formic acid, acetaldehyde, and small amounts of acrylic acid. However, a significant increase in selectivity to acrylic acid and acetaldehyde is observed for the catalytic reaction in addition to a moderate increase for acetic acid and CO_2 and an important decrease in CO production. Consequently, it seems that propenal oxidation leads preferentially to formation of acrylic acid as well as degradation products: acetaldehyde, acetic acid, CO, and CO_2.

Acetaldehyde: In homogeneous oxidation of acetaldehyde, carbon oxides, and formic acid predominates as reaction products while an increase of CO_2, acetic acid, ethylene, methane, and formaldehyde formation and a decrease of formic acid and CO production are observed in the catalyzed reaction. In catalytic reaction conditions, oxidation to acetic acid could take place simultaneously with two degradation pathways, the one leading to formaldehyde and methane and the other to total oxidation products.

Acetone: No homogeneous oxidation was detected in the case of acetone. Study of the nature of oxidation products was carried out by varying the contact time, W/F. CO_2, CO, formic acid, and acetaldehyde were the main reaction products in addition to small amounts of butandione, propenal, and ethylene.

In Table 2 the results obtained at 653 K for different contact times are given. From these results it can be concluded that both, CO and CO_2, are primary+secondary stable products; formic acid, acetaldehyde, and acetic acid are primary, unstable products, while ethylene, propenal, and butandione are secondary, unstable products.

Influence of Operation Conditions on Primary Products Formation. For the study of influence of reaction temperature and/or oxygen: propene ratio in the reaction mixture, changes in yield to the different reaction products and in initial selectivities (i.e., selectivities for $x_T \rightarrow 0$) to the primary reaction products were monitored. This study was carried out at temperatures ranging from 593 to 653 K, and oxygen: propene ratios varying from 1.5 to 6. The corresponding results are shown in Table 3.

No changes in nature of the primary reaction products were found. An increase of reaction temperature led to increase of initial selectivity to propenal and to an important decrease of initial selectivities to acetone and CO_2, the decrease being less marked the case of acetaldehyde. On the other hand, increase of oxygen: propene ratio in the reaction mixture caused a decrease of initial selectivities to propenal and acetone, and an increase of selectivities to acetaldehyde and CO_2.

Kinetics of Minor Primary Products Formation. The detailed kinetic analysis of propenal formation

Table 1. Propenal and Acetaldehyde Oxidation[a)]

Reactant	Type of reaction	x_T	S_i/%								
		%	CH_2=CHCOOH	CH_3CHO	CH_3COOH	HCOOH	HCHO	C_2H_4	CH_4	CO	CO_2
CH_2=CHCHO	Homogeneous	4.03	0.9	3.1	8.2	4.6	0	5.9	0	66.2	11.1
	Catalytic[b)]	6.32	15.1	20.2	12.1	4.8	0	4.6	0	32.4	10.8
CH_3CHO	Homogeneous	2.10	0	t[c)]	3.1	10.8	0.4	0.7	2.5	64.9	17.6
	Catalytic[b)]	4.05	0	t[c)]	6.2	5.3	2.1	3.1	6.8	47.1	29.4

a) Experimental conditions in text. b) W/F=1.00 g cat. h mol^{-1} C_3H_4O (or C_2H_4O). c) $CH_3COCOCH_3$. t=traces.

Table 2. Acetone Oxidation[a)]

W/F (g cat. h mol^{-1} C_3H_6)	X_T	S_i/%							
	%	$CH_3COCOCH_3$	CH_2=CHCHO	CH_3COOH	CH_3CHO	C_2H_4	HCOOH	CO_2	CO
0.30	5.34	0	0	33.9	11.1	0	4.0	37.8	13.3
0.92	9.94	t	t	29.3	9.8	0	4.6	43.5	13.1
1.62	17.45	0.9	0.3	27.6	8.1	t	5.0	43.7	14.4
4.31	42.87	1.0	1.4	23.8	7.5	0.4	2.8	44.6	18.5

a) Experimental conditions in text. t=traces.

Table 3. Initial Selectivities to Primary Products in the Oxidation of Propene on Mo-Pr-Bi-O/SiO_2

Product	S_i/%					
	A[a)]			B[b)]		
	593 K	623 K	653 K	593 K	623 K	653 K
CH_2=CHCHO	42	65	80	37	60	75
CH_3COCH_3	33	13	6	30	11	3.5
CH_3CHO	18	17	12	23	18.5	15.5
CO_2	7	5	2	10	7.5	6

a) Mixture A: oxygen/propene=1.5. b) Mixture B: oxygen/propene HL=6.0.

during propene oxidation over the same catalyst used in the present work was carried out previously and published elsewhere.[13)] However, the important differences found among the kinetics of formation of the rest of products justified to undertake a more detailed analysis, which was made by the initial rates technique, i.e., at total converisons lower than 7%. Influence of the main operation variables (temperature, contact time, and partial pressure) was examined. For studying the influence of reaction mixture composition, the conventional technique of modifying the concentration of one reactant while keeping constant the concentration of the rest of reactants was used.

Kinetic measurements were carried out in the following ranges: propene partial pressure, 0.047—0.374 atm (with oxygen partial pressure constant and equal to 0.280 atm); oxygen partial pressure, 0.065—0.470 atm (with propene partial pressure constant and equal to 0.190 atm); reaction temperature, 593—653 K. In all cases a constant water partial pressure of 0.190 atm was kept, as well as a helium partial pressure balance to 1 atm.

For the study of dependence of the rates of formation of the different reaction products on composition of the reaction mixture an empirical rate equation was used:

$$\ln r_i = \ln k_i + a \ln p_H + b \ln p_O, \qquad (1)$$

where k_i is the rate constant for formation of product i, and a and b are the apparent reaction orders for propene and oxygen, respectively. From plots of ln r_i vs. ln p_H or ln p_O (p_H and p_O being the partial pressures of propene and oxygen, respectively), straight lines were obtained whose slopes gave the apparent reaction order for a given reactant (Table 4).

In the cases of acetaldehyde and CO_2 and at temperatures of 593 and 623 K two different reaction orders for propene were found: at pressures lower than 0.19 atm the apparent order was greater than unity, while it was lower than 1 at pressures greater than 0.19 atm. This kind of behavior was not observed in the case of oxygen.

Values of k_i were determined by linear fitting of experimental and calculated rate values for the different products at 593, 623, and 653 K; they are given with their 95% confidence intervals (in parenthesis) in Table 4. In the case of acetaldehyde and CO_2 the values reported were determined at reaction temperatures of 593 and 623 K from results obtained at propene partial pressures lower than 0.19 atm, while at 653 K results correspond to the whole partial pressure range (0.047—0.374 atm). Finally, from plots of ln k_i vs. $1/T$, apparent activation energies for each product were calculated. Their values are given in Table 5.

Table 4. Power Law Model Parameters (k_i, a, b, with r in 10^{-4} mol g^{-1} h^{-1})

Product	Temp/K	$k_i \times 10^3$	a	b
CH_3COCH_3	593	1.34(0.02)	0.93	0.26
	623	1.37(0.04)		
	653	1.38(0.01)		
CH_3CHO	593	4.50(0.04)[a)]	1.05[a)] 0.42[b)]	0.75
	623	8.23(0.04)[a)]	1.20[a)] 0.81[b)]	0.52
	653	16.6(0.1)	1.26	0.50
CO_2	593	3.67(0.01)[a)]	1.31[a)] 0.47[b)]	0.26
	623	6.75(0.03)[a)]	1.31[a)] 0.73[b)]	0.34
	653	16.08(0.05)	1.41	0.29

a) p_H=0.047—0.190 atm. b) p_H=0.190—0.370 atm.

Table 5. Apparent Activation Energies for the Formation of Primary Products (593—653 K)

Product	E_a/KJ mol^{-1}
CH_2=CHCHO	117.0±15.5
CH_3COCH_3	1.7±1.3
CH_3CHO[a)]	69.4±10.2
CO_2[a)]	78.6±11.3

a) Calculated for $p_H \leqslant 0.19$ atm.

Discussion

Reaction Network. From the results of selectivity curves (Figs. 2 and 3), a first scheme can be drawn for propene oxidation:

$$\text{propene} \rightarrow \text{propenal} + \text{acetone} + \text{acetaldehyde} + CO_2.$$

Primary products containing three carbon atoms (propenal and actone) are both unstable. Therefore, increase of temperature influences unequally selectivities to these products (Table 3). Propenal is usually obtained at temperatures above 523 K, while acetone forms below this temperature.[1] This effect of reaction temperature on selectivities probably depends on the different ways of oxygen incorporation to the catalyst surface. In a previous study carried out in this laboratory, oxygen adsorption experiments were carried out on the same catalyst used in the present work in the temperature range corresponding to the catalytic reaction.[13] The oxygen adsorption isobar exibited an ascending branch; for example, oxygen coverages at 25 mmHg (1 mmHg=133.322Pa) increased from 0.05% (572 K) to 1.39% (621 K). This increase of oxygen adsorption with temperature is probably associated with the appearance of dissociative adsorption.

If both, oxyhydration and allylic oxidation reactions are competitive, selectivities to acetone or propenal will depend on the relative formation rates of these products.[17] The reactivity of either adsorbed species or oxygen ions present in the catalyst will monotonically increase with reaction temperature. Consequently, as reaction temperature increases, a change in the nature of reactive centers and, hence, in the reaction mechanism will take place.[18,19]

From results of studying catalytic oxidation of propenal, secondary reactions may be summarized as follows:

propenal → acrylic acid + acetic acid + acetaldehyde
+ CO_2 + CO.

Margolis[9] proposed that propenal oxidation leads preferentially to formaldehyde and carbon oxides. Cathala and Germain[6] found carbon oxides and acetaldehyde when this reaction was carried out on Mo-Bi-O catalysts. Indeed, reactions of propene methatesis are well characterized on MoO_3/SiO_2 catalysts working at high temperature, ethylene being formed.[20] The auto-oxidation processes proposed by Semenov[21] may explain formation of the different products. Finally, it is clear that acetic acid proceeds from propenal consecutively.

Catalytic oxidation of acetone leads to the following products:

acetone → acetic acid + acetaldehyde + formaldehyde
+ CO + CO_2.

Acetone forms by propene oxidation; however, 2-propanol was not detected, contrary to reports of some authors[22,23] concerning both, propene and acetone oxidation. This absence of 2-propanol may be due either to a small yield to acetone in propene oxidation, and/or to a rapid conversion of this alcohol into ketone.[22,24]

Acetaldehyde is a primary product (from propene degradation), but it also forms by decomposition of C_3-oxygenated products. Different possible pathways have been suggested for acetaldehyde formation, either from propene via allylic intermediate,[9] or by double-bond break[25] and/or by propenal oxidation.[6,26] In catalytic oxidation of acetaldehyde:

acetaldehyde → acetic acid + formic acid + CO + CO_2,

carbon oxides formation seems to be the main reaction pathway, and takes place through decomposition of the different secondary products.[6,27]

In summary, carbon oxides seem to be the only stable reaction products. However, while CO_2 is a primary+secondary product, CO is merely a secondary product (Fig. 3). On the other hand, the possibility that at higher temperatures CO may be produced directly from propene cannot be discarded. In any case, CO production at high temperatures by consecutive reaction is higher than that of CO_2; this fact could explain why, at high conversions, the amount of CO produced is higher than that of CO_2.

Concerning the main secondary reaction products, formation of acrylic acid may be ralated to propenal oxidation on the catalyst surface; this is in agreement with IR spectroscopic studies of propenal adsorption on different catalysts.[28] Acetic acid comes from oxidation of primary products,[23,24] but the most favorable route is acetaldehyde oxidation. Finally, the presence of large amounts of acetic acid can be explained as due to consecutive oxidation of acetaldehyde.

From the above consideration, the overall reaction network given in Fig. 4 is proposed. Formation of ethylene and methane was not taken into account in this scheme because these products appeared in very minor concentrations. Formation of these products seems to take place through a pathway very different from those observed for the rest of reaction products. Their appearance could be explained on the basis of auto-oxidation processes of propenal and acetaldehyde, respectively.[6,10,21]

Kinetic Results. In a previous work[13] the activation energy for propenal formation from propene oxi-

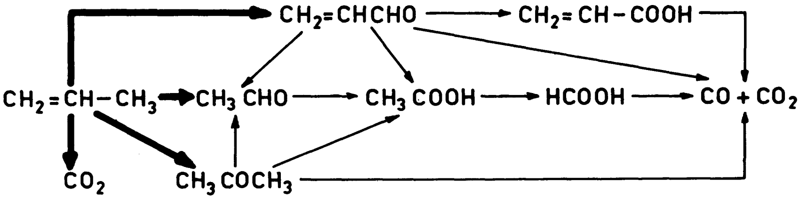

Fig. 4. Simplified reaction network for the oxidation of propene on $Mo_4Pr_{0.5}Bi_{0.5}O_x/SiO_2$ catalyst. ➧, primary reactions; →, secondary reactions.

dation over the $Mo_4Pr_{0.5}Bi_{0.5}O_x/SiO_2$ catalyst was determined, its value being similar to that one obtained for USb_3O_{10}[5] but much lower than that one reported for bismuth molybdate.[29]

An important feature is the low activation energy (1.7 kJ mol^{-1}) found for acetone formation, in contrast to values obtained for the rest of products. This can be interpreted as due to a decrease of the number of active centers present in catalyst surface with increasing temperatures. Moreover, increase of reaction temperature favorises acetone elimination via secondary reactions. The poor fit obtained for the influence of temperature on the rate constant, for acetone formation is due to the combined effect of these two phenomena.

Apparent reaction orders for acetaldehyde and CO_2 formation were strongly dependent on the hydrocarbon partial pressure; only at a temperature of 653 K constant values were obtained for the apparent reaction orders along the whole propene partial pressure range, their values being 1.26 for acetaldehyde and 1.41 for CO_2. It is rather unusual to obtain values for reaction orders greater than unity; however, such values have been previously reported in both, acetaldehyde[7] and carbon oxides[4,30] formation. This fact could be explained by simultaneous presence of both, consecutive and parallel pathways in propene degradation. However, this fact alone cannot explain the effect observed if a value of 1 is considered for the reaction order corresponding to both pathways.

It seems logical to conclude that acetaldehyde and CO_2 formation on our catalyst follow similar pathways, namely both, consecutive reaction (from primary products), and parallel reaction (from propene). Consequently, a complex kinetic equation results taking into account these two different pathways. On the other hand, the similarity of values obtained for activation energies for acetaldehyde and CO_2 formation (69.4 and 78.6 kJ mol^{-1}, respectively) is a further evidence for the similarity of these phenomena.

Finally, it seems convenient to recall some characterization results in order to compare our catalyst with the well-known bismuth molybdate catalyst. The $Mo_4Pr_{0.5}Bi_{0.5}O_x$ catalyst shows a high selectivity for propene oxidation to propenal[13] (redox mechanism) but a low selectivity for 2-methyl propene oxidation to 2-methyl propenal[31,32] (competitive redox and stationary state of adsorption mechanism). The most active and selective binary Mo-Pr oxide catalysts (i.e., those with Mo/Pr=4—6.7) for propene oxidation contain Pr_2O_3 instead of Pr_6O_{11}, as well as a highly dispersed MoO_3 phase.[33] For a Mo/Pr ratio equal to 4, the most active and selective ternary Mo-Pr-Bi catalysts (those with Mo/Bi=13.3) show the highest surface acidity in this series.[34] The increase of selectivity is ascribable to the well-known ability of bismuth to active propene in the form of allylic species.[35] On the other hand, ESR studies on Mo-Pr-Bi/SiO_2 catalysts, indicate that the presence of Pr in the Mo/Bi catalysts increase the dispersion of bismuth molybdates.[36] Additional work is in progress in our laboratories in order to get some further insight on the role of praseodimium in selective oxidation catalysts.

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