Catalytic decomposition of formic acid on oxide catalysts—an impulse-oscillation model approach to the unimolecular mechanism

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Abstract

An impulse-oscillation model (IOM) was used for a time description of catalytic acts in the reactions of catalytic decomposition of formic acid on oxide catalysts. The results of computation using the model show that for the dehydrogenation reaction the most important modes are the OCO bending in bidentate adsorbed formate ion and OH stretching on the catalyst surface while for the dehydration the asymmetric stretching OCO mode in the monodentate adsorbed formate ion and metal–oxygen stretching mode on oxide catalysts. These findings confirm the results obtained [R. Larsson, M.H. Jamróz, M.A. Borowiak, J. Mol. Catal. A: Chem. 129 (1998) 41] in our previous analysis of the SET model. Assuming the synchronization of eight vibrators to be important in the reactions system considered in the present paper, the IOM method predicted ranges of wavenumbers which are close to those wavenumbers found starting from the idea of a stepwise variation of activation energies. The best ranges for the dehydrogenation reaction are proposed. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Impulse oscillation model; Catalytic decomposition; Formic acid

1. Introduction

The decomposition of formic acid over solid phase catalysts is a classical reaction in heterogeneous catalysis. Many problems concerning this reaction have been highlighted through the years. In our recent paper [1] the selective energy transfer model (SET) [2] was used to address a question whether it is possible to use the activation energies to describe the mechanisms of dehydration and dehydrogenation reactions of formic acid decomposition. It was found that for the dehydration reaction the asymmetric stretching O–C–O mode and for the dehydrogenation reaction the O–C–O in plane bending mode are the modes which must be excited for the reactions to occur. In this paper we will present results of the same reactions with the impulse-oscillation model (IOM) making the assumption that the decomposition reaction is a unimolecular one.

Several models are commonly used for describing separately spatial, energetistic and time aspects of catalysis at molecular level. In a

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concept of an elementary catalytic system [3–9] all these aspects are combined together using spatial, energetistic and temporal molecular properties of the reactant and the catalytic center to describe the catalytic act. In particular, time conditions of a catalytic act are considered by the impulse-oscillation model (IOM) [3,5–9]. In this model frequencies of internal vibrations of the reactant and the center are the primary molecular parameters. The 'time parameters' (vibrational periods) contain also information on energy, chemical composition and geometry of the oscillators. The IOM model treats the molecule of reactant and the center as a set of their vibrational modes. The model calculates possible sets of vibration ranges within which synchronization of the appropriate momentary electron density distribution in reactant and in the center can be reached during the vibrations. The distribution is assumed to be important for the considered reaction step. Consequently, for a given reaction path, the reaction occurs at the time of synchronization if the necessary spatial and energy conditions are fulfilled.

2. Methods

The IOM model is based on a set of equations connecting the wavenumbers of the considered modes with moments of appearance of electron density distribution in the reactant and in the catalytic center, favourable for the reaction to occur. The momentary distribution of the electron density for each oscillator varies during the vibration, with a periodical reappearance in consecutive periods of vibration. The distribution can be related to momentary lengths of bonds in the different stages of the vibration. In practice, in the IOM model only three particular electron density distributions are used: the two extreme ones and the equilibrium distribution corresponding to three bond lengths, namely the shortest (stage 0), the longest (stage 1), and the equilibrium length (stage 0.5). The zero of the time scale is arbitrarily set. The favourable dis-

tribution of electron density is called the *reactivity impulse*. It appears periodically with consecutive vibrations. The time between two consecutive impulses—called the *oscillation* time —is characteristic for a given molecule.

To model a reaction with the IOM method a moment when the reactivity impulses for both reactant and catalytic center appear simultaneously should be found. This requires the definition of the beginning of the system time scale ($t = 0$). The moment of adsorption of reagent on the catalytic center (in heterogeneous catalysis), or the moment of formation of reactant–catalyst complex (in homogeneous and enzymatic catalysis) is assumed as $t = 0$. At this moment the states of both reactant and the center must be described by means of the stages (0; 0.5; 1) for each vibrator considered in the model. Now, the time of the first appearance of the reactivity impulse of the reactant and of the center can be determined. Finally, the time of synchronization of these impulses can be calculated. According to the IOM approach [9] this is the time condition for the reaction to occur.

For each vibrator considered in the model a reasonable range of frequency is assumed. Next, the synchronization condition is tested for all combinations of these ranges of all vibrators. In calculation the used ranges are wider than what is usually experimentally found—in order to include a variety of systems that potentially can be used as catalysts for the considered reaction. For instance, in the calculation of metal–oxygen vibrations a large enough range to include many different metal oxides it can be possible to predict which oxides are the most efficient catalysts.

Usually, a set of vibrations is resulting for which the synchronization condition is fulfilled only for a narrow part of the initial wide ranges. These vibration modes are reactive modes from the point of view of the model. However, for a few of the vibrators, the synchronization condition is fulfilled in the whole wide range of wavenumbers. According to the model, those vibrators are non-reactive modes because they

do not limit the synchronization condition. Thus, the model naturally eliminates the vibrators of no importance for the mechanism of the reaction.

The IOM calculations are performed using the IOMOS software [10] for PC, yielding some sets of wavenumbers for a specific reaction path. These results can be used as input data for the IOMAB program [11] in order to determine the selectivity for two distinct reaction paths A and B if such are assumed to occur. The IOMAB software finds subsets of the ranges where the synchronization for only one path is possible (A or B) and the subsets where synchronization for both paths is possible. In the latter case IOMAB distinguishes the situation when the synchronization time for the A path is shorter than for the path B (AB case) and the case when time for path B (BA case) is the shorter one. The selectivity S_a (choice of the path A) is calculated from the formula:

$$S_a = (A + AB + BA)100$$

$$/[A + B + 2(AB + BA)]$$

where: A, B, AB, BA—sums (in wavenumbers) of ranges for which the above described cases of synchronization are found. For instance, if for the A path ranges 720–725 cm^{-1} and 743–755 cm^{-1} are found then $A = 5 + 12 = 17$ cm^{-1}.

3. Results and discussion

3.1. Model of the reaction

It is commonly considered [12] that the formate ion is the reactive intermediate in HCOOH decomposition reaction. Three different forms of adsorbed formate ion, namely, monodentate, bidentate and bridged [13] were taken into account in our present approach. For each of the forms two reaction paths were considered. The dehydrogenation path is named A and the dehydration path is named B.

In Table 1 the assumed initial states ($t = 0$) and the reactivity impulses are defined for the three types of adsorption and for the two paths. A set of eight vibrational modes is considered in the model: the 5 internal modes of formate ion adsorbed on the surface, surface OH group and the bond between oxygen in formate and metal as well as metal–oxygen surface vibrations. As the initial state ($t = 0$) we assumed a moment when the bonds $\nu6$ (CO–M.) and the $\nu7$ (O–H) have just been formed. The momentary lengths are designed as 1—i.e., the longest—see Table 1. The electron density on the metal at that moment is assumed to be minimal. Therefore, the momentary length O–M. ($\nu8$) is designed as 0—i.e., the shortest. For the bidentate case, the OCO angle is assumed smallest and the HCO angle largest while for the monodentate

Table 1

Definition of the initial states ($t = 0$) and reactivity impulses for the dehydrogenation (A) and the dehydration (B) reactions

Modes	Monodentate			Bidentate			Bridged		
	$t = 0$	A	B	$t = 0$	A	B	$t = 0$	A	B
$\nu1$ OCO asymmetric[a]	1; 0	0; 1	0; 1	0.5; 0.5	0; 1	1; 0	1; 0	0; 1	0; 1
$\nu2$ OCO symmetric	1	0	1	0.5	0	1	0	0	1
$\nu3$ OCO bending[b]	-1	-1	$+1$	$+1$	-1	$+1$	-1	-1	$+1$
$\nu4$ H–C stretching	0	1	1	0	1	1	0	1	1
$\nu5$ HCO bending[b]	-1	$+1$	$+1$	-1	$+1$	$+1$	-1	$+1$	$+1$
$\nu6$ CO–M stretching	1	1	1	1	1	1	1	1	1
$\nu7$ O–H stretching	1	1	1	1	1	1	1	1	1
$\nu8$ O–M	1	0	1	1	0	1	0	0	1

[a] The pair of stages (0.5; 0.5 or 0;1) corresponding to the pair of bonds in the moiety.
[b] The stage 0.5 means the equilibrium angle in the moiety, the stage -1—the maximum angle, the stage $+1$—the minimum angle.

Table 2
Ranges (in wavenumbers) of modes used in the IOM calculation

Modes	Range [cm^{-1}]
$\nu 1$ OCO asymmetric	1679–1521
$\nu 2$ OCO symmetric	1399–1301
$\nu 3$ OCO bending	910–701
$\nu 4$ H–C stretching	2980–2820
$\nu 5$ HCO bending	1099–1001
$\nu 6$ CO–M stretching	1199–1080
$\nu 7$ O-H stretching	3499–3201
$\nu 8$ O–M	799–351

and bridged both the HCO and OCO angles are largest. The reactivity impulse of the formate ion for the path *A* (dehydrogenation) is defined from the assumption of a symmetry of OCO bonds system (the same lengths of the bonds). For the path *B* (dehydration)—the assumption of asymmetry of the bonds system is made. The need of the different momentary electron density on metal for the two paths is taken into account as well as appropriate deformations of the formates.

In order to determine the time of first appearance of the desired electron density distribution in each of the eight modes taken into account in this model one has to note that momentary state 0.5 (equilibrium length of bond) appears two times during one full vibration. One moment is when the vibration is during expansion (let sign this phase as R), the second is during contraction (the phase K). In the present application of the IOM model there are two modes in such situations for the case of bidentate adsorbed formate ion. The first mode $\nu 1$ asymmetric stretching O–C–O and the second $\nu 2$ mode symmetric stretching O–C–O. Four combinations of the phases for each of the paths are considered. The full model is presented in Appendix A. The ranges of wavenumbers used in the calculation are presented in Table 2.
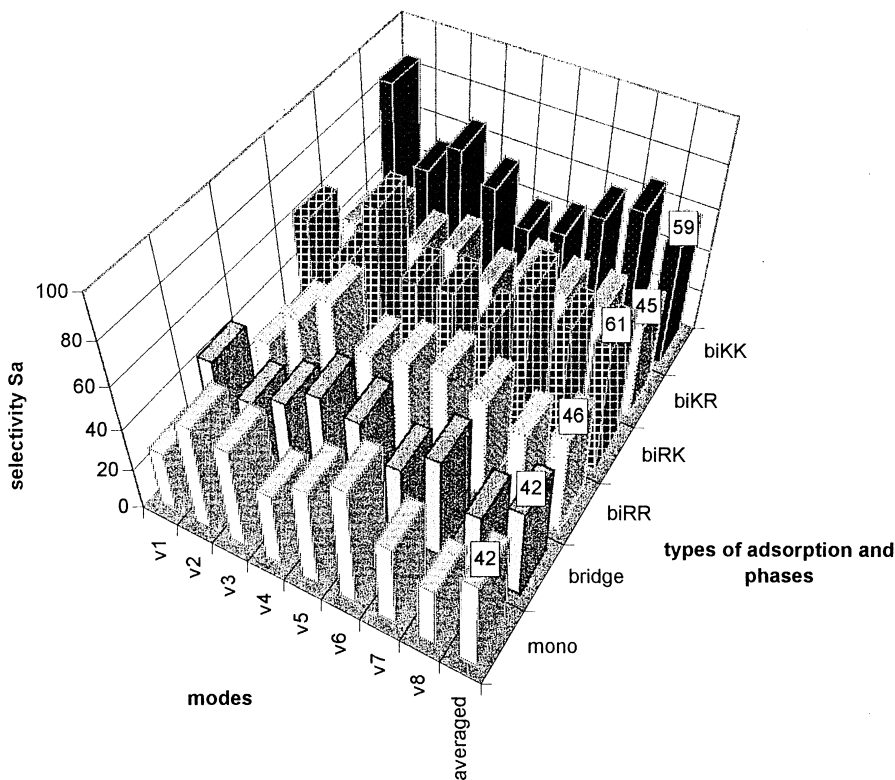

Fig. 1. Selectivities of the dehydrogenation reaction, including the average values for bidentate.

3.2. Results of calculations

The selectivities of the path A (dehydrogenation) for each of the modes and each of the calculated cases are presented on Fig. 1. Only for bidentate for the combination RK and KK (the phases of the $\nu1$ mode—asymmetric stretching OCO and of the $\nu2$ mode—symmetric stretching OCO), selectivities for dehydrogenation reaction is higher than 50%. The selectivity 61% is obtained for the RK combination, i.e., for the initial situation when one of the C–O bonds, viz., the one near the surface OH group is expanded in the $\nu1$ mode and the O–C–O bonds contract in the $\nu2$ mode. For the situation KK when the above mentioned bonds are contracting the selectivity is 59%. All of the other cases result in selectivities of the dehydrogenation reaction lower than 50%, i.e., the dehydration reaction is preferred. In Fig. 2 the averaged selectivities for monodentate, biden-

tate and bridged formate ions are presented. Both the average for all ion forms and for the bidentate ion selectivities indicated that the $\nu3$ mode (OCO bending) has the highest value of selectivity. The next important mode is the $\nu7$ vibration of OH surface group. Taking into account the selectivities values one can order the decreasing importance of the rest modes for the bidentate ion as following: $\nu1$ (OCO asymmetric stretch); $\nu8$ (O-M. stretch); $\nu4$ (HC stretch); $\nu2$ (OCO symmetric stretch); $\nu6$ (CO–M. stretch); $\nu5$ (HCO bend). The monodentate and bridged forms prefer the dehydration reaction (the averaged selectivity of the dehydrogenation reaction is 42%). Therefore, for these forms the sequence of decreasing importance of the modes is different than for the bidentate form. For the monodentate ion the highest selectivity of the dehydrogenation reaction is for the $\nu6$ mode (CO–M stretch) (57%), next for the $\nu2$ mode (OCO symmetric stretch)
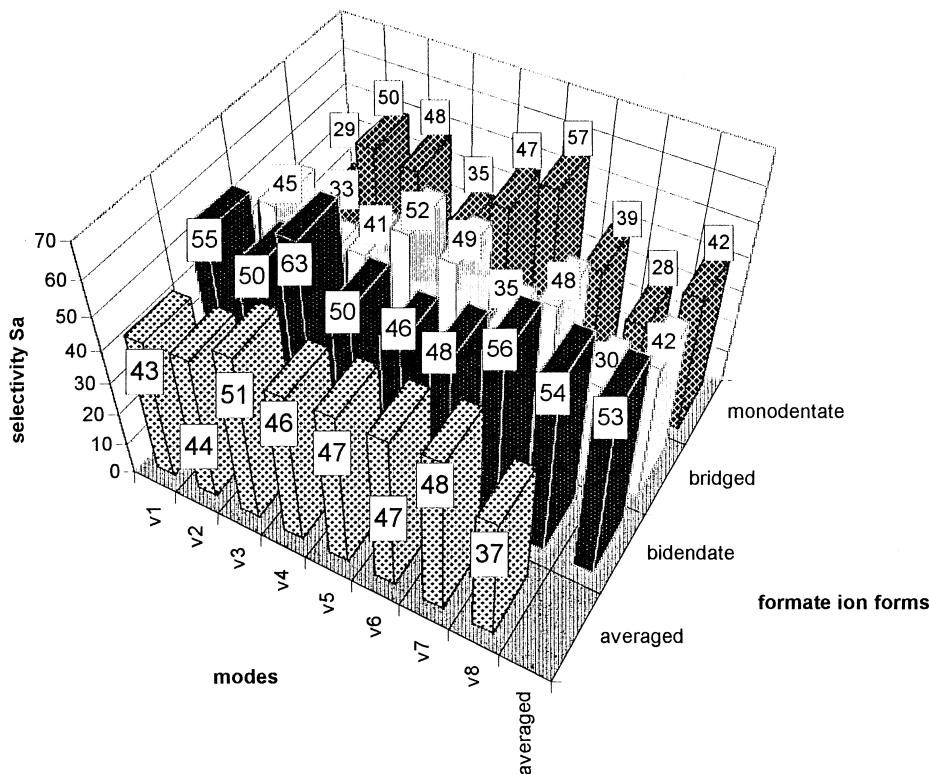

Fig. 2. Selectivities of the dehydrogenation reaction, including the average values for bidentate.

(50%) and for the $\nu 3$ mode (OCO bending) (48%). The lowest selectivities are for the $\nu 8$ (O–M stretch) (28%) and for $\nu 1$(OCO asymmetric stretch) (29%) modes. For the bridged form the most important modes in the dehydrogenation reaction are the $\nu 4$ (HC stretch) (52%), the $\nu 5$ (HCO bending) (49%) and the $\nu 7$ (OH surface group) (48%). The lowest selectivity is for the $\nu 8$ mode (O–M stretch) (30%).

In Fig. 3 the selectivities of choice of the dehydration reaction are presented. The average values are calculated for the three formate ions forms of adsorbed species. For the average values of selectivities the most important mode is $\nu 8$—the metal-oxygen vibration of oxide catalysts. In the formate the most important mode is the $\nu 1$—asymmetric stretching vibrations of O–C–O bonds. The decreasing importance of the rest modes is ordered as following: $\nu 2$ (OCO symmetric stretch); $\nu 4$ (HC stretch); $\nu 6$

(CO–M stretch); $\nu 5$ (HCO bend); $\nu 7$ (OH surface group); $\nu 3$ (OCO bend). The same two most important modes ($\nu 8$ and $\nu 1$) are in the case of monodentate, and the rest modes is ordered as following: the $\nu 4$; $\nu 7$; $\nu 5$; $\nu 3$; $\nu 2$; $\nu 6$ modes, while for the bridged form the order: $\nu 8$; $\nu 2$; $\nu 6$; $\nu 3$; $\nu 1$; $\nu 5$; $\nu 7$ and $\nu 4$ modes is found.

3.3. Discussion

The IOM model suggests that the most important mode for the dehydrogenation reaction is the OCO bending mode in formate and O–H stretching mode on catalyst surface while for the dehydration reaction the asymmetric stretching mode OCO in the adsorbed formate and the metal–oxygen stretching mode on oxide catalysts are the most important ones. In our recent paper [1] the same conclusions were obtained
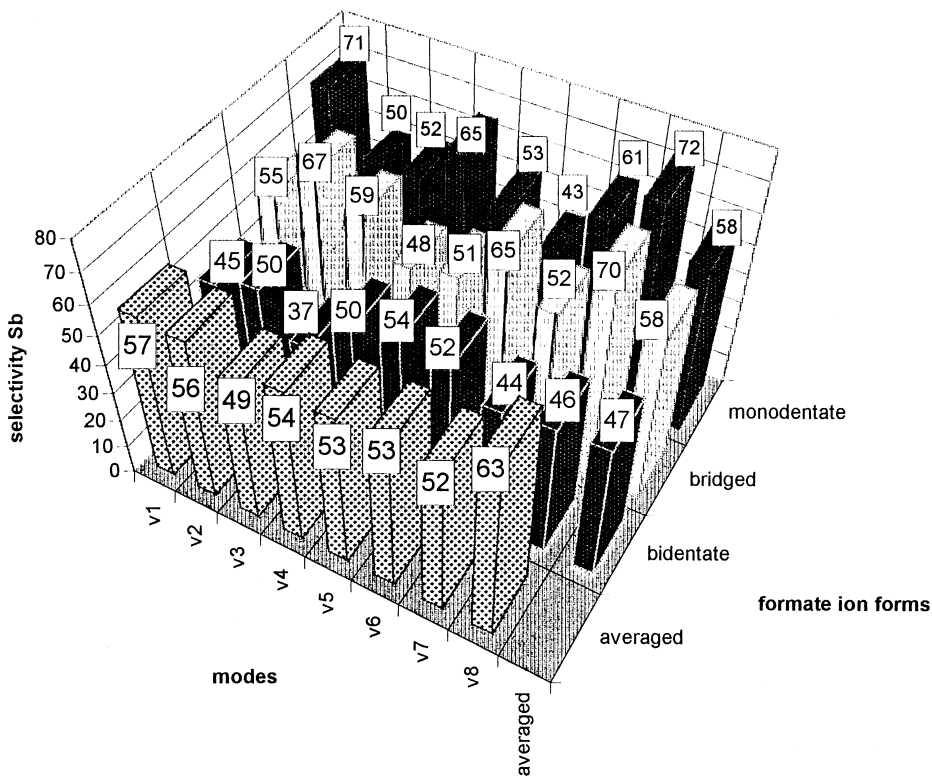

Fig. 3. Selectivities of the path *B*—dehydration.

Table 3
The best ranges for the dehydrogenation reaction

Mode	The best ranges for the dehydrogenation reaction [cm^{-1}]
$\nu 1$ OCO asymmetric	1580–1565
$\nu 2$ OCO symmetric	1325–1310
$\nu 3$ OCO bending	900–860; 760–720
$\nu 4$ H–C stretching	2980–2970; 2850–2830
$\nu 5$ HCO bending	1050–1040
$\nu 6$ CO–M stretching	1165–1150; 1130–1120
$\nu 7$ O–H	3500–3460; 3260–3200
$\nu 8$ O–M	750–720 (TiO_2); 670–660 (SnO_2; NiO); 580–550 (Fe_2O_3; Cr_2O_3); 420–400 (CuO; Cr_2O_3; MnO_2)

from the SET model analysis of the reactions. In particular, for the dehydrogenation reaction, according to the SETOS computation, the OCO bending mode appears at 765 cm^{-1} and some extra peaks were found at approximately 1040 cm^{-1}, 1130 cm^{-1}, 1200 cm^{-1} and perhaps at 1245 cm^{-1}.

The best ranges of wavenumbers for the considered modes in the IOM for the dehydrogenation reaction are presented in Table 3. The model predicts the range 760–720 cm^{-1} which is close to 765 cm^{-1} found [1] for the OCO bending mode. The range 1050–1040 cm^{-1} for the $\nu 5$ (HCO bending) mode corresponds to the peak 1040 cm^{-1} resulting from the SETOS calculation. Moreover, it is predicted (Table 3) that the $\nu 6$ (CO–M) mode is located in the range 1130–1120 cm^{-1}, i.e., close to the peak 1130 cm^{-1} found in our previous work [1]. The assigned metal oxides for the $\nu 8$ mode are proposed based on the spectroscopic data collected by Davidov [14]. It must be pointed out that from the point of view of the IOM method a choice of metal oxide catalyst should be based primarily on the predicted ranges of wavenumbers of the O–M vibration. Therefore, spectroscopic characteristics of a given metal oxide is necessary in order to make the good choice.

Acknowledgements

Appendix A

A.1. The IOM for bidentate form for the dehydrogenation reaction

	( )/$\nu 1$	( )/$\nu 2$	( )/$\nu 3$	( )/$\nu 4$	( )/$\nu 5$	( )/$\nu 6$	( )/$\nu 7$	( )/$\nu 8$
RR	$0.75 + n1$	$0.75 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0.5 + n8$
RK	$0.75 + n1$	$0.25 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0.5 + n8$
KR	$0.25 + n1$	$0.75 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0.5 + n8$
KK	$0.25 + n1$	$0.25 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0.5 + n8$

A.2. The IOM model for bidentate for the dehydration reaction

	$(\ )/\nu 1$	$(\ )/\nu 2$	$(\ )/\nu 3$	$(\ )/\nu 4$	$(\ )/\nu 5$	$(\ )/\nu 6$	$(\ )/\nu 7$	$(\ )/\nu 8$
RR	$0.25 + n1$	$0.25 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0 + n8$
RK	$0.25 + n1$	$0.75 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0 + n8$
KR	$0.75 + n1$	$0.25 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0 + n8$
KK	$0.75 + n1$	$0.75 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n4$	$0 + n6$	$0 + n7$	$0 + n8$

A.3. The IOM model for monodentate for the dehydrogenation (A) and dehydration (B) reactions

	$(\ )/\nu 1$	$(\ )/\nu 2$	$(\ )/\nu 3$	$(\ )/\nu 4$	$(\ )/\nu 5$	$(\ )/\nu 6$	$(\ )/\nu 7$	$(\ )/\nu 8$
A	$0.5 + n1$	$0.5 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n5$	$0 + n6$	$0 + n7$	$0.5 + n8$
B	$0.5 + n1$	$0 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n5$	$0 + n6$	$0 + n7$	$0 + n8$

A.4. The IOM for bridged for the dehydrogenation (A) and dehydration (B) reactions

	$(\ )/\nu 1$	$(\ )/\nu 2$	$(\ )/\nu 3$	$(\ )/\nu 4$	$(\ )/\nu 5$	$(\ )/\nu 6$	$(\ )/\nu 7$	$(\ )/\nu 8$
A	$0.5 + n1$	$0 + n2$	$0 + n3$	$0.5 + n4$	$0.5 + n5$	$0 + n6$	$0 + n7$	$0 + n8$
B	$0.5 + n1$	$0.5 + n2$	$0.5 + n3$	$0.5 + n4$	$0.5 + n5$	$0 + n6$	$0 + n7$	$0.5 + n8$

Program IOMOS is used to solve the parametrized equations: $(w_1 + k_1 * n_1)/\nu 1 = \ldots = (w_8 + k_8 * n_8)/\nu 8$, where ν—IR frequencies; n—integer number of vibration cycles; k, w—phase coefficients due to model formalism. '$(\ )$' $= (w_i + k_i * n_i)$.

References

[1] R. Larsson, M.H. Jamróz, M.A. Borowiak, J. Mol. Catal. A: Chem. 129 (1998) 41.

[2] R. Larsson, J. Mol. Catal. 55 (1989) 70.

[3] M.A. Borowiak, ISSOL 86, Berkeley, USA, 1986, Abstracts, p. 306.

[4] M.A. Borowiak, in Prep. Pap. Pres. 196th Am. Chem. Soc. Nat. Meeting, Los Angeles, USA, 33 (4)(1988) 647.

[5] M.A. Borowiak, Biophys. Chem. 32 (1988) 21.

[6] M.A. Borowiak, Introduction to Modelling of Catalytic System (in Polish), Ossolineum, Wrocław, 1990.

[7] M.A. Borowiak, Acta Pharm. Pol.- Drug Res. 48 (3–4) (1991) 75.

[8] M.A. Borowiak, Elementary Catalytic System Model for Rational Design of Catalysts at Atomic/Molecular Levels, Ossolineum, Wrocław, 1991.

[9] M.A. Borowiak, J. Haber, J. Mol. Catal. 82 (1993) 327.

[10] M.H. Jamróz, ICRI Internal Report 1995, unpublished.

[11] M.A. Borowiak, M.H. Jamróz, Internet J. Chem.: www.ijc.com./articles/1998v1/17.

[12] Y.N. Trillo, G. Munuera, J.M. Criado, Catal. Rev. 7 (1972) 51.

[13] P.A. Dilare, J.M. Vohs, J. Phys. Chem. 47 (1993) 12922.

[14] A.A. Davidov, IR Spectroscopy in Oxide Surface Chemistry (in Russian), Nauka, Novosibirsk, 1984.