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Szarawara–Kozik’s temperature criterion in the context of three-parameter equation for modeling ammonia or methanol decomposition during heterogenous catalysis

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Abstract Szarawara–Kozik’s temperature criterion, suggested many years ago, has been reinterpreted as three-parameter fitting equation. We demonstrated interpretation of the chemical reactions of ammonia and methanol catalytic decomposition (to produce syngas and hydrogen) by associating two parameters with the activation energy and the average enthalpy of reaction for the equilibrium conversion degrees. It was proved that the three-parameter equation can be applicable to studying a wide variety of catalytic/enzymatic processes in isothermal conditions.

Keywords Ammonia · Methanol · Decomposition · Three-parameter equation · Equilibrium constant

List of symbols

A	Preexponential factor in the Arrhenius equation, min^{-1}
a, b	Constants in $g(\alpha)$ function
a_0, a_1, a_2	Coefficients in three-parameter Eq. 3
α	Conversion degree, $0 < \alpha \leq 1$,
C	Constant in Eq. 1
E	Activation energy of decomposition reaction, J mol^{-1}
φ	Proportional constant in Eq. 21
$g(\alpha)$	Mass integral
$\Delta_r H$	Enthalpy of reaction, J mol^{-1}
K	Equilibrium constant of reaction
N	Number of measurements/observations
q	Heating rate, K min^{-1}

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Q	Energetic value, J mol^{-1}
$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	Universal gas constant
R^2	Determination coefficient in nonlinear regression, $0 \leq R^2 \leq 1$
sl	Significance level
T	Temperature of reaction, K
ν	Stoichiometric coefficient
τ	Time, s
τ_z	Equivalent time, g min/mol

Subscripts

av	Average
c	Vaporization
eq	Equilibrium
iso	Isokinetic
min	Minimal
r	Reaction

Introduction

Kinetic considerations and interpretations of catalytic and non-catalytic reactions have been performed in many publications. Isoconversional methods are most often applied for this purpose [1–7].

Interesting temperature and turbulence criteria for the reactions on heterogeneous catalysts have been published in seventies [8–10]. The above mentioned references, which are available only in Polish, were based on extensive experimental results, described originally in the unpublished PhD dissertation [11].

The comparison of the temperature and turbulence criterion indicates that the temperature criterion, that is correct for low conversion degree α , are of greater importance:

$$\ln \alpha = C - E/RT, \quad 0 < \alpha < 0,2 \quad (1)$$

This enables one for the estimation of activation energy.

On the other hand, the constant C has a quite complex origin and depends on the equivalent time of reaction, initial concentrations and grain size of catalyst, but in any case, it does not simply contain the pre-exponential factor (A) in the Arrhenius equation. In this context, in publications [8–11] a discussion is presented on the decomposition of ammonia, methanol, some inorganic salts or solids as well as SO_2 oxidation to SO_3 .

Therein, the temperature criterion 1 was used to analyze the thermal dissociation of a condensed phase assigning a particular form for C constant in dynamic conditions, that is, for heating rate $q > 0$ [12]:

$$\ln \alpha = \ln \left(\frac{0,005AE}{qR} \right) - E/RT, \quad 0 < \alpha < 0,2 \tag{2}$$

In this approach it is possible to designate the pre-exponential factor (A) in the Arrhenius equation, which enables the KCE (kinetics compensation effect) analysis.

According to the Ortega considerations [13], Eq. 2 is useful when we consider that for many known functions integral $g(\alpha)$ for low degrees of conversion of $g(\alpha)$ takes a value of $g(\alpha) = a\alpha^b$, where specific values for models a and b were proposed in work [14]. Thus, comparing the obtained values of the activation energy from Eq. 2 with specific thermokinetic models requires a conversion according to ratio (E/b) , where $b = 2$ for D-type models, $b = 1/2$ form A2 and $b = 1/3$ for A3.

Finally, we developed [14] a three-parameter thermokinetic equation with the signs consistently compatible a_1, a_2 in comparison to a_0 :

$$\ln \alpha = a_0 - \frac{a_1}{T} - a_2 \ln T \quad \alpha > 0 \tag{3}$$

Equation 3 was used in a number of models, whereas this can be concluded more or less by the results presented in [15].

From the formal point of view Eqs. 1 and 2 differ from Eq. 3 by the additional element $(-a_2 \ln T)$.

Aim of work

The aim of the work is to demonstrate that the three-parameter Eq. 3 is a generalization of temperature relation 1 for isothermal conditions. In such an approach, it is also important how to interpret the Eq. 3 under these conditions, extending the formalism presented in the work [15] for dynamic conditions. Thus, it becomes necessary to interpret the correlation Eq. 4.

$$a_1 = \frac{Q}{R} + a_2 T_{iso} \tag{4}$$

Where Q means:

- (a) activation energy $E = Q$, for chemical reactions performed far away from equilibrium state DFE (Distance From Equilibrium).
- (b) average enthalpy of reaction $\Delta_r H/\nu = Q$ for chemical reactions exhibiting formal and mathematical relationship with equilibrium constant.

Experimental

The two types of catalytic reactions were used for the analysis: the isothermal decomposition of ammonia and methanol.

The decomposition of ammonia were considered for:

1. Archival results obtained on Pt/Rh catalytic grid in terms of equivalent time 22.5–2256 min g/mol, given in [11], and discussed in [8–10].
2. Our study on nanoparticles of active metals on mineral and metallic carriers provided in [16].

On the other hand, the methanol decomposition were analyzed only for archival results [8–11].

Results

Ammonia Decomposition $\text{NH}_3 \rightarrow 1/2\text{N}_2 + 3/2\text{H}_2$

For series experimental data $N = 16$ for equivalent time $\tau_z = 22.5\text{--}2256$ g min mol⁻¹ on the Pt/Rh catalyst grid (weight of 10.22 g), three-parameter Eq. 3 was valid for the determination coefficient $R^2 = 0.9633\text{--}0.9984$ (significance level of at least 0.001) with a clear trend of increase in R^2 with increasing equivalent time or otherwise—with a more complete decomposition in a wider temperature range.

Then, the obtained coefficients of Eq. 4 were correlated according to [15], for the positive signs, but rather kinetic than thermodynamic nature was assigned to intercept:

$$a_1 - a_2 T_{iso} = \frac{E}{R} \quad (5)$$

Equation 4, which is also another form of KCE, can be used twice:

1. for each individual case ($N = 16$) using the designated isokinetic temperature for the calculation of activation energy E_i ,
2. directly by considering the intercept as an average activation energy E .

Fig. 1 illustrates the relationship between the obtained activation energy values and the equivalent time for archival data.

Equation 4 takes a following analytical form:

$$a_1 = 14290.9 + a_2 T_{iso}, \text{ where } T_{iso} = 885.34 \text{ K}, \quad E = 118.8 \text{ kJ mol}^{-1} \quad (6)$$

The occurrence of the maximum, amounting to $E = 136.9$ kJ mol⁻¹ with a minimum values at the level $E \approx 100$ kJ mol⁻¹ and the average value of 118.8 kJ mol⁻¹ is a characteristic feature of the plot shown in Fig. 1. The results of these analyses are in accordance with the temperature criterion resulting from Eq. 1 for $\alpha \leq 0.2$.

For studies using nanocatalysts [16] with a constant flow rate of 2 dm³ h⁻¹ ammonia in isothermal conditions temperature criterion 1 was used for calculation of activation energies as shown in Fig. 2.

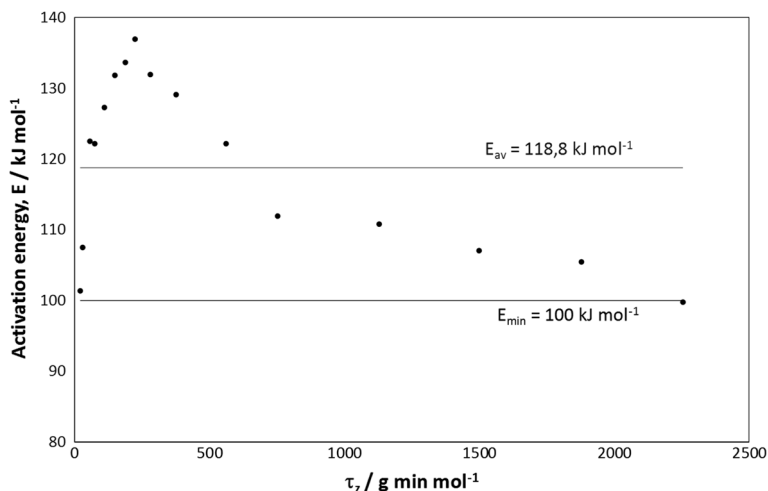


Fig. 1 Relationship between obtained activation energy and equivalent time (for archival data [11])

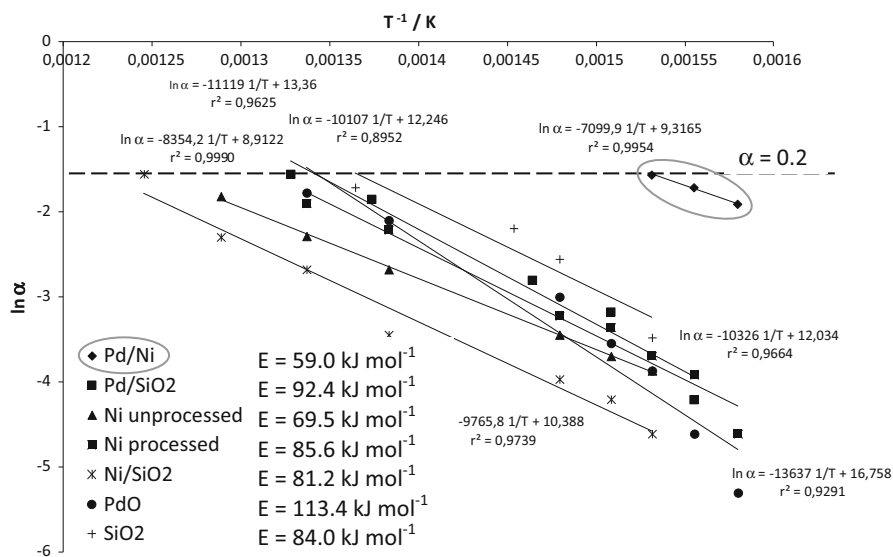


Fig. 2 The analysis of ammonia decomposition on the selected catalysts on the basis of the temperature criterion 1—(relation α vs T in [16], see Fig. S1 in Supplementary Materials)

As previously the coefficients of the three-parameter Eq. 4 were determined with high determination coefficients R^2 above 0.9555, while the analytical model takes a form of Eq. 5:

$$a_1 = 8723,8 + a_2 T_{iso}, \text{ where } T_{iso} = 786.03 \text{ K}, \quad E = 72.5 \text{ kJ mol}^{-1} \quad (7)$$

A comparison of these data clearly indicates a very beneficial effect of nanocatalysts, the average activation energy significantly approaching to the enthalpy of this reaction, which also means shortening the DFE.

Individual values are consistent assuming ammonia decomposition on the nickel and ruthenium catalysts for the mechanism consisting of four steps, wherein that for the reactions 2 to 4 according to [17], the activation energies vary in the range $E = 144 \rightarrow 109 \text{ kJ mol}^{-1}$ (Ni catalyst), and $E = 105.8 \rightarrow 67.8 \text{ kJ mol}^{-1}$ (Ru catalyst). The results presented in work [16] are very interesting, but obviously there are other works, where valuable results had also been obtained [18].

The appropriate thermodynamic relationship for the equilibrium chemical constant were determined on the basis of Barin's tables [19]:

$$\ln K_1 = 13.122 - 5912.35/T, \quad 298.15 \text{ K} \leq T \leq 900 \text{ K}, \quad (8)$$

$$\Delta_r H = 49.2 \text{ kJ mol}^{-1}, \text{ acc. to [20–22]} \quad \Delta_r H = 46\text{--}49.2 \text{ kJ mol}^{-1}.$$

The interpretation of Eq. 4 in the form of Eq. 5 complies with the general principle that $E \geq \Delta_r H$.

Methanol decomposition $\text{CH}_3\text{OH}^{(c,g)} \rightarrow 2\text{H}_2 + \text{CO}$

The results of studies of this reaction are presented in Ref. [11], mainly in two aspects:

1. for Zn/Cr catalyst where equivalent time τ_z amounted to $\tau_z = 9.74\text{--}156 \text{ g min/mol}$, catalyst weight of 30 g and 5 mm grinding (I variant),
2. as in the first variant but for $\tau_z = 26 \text{ g min mol}^{-1}$ and variable catalyst grinding of 0.5–1 mm, 0.385–0.6 mm, 0.385–0.1 mm, < 0.1 mm (II variant).

In all cases Eq. 3 was found to be correct with the determination coefficients $R^2 = 0.9929\text{--}0.9991$ and a significance level of at least 0.0001.

A value of activation energies E_i were determined by applying Eq. 4 in formula 5:

1. for the I variant: $\tau_z = \text{var}$, catalyst grinding = *const*: $E_i = 18.7\text{--}28.3 \text{ kJ mol}^{-1}$, and average activation energy E from analytical form:

$$a_1 = 3216.86 + a_2 T_{iso}, \text{ where } T_{iso} = 587.43 \text{ K}, \quad E = 26.7 \text{ kJ mol}^{-1} \quad (9)$$

2. for the II variant, $\tau_z = \text{const}$, catalyst grinding = *var*: $E_i = 24.6\text{--}39.3 \text{ kJ mol}^{-1}$, and average activation energy E from analytical form:

$$a_1 = 3687.18 + a_2 T_{iso} \text{ where } T_{iso} = 610.82 \text{ K}, \quad E = 30.7 \text{ kJ mol}^{-1} \quad (10)$$

After combining both groups of results in Eqs. 9 and 10 one can obtain:

$$a_1 = 3234.94 + a_2 T_{iso} \text{ where } T_{iso} = 614.66 \text{ K, } E = 26.9 \text{ kJ mol}^{-1} \quad (11)$$

In the case of variant I (variable equivalent time), the a_2 coefficient is small, taking a maximal value of $a_2 = 16.5$, while for variant II (variable catalyst grinding and fixed equivalent time) it reaches a maximum value of $a_2 = 117$. Fig. 3 illustrates a dependence of activation energy on the equivalent time for variant I.

At the same time, a reduction of three-parameter Eq. 3 to the temperature criterion 1 for a low degree of methanol conversion, $\alpha < 0.2$ a high activation energy values are obtained $E = 60\text{--}90 \text{ kJ mol}^{-1}$ (the II variant).

The appropriate thermodynamic relations for chemical equilibrium constant were determined from the Barin’s tables [19] to broaden the obtained results:

- methanol decomposition (to synthesis gas) in the gaseous form:

$$\ln K_2 = 28.7024 - 11652.623/T, \text{ for } 298.15 \text{ K} \leq T \leq 1000 \text{ K} \quad (12)$$

$$\Delta_r H = 96.9 \text{ kJ mol}^{-1}.$$

- methanol decomposition in the liquid form:

$$\ln K_3 = 40.074 - 15431.710/T, \text{ for } 298.15 \text{ K} \leq T \leq 400 \text{ K} \quad (13)$$

$$\Delta_r H = 128.9 \text{ kJ mol}^{-1}.$$

The enthalpy difference given by the Eqs. 13 and 12 is the vaporization enthalpy of methanol in a temperature range 298.15–400 K:

$$\Delta_c H = 31.4 \text{ kJ mol}^{-1} (\Delta_c H = 35.3 \text{ kJ mol}^{-1}, \text{ when } T_b = 337.85 \text{ K [23]})$$

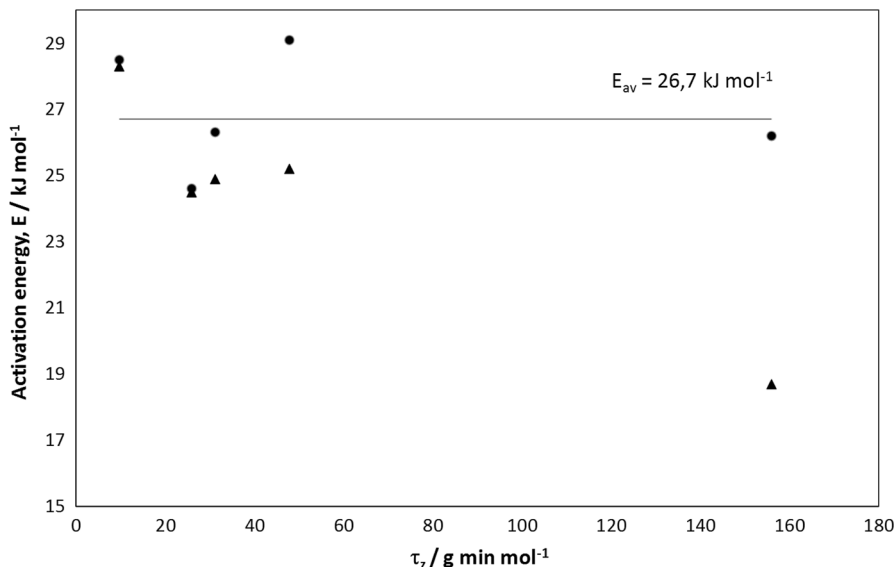


Fig. 3 Dependence of activation energy from the equivalent time for the I variant (triangles—from temperature criterion 1)

The first observation which arises from the comparison of the activation energy and enthalpy of vaporization is that there are comparable values ($E = \Delta_c H$), while the additional cases of the high activation energy ($E = 60\text{--}90 \text{ kJ mol}^{-1}$) are close in a value to the average enthalpy of the reaction ($E \approx \Delta_c H$).

This observation will be explained in the next part of work.

Discussion

Discussion on the results in the aspect of thermodynamic

The obtained results suggest another interpretation of Eq. 4 which further gives the kinetic form (5). According to the works [15, 24] Eq. 4 appears substantial for the dissociation of solid phase, particularly, in dynamic conditions, where it takes a form:

$$a_1 - a_2 T_{iso} = \frac{\Delta_r H}{\nu R} \quad (14)$$

Here the stoichiometric ratio ν should be understood as total only for the gaseous products. Practically, in the decomposition of ammonia and methanol the substrates and products are gaseous, except where from ambient temperatures up to the boiling point the substrate (methanol) is in the liquid state.

Ammonia decomposition

Equilibrium constant for the ammonia decomposition can be expressed by the following equation:

$$K_1 = c \frac{\alpha_{eq}^2}{1 - \alpha_{eq}^2} \quad (15)$$

This can be reduced to the relation of equilibrium conversion degree of ammonia

$$\alpha_{eq} = \sqrt{\frac{cK_1}{1 + cK_1}} \quad (16)$$

Here $c = \sqrt{16/27} = 0.7698$ and K_1 can be expressed by Eq. 8.

For a small conversion degree of decomposition ($\alpha_{eq} < 0.2$) Eq. 15 approximately equals $K_1 \approx c\alpha_{eq}^2$, and from relation: $\ln \alpha_{eq}$ vs. $1/T$ (Fig. 4) there was determined $\Delta_r H/\nu = 24.36 \text{ kJ mol}^{-1}$, and $\Delta_r H = 48.7 \text{ kJ mol}^{-1}$ ($\nu = 2$), where the designated value is consistent with Eq. 8.

Gaseous methanol decomposition

Equilibrium constant for the gaseous methanol decomposition can be expressed by the equation:

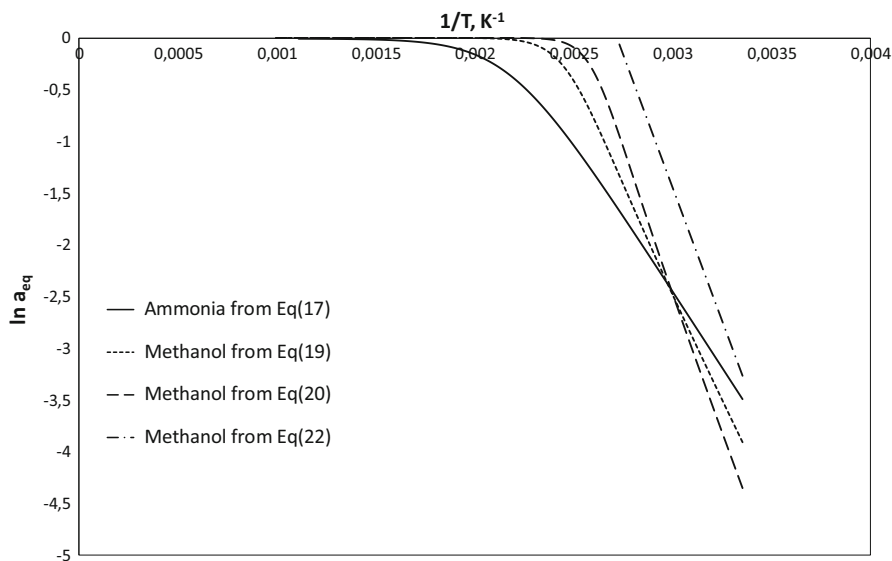


Fig. 4 Relationship $\ln \alpha_{eq}$ versus $1/T$ for ammonia and methanol decomposition

$$K_2 = \frac{4\alpha_{eq}^3}{(1 + 2\alpha_{eq})^2(1 - \alpha_{eq})} \tag{17}$$

This can be transformed by solving equation to dependence of equilibrium conversion degree:

$$\alpha_{eq} = 1/2 \left(\frac{K_2}{1 + K_2} \right)^{\frac{1}{3}} \left[\left(1 + \frac{1}{\sqrt{1 + K_2}} \right)^{\frac{1}{3}} + \left(1 - \frac{1}{\sqrt{1 + K_2}} \right)^{\frac{1}{3}} \right] \tag{18}$$

Here K_2 is expressed by Eq. 12.

For small conversion degree of decomposition ($\alpha_{eq} < 0.2$) relation 18 is regulated with regard to the equilibrium value $K_2 \propto \alpha_{eq}^3$, and from relation: $\ln \alpha_{eq}$ vs $1/T$ (Fig. 4) there was determined $\Delta_r H/v = 34.19 \text{ kJ mol}^{-1}$, and $\Delta_r H = 102.6 \text{ kJ mol}^{-1}$ ($v = 3$) and the designated value is consistent with Eq. 12.

Liquid methanol decomposition

Although methanol under atmospheric pressure and at temperatures below $T_b = 337.85 \text{ K}$ [23] is in liquid form, the discussion can be carried out for two cases.

In a first, we assume the validity of Eq. 18 except that it contains a constant thermodynamic constant K_3 expressed by Eq. 13:

$$\alpha_{eq} = 1/2 \left(\frac{K_3}{1 + K_3} \right)^{\frac{1}{3}} \left[\left(1 + \frac{1}{\sqrt{1 + K_3}} \right)^{\frac{1}{3}} + \left(1 - \frac{1}{\sqrt{1 + K_3}} \right)^{\frac{1}{3}} \right] \quad (19)$$

Equation 19 assumes that despite the existence of the liquid phase, there are three gas components in its surrounding: CH₃OH, CO and H₂.

According to procedure describe above (Fig. 4) there was determined $\Delta_r H/\nu = 44.89 \text{ kJ mol}^{-1}$, and $\Delta_r H = 134.7 \text{ kJ mol}^{-1}$ for the $\nu = 3$. This value is acceptable in comparison to the value specified in the supplement to Eq. 13.

For the second case of the low temperature decomposition of methanol in the liquid phase (298.15–400 K), a model described in work [15] was used, assuming that the chemical equilibrium constant refers only to gaseous products (CO and H₂), and in this case $\nu = 3$:

Thus

$$K_3 = \varphi \alpha_{eq}^{\nu} \quad \text{where} \quad \varphi = 0.1481, \quad \text{and} \quad \nu = 3 \quad (20)$$

Finally:

$$\alpha_{eq} = 1,89(K_3)^{1/3} \quad (21)$$

Here K_3 expresses relation (13) in the range: $298.15 \text{ K} \leq T \leq 337.85 \text{ K}$.

In the same way (Fig. 4) $\Delta_r H/\nu = 42.77 \text{ kJ mol}^{-1}$, and $\Delta_r H = 128.3 \text{ kJ mol}^{-1}$ was calculated, and this value was in accordance with the supplement to the Eq. 13.

The differences indicate the enthalpy of evaporation enthalpy in the range of: $\Delta_c H = 25.7\text{--}32.1 \text{ kJ mol}^{-1}$ (in the previous case $\Delta_c H = 31.4 \text{ kJ mol}^{-1}$).

In relation to the received values of activation energy, it can be assumed that in the catalytic process activation energy is minimal and similar to evaporation enthalpy $E = \Delta_c H$ and these values are approx. 30 kJ mol^{-1} .

The higher activation energies, approaching the average enthalpy of reaction $E = 60\text{--}90 \text{ kJ mol}^{-1}$ are the result of two effects:

- according to the authors [10], this is a typical KCE,
- according to these considerations, poorly prepared catalyst with low activity is expressed in increased activation energy, at the level of enthalpy of decomposition, according to a relation for the endothermic processes $E \rightarrow \Delta_r H$.

It should be appreciated that thermodynamic considerations provided here relate to decomposition of methanol to synthesis gas, and in this regard there are many other possibilities, such as dehydration (DME), dehydrogenation or formation of esters of formic acid etc. [25].

Conclusion

1. For the experimental data of decomposition type reactions under isothermal conditions three-parameter Eq. 3 can make wider the understanding of Szarawara–Kozik's temperature criterion 1. We proposed here other interpretation of the coefficients in Eq. 3 for these conditions, by determining the activation energy.
2. Criteria used for the obtained results of catalytic decomposition of ammonia indicate a considerable more efficient activity of nanocatalysts [16] in relation to the earlier studies [11] and the DFE. The numerical scale DFE can be determined by the average values: $\Delta_r H = 49.2 \text{ kJ mol}^{-1}$, activation energy for data from [11] $E = 118.8 \text{ kJ mol}^{-1}$ and on nanocatalysts [16] $E = 72.5 \text{ kJ mol}^{-1}$.
3. In the case of methanol decomposition averaged activation energy is at the level of evaporation enthalpy of methanol $E = \Delta_c H$, and these values are approx. 30 kJ mol^{-1} . It is interesting that reaction enthalpy was determined by two routes of thermodynamic analysis and they differing by evaporation enthalpy of methanol, ie. $\Delta_r H = 96.9 \text{ kJ mol}^{-1}$ for the gaseous substrates and $\Delta_r H = 128.3 \text{ kJ mol}^{-1}$ for the liquid methanol. This result was confirmed by the simplification introduced by adapting thermodynamic equations in a similar manner to the temperature criterion inserting the equilibrium conversion degree, instead of experimental conversion degree even for $\alpha_{eq} < 0.2$.

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References

1. Brown ME, Maciejewski M, Vyazovkin S, Nomen R, Sempere J, Burnham A, Opfermann J, Strey R, Anderson HL, Kemmler A, Keuleers R, Janssens J, Desseyn HO, Li C-R, Tang TB, Roduit B, Malek J, Mitsuhashi T (2000) Computational aspects of kinetic analysis: part A: the ICTAC kinetics project-data, methods and results. *Thermochim Acta* 355:125–143
2. Maciejewski M (2000) Computational aspects of kinetic analysis: Part B. The decomposition kinetics of calcium carbonate revisited, ore some tips on survival in the kinetic minefield. *Thermochim Acta* 355:145–154
3. Vyazovkin S (2000) Computational aspects of kinetic analysis: Part C. The light at the end of the tunnel. *Thermochim Acta* 355:155–163
4. Burnham AK (2000) Computational aspects of kinetic analysis: Part D. The ICTAC kinetics project—multi-thermal-history model-fitting methods and their relation to isoconversional methods. *Thermochim Acta* 355:165–170

5. Roduit B (2000) Computational aspects of kinetic analysis: Part E: The ICTAC kinetics project - numerical techniques and kinetics of solid state processes. methods. *Thermochim Acta* 355:171–180
6. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N (2011) ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta* 520:1–19
7. Vyazovkin S, Chrissafis K, di Lorenzo ML, Koga N, Pijolat M, Roduit B, Sbirrazzuoli N, Suñol JJ (2014) ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim Acta* 590:1–23
8. Szarawara J, Cz Kozik (1973) The issue of area of catalytic processes (Zagadnienie obszaru procesów kontaktowych). *Chem Stosow* 17:279–294 (in Polish)
9. Szarawara J, Cz Kozik (1973) Attempt at the potential interpretation of chemical kinetics equations (Próba potencjalowej interpretacji równań kinetyki chemicznej). *Chem Stosow* 17:295–3014 (in Polish)
10. Szarawara J, Cz Kozik (1976) Application of a new method for studies on the area of selected heterogeneous processes (Zastosowanie nowej metody badania obszaru do wybranych procesów heterogenicznych). *Chem Stosow* 20:45–69 (in Polish)
11. Kozik Cz (1973) Studies on the area of heterogeneous processes (Studia nad obszarem procesów heterogenicznych). PhD thesis, Silesian University of Technology, Faculty Chemistry (in Polish)
12. Mianowski A, Radko T (1994) The possibility of identification of activation energy by means of the temperature criterion. *Thermochim Acta* 247:389–405
13. Ortega A (1996) The incorrectness of the temperature criterion. *Thermochim Acta* 276:189–198
14. Mianowski A (2000) Thermal dissociation in dynamic conditions by modeling thermogravimetric curves using the logarithm of conversion degree. *J Therm Anal Cal* 59:747–762
15. Mianowski A, Siudyga T (2012) Analysis of relative rate of reaction/process. *J Therm Anal Cal* 109:751–762
16. Polanski J, Bartczak P, Ambroźkiewicz W, Sitko R, Siudyga T, Mianowski A, Szade J, Balin K, Lelątko J (2015) Ni-supprted Pd nanoparticles with Ca promoter: a new catalyst for low-temperature ammonia cracking. *PLoS ONE*. <https://doi.org/10.1371/journal.pone.0136805>
17. Takahashi A, Fujitani T (2016) Kinetic analysis of decomposition of ammonia over nickel and ruthenium catalysts. *J Chem Eng Jpn* 49:22–28
18. Guo J, Chen Z, Wu A, Chang F, Wang P, Hu D, Wu G, Xiong Z, Yu P, Chen P (2015) Electronic promoter of reaction species? The role of LiNH_2 on Ru in catalyzing NH_3 decomposition. *Chem Commun* 51:15161–15164
19. Barin I (1989) Thermochemical data of pure substances, vol 1. VCH Verlagsgesellschaft, Weinheim
20. Klerke A, Christensen CH, Nørskov JK, Vegge T (2008) Ammonia for hydrogen storage: challenges and opportunities. *J Mater Chem* 18:2304–2310
21. Atsumi R, Noda R, Takagi H, Vecchione L, di Carlo A, del Prete Z, Kuramoto K (2014) Ammonia decomposition activity over Ni/SiO_2 catalysts with different pore diameters. *Int J Hydrogen Energy* 39:13954–13961
22. Okura K, Okanishi T, Muroyama H, Matsui T, Eguchi K (2015) Promotion effect of rare-earth elements on the catalytic decomposition of ammonia over $\text{Ni/Al}_2\text{O}_3$ catalyst. *Appl Catal A* 505:77–85
23. Knovel Critical Tables (2nd edn). <https://app.knovel.com/web/>
24. Mianowski A, Urbańczyk W (2016) Thermal dissociation in terms of second law of chemical thermodynamics. *J Therm Anal Cal* 126:863–870
25. Vedyagin A, Kotolevich Y, Tsyrl'nikov P, Khramov E, Nizovskii A (2016) Methanol dehydrogenation over Cu/SiO_2 catalysts. *Int J Nanotechnol* 13:183–197