

Hydrogenolysis of ethane on silica-supported cobalt catalysts

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Abstract

The kinetics of ethane hydrogenolysis over cobalt catalysts supported on silica has been investigated. The results compare well with previous data from Sinfelt et al., Haddad and Goodwin, and Babernics et al. The data were found to be characterized by an isokinetic temperature, $T_{\text{iso}} = 490 \pm 40$ K and it was therefore possible to apply the model of selective energy transfer (SET). This approach indicates that either there is an energy transfer from the catalyst by full resonance to a vibration mode of the reactant with $\nu = 680 \text{ cm}^{-1}$ corresponding to a metal (M)=CH₂ bond, or there is an energy transfer to an M–CH₃ vibration mode in the region of 400 cm^{-1} , most likely at 355 cm^{-1} . In any case, these interpretations indicate that it is the breaking of one or two metal–carbon bonds that determine the reaction, not the cleavage of the carbon–carbon bond of ethane. This is in agreement with recent views of Sinfelt. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Ethane hydrogenolysis; Silica supported catalysts; Selective energy transfer

1. Introduction

In a previous paper [1] the relation between the so-called isokinetic effect and reaction mechanism was exemplified with data from metal catalyzed hydrogenolysis of ethane. These results were discussed in terms of a recent categorization by Sinfelt [2] which means that there is a gradual change in M–C bonding strength, passing from high to low electronegativities of the metals. This change makes the C–C bond breaking rate determining for Pt metals, whereas the more electropositive elements (Co, Fe, etc.) form such a strong M–C bond that the C–C bond breaking is made fast and the rate determining step of the reaction is the M–C bond breaking. One should note

that this categorization is contrary to the mechanism of hydrogenolysis previously suggested by the same author [3]. It was suggested [1] that some metals, like Pt, for which the carbon–carbon bond splitting was rate determining according to Sinfelt [2] showed an isokinetic temperature, T_{iso} , that could be analyzed in terms of a vibrational frequency (around 1000 cm^{-1}) that indeed corresponded to a C–C vibrational mode. Conversely, metals with a high electropositive character (e.g. Co, Fe) and which according to Sinfelt [2] had the metal–carbon splitting as rate determining, showed isokinetic temperatures 330 K for Fe and 320 K for Co [1], that could be analyzed as indicating M–C vibrational frequencies.

The “isokinetic effect” is phenomenologically described [4,5] by

$$\ln k_0 = \ln k_{\text{iso}} + \frac{E_a}{RT_{\text{iso}}} \quad (1)$$

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where k_0 is the pre-exponential factor of the Arrhenius equation

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (2)$$

and E_a the activation energy, k_{iso} the isokinetic rate constant, T_{iso} the isokinetic temperature. Eqs. (1) and (2) can be combined to

$$\ln k = \ln k_{\text{iso}} - \frac{E_a}{RT} \left(\frac{1}{T} - \frac{1}{T_{\text{iso}}} \right) \quad (3)$$

indicating that $\ln k$ is independent of E_a at $T = T_{\text{iso}}$.

However, the kinetic data used for the analysis for cobalt and iron were of very old record [6] and furthermore extensive extrapolations had to be made [1]. In order to improve the accuracy and reliability of available data, we have made new, careful measurements of ethane hydrogenolysis over supported cobalt catalysts. The results of these measurements will be compared with other recent investigations of similar art. Especially, as the data of Haddad and Goodwin [7] indicated an isokinetic relationship, we felt encouraged to look for isokinetic relations also with our data.

1.1. The SET model

The basis for the above-mentioned analyses is a model proposed by one of us [8], implying a selective energy transfer (SET) from the catalyst system to the reacting molecule. This transfer is assumed to operate through vibrational resonance so that a certain vibrator in the catalyst system has a frequency (ω , cm^{-1}) that agrees with the frequency (ν , cm^{-1}) of precisely that vibrational mode of the reacting molecule that most closely corresponds to the reaction coordinate. Applying the rules for a coupled damped oscillation system of classical physics it was deduced that the isokinetic temperature could be expressed as a function of ν and ω . This semi-classical resonance model relates the activation of the reacting molecule to a steady gain of energy of the vibration mode leading towards reaction (ν) in spite of a likewise steady loss of energy from the excited levels of this vibration mode by a series of dissipation processes. The main energy input comes from vibrations (ω) of the “heat bath” of a frequency similar to that of the reacting molecule. If this resonance process is more effective than the energy

dissipation process, the molecule can be excited in the critical mode to such an extent that it reacts.

If the frequency of reacting molecule is denoted as ν and that of the heat bath as ω , as indicated above, the following relation can be deduced from an analogy with the classical physics treatment of coupled, damped oscillator systems [8]:

$$T_{\text{iso}} = NhcR^{-1}(\nu^2 - \omega^2)\omega^{-1} \times \left\{ \pm \frac{1}{2}\pi - \arctg[0.5\nu\omega(\nu^2 - \omega^2)]^{-1} \right\}^{-1} \quad (4)$$

Especially, if $\omega = \nu$, in which case one has maximum efficiency of resonance energy transfer, it holds [8] that

$$T_{\text{iso}} = \frac{Nhc}{2R\nu} = 0.719\nu \quad (5)$$

In this formula, T_{iso} is expressed in K, and ν and ω are expressed in cm^{-1} .

It was from this simple formula (Eq. (5)) that the conclusions of the first-mentioned paper [1] were drawn. This means that complete resonance was assumed.

2. Experimental

2.1. Catalyst preparation

Davison Grade 62 silica gel was used as a support. Support pretreatment consisted of sieving (75–120 mesh), fines removal, acid and redistilled water washing and, finally, drying in air at 393 K overnight.

Co/SiO₂ catalysts preparation was realized by impregnation of silica gel with an aqueous solution of CoCl₂ (analytical reagent from POCh, Gliwice, Poland) using an incipient wetness technique. Thereafter, drying in an air oven at 393 K for 16 h was applied. Three variously metal loaded catalysts were prepared with 3, 6 and 10 wt.% Co. We had also at our disposal another silica-supported cobalt catalyst (10 wt.% Co) originating from our earlier study. It was prepared in a similar way as the above-mentioned catalysts, using SiO₂ (puriss, 80–100 mesh) from Serva.

2.2. Catalyst characterization

Reducibility of the cobalt precursors was investigated by TPR (temperature programmed reduction) in

a flow system. A Gow-Mac thermal conductivity detector, temperature ramp 8 K/min, and a 10% H₂/Ar reducing mixture (at 25 cm³/min) were used. The gases were purified by passing over MnO/SiO₂ and drying traps.

Prior to catalytic runs, the catalysts were reduced at 653 K for 16 h. Since TPR profiles showed maxima at somewhat higher temperatures (between 673 and 773 K), one had to check if the H₂/Ar treatment at 653 K for 16 h led to a complete reduction of the cobalt precursor. Such additional TPR runs showed that indeed 653 K in H₂/Ar for 16 h led to a full reduction.

X-ray diffraction (XRD) was performed with a Rigaku-Denki instrument using Ni-filtered Cu K α radiation.

Metal (cobalt) dispersion was determined by hydrogen chemisorption following the procedure recommended by Reuel and Bartholomew [9]. A reduced and outgassed catalyst was saturated with hydrogen at 423 K, and the amount of adsorbed hydrogen was measured by temperature programmed desorption in an argon stream, ramping the temperature at 20 K/min.

2.3. Reaction procedure

Ethane (Matheson; chemical purity, 99.3%) hydrogenolysis was followed over the thus prepared catalysts in a flow system under atmospheric pressure by gas chromatography (HP 5890 series II with 6 m squalane/Chromosorb P column and FID). The partial pressures of reactants were: 10 Torr (ethane) and 100 Torr (H₂) (1 Torr = 133.32 N m⁻²) with helium as balance gas. The reaction was carried out at 553–634 K.

3. Results

3.1. Catalyst characterization

Fig. 1 collects TPR profiles of investigated Co/SiO₂ catalysts. The appearance of TPR maxima at 673–773 K is in general agreement with other works [7,10,11]. One observes that the low metal loaded sample (3 wt.%) reduces at somewhat lower temperature compared to high loaded catalysts (6 and 10 wt.%). However, taking into account that similar charges of all catalysts were used in TPR experiments

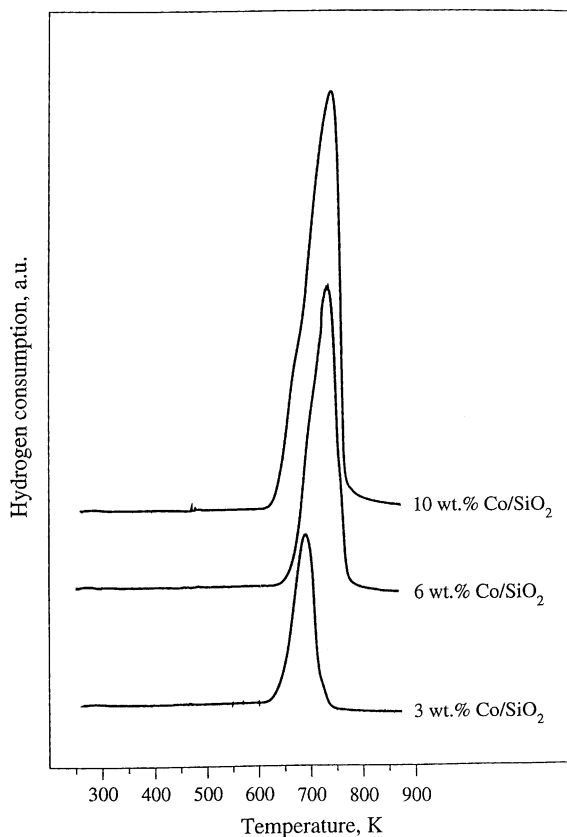


Fig. 1. Hydrogen TPD results from Co/SiO₂ catalysts.

(~0.25 g), it seems possible that in the case of high metal loaded samples, the TPR experiments were not carried out in an optimum regime, i.e. when the hydrogen content in a reducing gas mixture (H₂/Ar) is not too extensively diminished over the catalyst bed. The TPR experiments were intentionally performed in this way because catalysts' weights employed in reaction studies were roughly of the same order (0.2–0.3 g), so it was important to learn how the reduction proceeds with similar catalyst's charges. Nevertheless, the overall picture from TPR experiments (including difference TPR spectra for catalysts prerduced at 653 K for 16 h, profiles not shown) displayed that the reduction time used prior to catalytic measurements was sufficient to reduce the cobalt precursor (CoCl₂/SiO₂) to zerovalent cobalt species.

Hydrogen chemisorption showed that metal dispersion of all three Co/SiO₂ catalysts was very low, lower

Table 1
Results of dispersion measurements

Catalyst	H/Co from H ₂ chemisorption
3 wt.% Co/SiO ₂ (Davison 62)	0.0068
6 wt.% Co/SiO ₂ (Davison 62)	0.0032
10 wt.% Co/SiO ₂ (Davison 62)	0.0024
10 wt.% Co/SiO ₂ (Serva)	0.0124

than 1% (Table 1). The XRD experiments of reduced Co/SiO₂ samples showed very sharp and narrow XRD reflections characteristic of very big metal crystallites (>60 nm) corresponding to low metal dispersion, supporting the results from H₂ chemisorption. Fig. 2 illustrates the results for 3 wt.% Co/SiO₂, showing the appearance of two crystallographic forms of metallic cobalt: α -Co and β -Co.

CoCl₂ was chosen as a precursor salt as its use leads to complete (100%) reduction to zerovalent cobalt species at relatively mild reduction temperatures. This would not be the case for other precursor salt, such as cobalt nitrate. In addition, one has to avoid too high reduction temperatures as those would lead to the formation of cobalt silicate. As it is seen from Table 1, our catalysts had quite poor metal dispersion. Such low

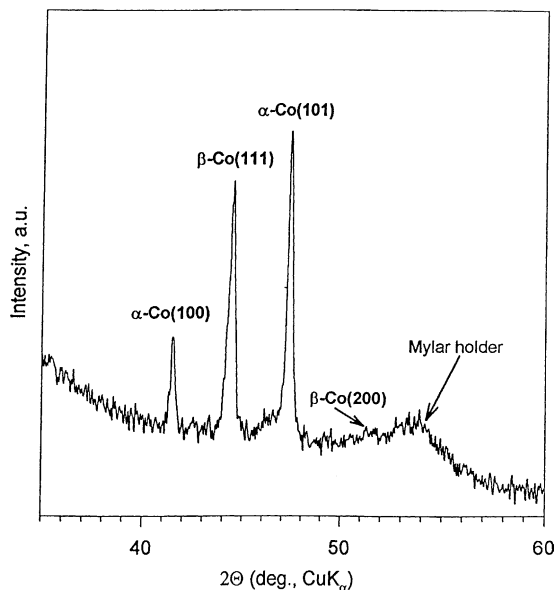


Fig. 2. XRD data for one of the catalyst preparations (3 wt.% Co/SiO₂) showing the presence of both α - and β -cobalt.

Table 2
Catalytic conversion of ethane on 3 wt.% Co/SiO₂

Reaction temperature (K)	TOF ($\times 10^4$ s ⁻¹)	Activation energy (kJ/mol)	ln(TOF) ₀
634	17.52		
613	8.82		
613	9.15		
593	4.07		
593	4.13	118.0 \pm 1.3	16.11 \pm 0.27
573	1.74		
573	1.72		
553	0.69		
553	0.70		

Table 3
Catalytic conversion of ethane on 6 wt.% Co/SiO₂

Reaction temperature (K)	TOF ($\times 10^4$ s ⁻¹)	Activation energy (kJ/mol)	ln(TOF) ₀
634	8.76		
613	4.52		
613	4.69		
593	2.16	113.8 \pm 9.4	14.61 \pm 0.88
593	2.44		
573	1.14		
573	0.71		

dispersions resulted from the use of chloride as the anion. Similar effects have also been found in Co/SiO₂ catalysts prepared from CoCl₂ by Nitta et al. [10] and by Rosynek and Polansky [11] who report dispersions of the order 0.002–0.003, in a very good agreement with our data (Table 1). Incidentally, one might estimate a somewhat higher dispersion (H/Co \sim 0.08¹) for the catalyst systems used by Sinfelt et al. [3,12] prepared from cobalt nitrate.

3.2. Kinetic measurements

The results of kinetic runs are reported in Tables 2–5. We obtained the activation energy value for all four cobalt catalysts in the range of 104–118 kJ/mol. This level is similar to that obtained by Sinfelt et al. (125 kJ/mol, [12]). Haddad and Goodwin [7] reported somewhat lower values, between 88

¹ Estimation of cobalt dispersion in 10 wt.% Co/SiO₂ catalyst based on data presented in Ref. [12] (5.6 m²/g_{cat}, 6.5 Å²/Co atom).

Table 4
Catalytic conversion of ethane on 10 wt.% Co/SiO₂ (Davison 62)

Reaction temperature (K)	TOF ($\times 10^4 \text{ s}^{-1}$)	Activation energy (kJ/mol)	$\ln(\text{TOF})_0$
634	15.33		
593	3.39		
593	3.54	118.6 ± 6.3	16.04 ± 1.27
573	1.25		
573	1.57		
574	1.24		

and 100 kJ/mol. One should also note that Babernics et al. [13] obtained 111 kJ/mol for unsupported Co catalysts. These data will be analyzed further in Table 6.

Plots of $\ln A$ versus E_a are shown in Fig. 3. They contain the present results together with the data furnished by Haddad and Goodwin [7]. In the latter case, $\ln A$ was calculated from TOF at 493 K and the activation energy supplied. However, one must note that the error of TOF is $\pm 20\%$. Our catalysts were less active than those of Sinfelt et al. [12] and Haddad and

Table 5
Catalytic conversion of ethane on 10 wt.% Co/SiO₂ (Serva)

Reaction temperature (K)	TOF ($\times 10^4 \text{ s}^{-1}$)	Activation energy (kJ/mol)	$\ln(\text{TOF})_0$
614	5.23		
613	5.18		
604	3.83		
604	3.81		
593	2.73		
594	2.66	104.5 ± 1.4	12.93 ± 0.29
584	1.84		
583	1.83		
573	1.26		
573	1.24		
574	1.24		

Goodwin [7], but more active than the unsupported Co samples of Babernics et al. [13].

The slopes of the two lines of Fig. 3 yields the isokinetic temperature, T_{iso} , from Eq. (1). The present data gives $T_{\text{iso}} = 530 \text{ K}$, whereas those of Haddad and Goodwin [7] gives $T_{\text{iso}} = 453 \text{ K}$. One notes that both

Table 6
Activation energies of this and other investigations on ethane hydrogenolysis

Reference	E_a (kJ/mol)	D^a	$\log(D)$	ΔE_a^b (kJ/mol)	$\Delta E_a/4.2^c$	n^d
Sinfelt et al. [12]	125.1	0.08	-1.097			
Babernics et al. [13]	111.0	0.0069	-2.161	14.1	3.357	3
This work						
3% Co/Davison	118.0	0.0068	-2.167	7.0	1.667	2
6% Co/Davison	113.8	0.0032	-2.495	4.2	1.000	1
10% Co/Davison	118.6	0.0024	-2.620	4.8	1.143	1
10% Co/Serva	104.5	0.0124	-1.907	14.1	3.357	3
Haddad and Goodwin [7]						
B4,5 (20%)	96.2	0.0740	-1.131	8.3	1.976	2
W6-25	92.0	0.0670	-1.174	4.2	1.000	1
W6-50	100.4	-	-	8.4	2.000	2
W6-90	83.7	0.1000	-1.000	16.7	3.976	4
W6-110	92.0	0.1520	-0.818	8.3	1.976	2
				33.1	7.881	8
Sum				123.2		29
Mean increment = $123.2/29 = 4.25 \text{ kJ/mol} = 355 \text{ cm}^{-1}$						

^a Dispersion estimated as either $1/d$ (d particle size in nm, Ref. [7]) or H/Co (from H₂ chemisorption, Ref. [12] and this work) or from BET surface area (Ref. [13]). See also footnote 2.

^b Absolute values of the successive differences of E_a , e.g. $125.1 - 111.0 = 14.1$, and $|92.0 - 100.4| = 8.4$.

^c Divided by the least number in the previous column, 4.2 kJ/mol, in this case appearing twice.

^d The nearest digit of the value in the preceding column.

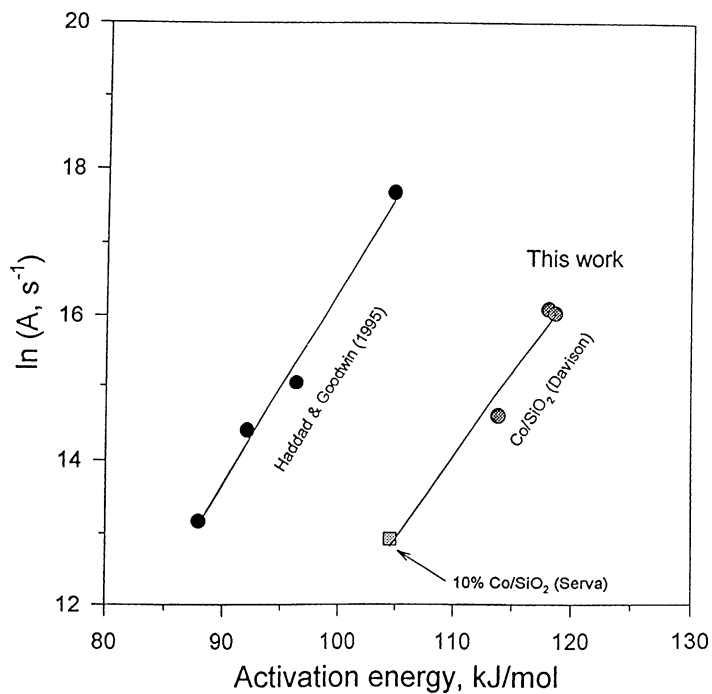


Fig. 3. Compensation line for the present data (lower line; $R^2 = 0.977$) and those by Haddad and Goodwin [7] (upper line).

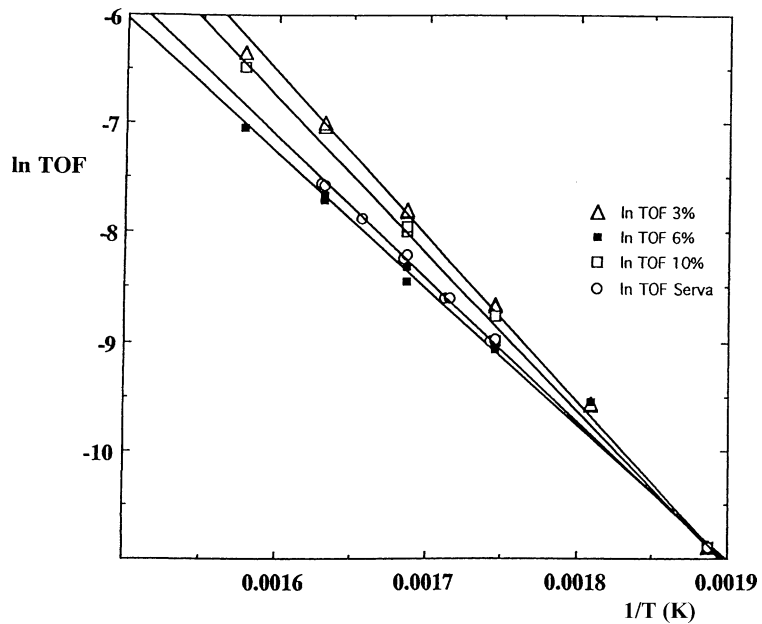


Fig. 4. Arrhenius lines for the present data, including the isokinetic point ($R^2 = 0.998, 0.996, 0.999$ and 1.000).

these values are significantly larger than the one estimated before [1], viz. $T_{\text{iso}} = 320$ K. In the continued discussion we will use the mean value of our result and that of Haddad and Goodwin [7]; $T_{\text{iso}} = 490 \pm 40$ K.

To test the significance of the estimated T_{iso} (that rested on the error-sensitive $\ln A$ versus E_a plot) we constructed Arrhenius plots for each of the four systems including the point for the isokinetic relation (530 K, -10.891). The lines were drawn with a 5-fold weight for the isokinetic point. As seen from Fig. 4, the lines fitted the points with good correlation factors.

4. Discussion

4.1. The isokinetic data

From the above data one can, for the purpose of this investigation, be satisfied with writing $T_{\text{iso}} = 490 \pm 40$ K. What does this figure imply about the vibration mode ν and the mechanism of the reaction in the light of the SET model (see Section 1)?

At first, one should try the assumption that there is a full resonance. In this case, Eq. (5) is applicable,

so $\nu = (490 \pm 40)/0.719 = 680 \pm 55 \text{ cm}^{-1}$. Such a value is not inconsistent with spectroscopic data. According to the survey of vibrational spectra of alkane adsorption products by Sheppard and de la Cruz [14] it should probably correspond to a double bonded CH_2 group. These authors quote, e.g. the $\nu \text{ CM}_2$ mode of adsorbed CH_2 on Fe as 640 cm^{-1} [14].

Another possibility should also be considered, viz. that the single bond stretching of the $\nu \text{ M-CH}_3$ mode is involved, which is found, e.g. at 385 cm^{-1} for Ni [14] and at 360 cm^{-1} for Cu [14]. In such a case, full resonance is not operating, and one has to use the complete form of the relation for T_{iso} , i.e. Eq. (4). In Fig. 5 we have calculated the appropriate curve for $\nu = 400 \text{ cm}^{-1}$, and also, for comparison, the curve for $\nu = 680 \text{ cm}^{-1}$. $\nu = 400 \text{ cm}^{-1}$ was chosen from an extrapolation of the frequencies for Ni and Cu [14] using the Allred–Rochow electronegativities [15] of the metals (Fig. 6). In the same figure we have used also the Pauling electronegativities [15]. Extrapolation to the proper Pauling value for Co gives $\nu = 362 \text{ cm}^{-1}$. Because of the different outcome of the extrapolations and for reasons to be given below, we also include a curve based on $\nu = 355 \text{ cm}^{-1}$. One notes that a value

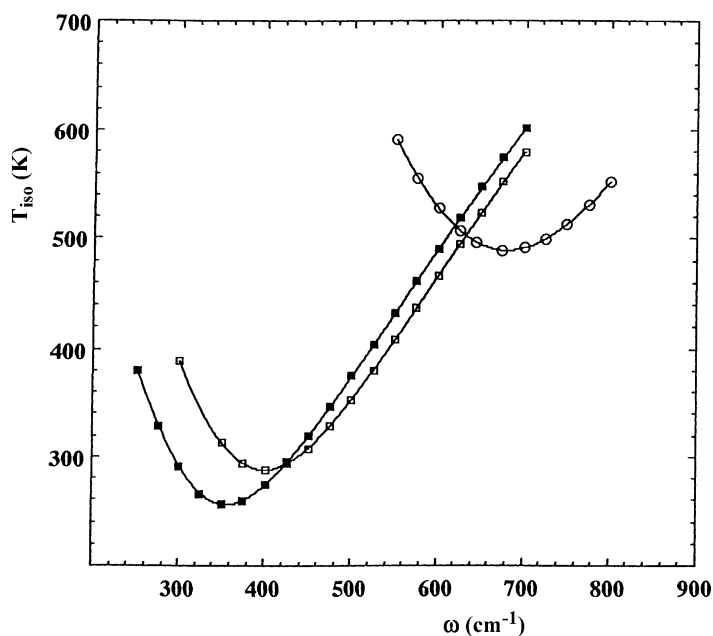


Fig. 5. T_{iso} as a function of the energy supply vibration frequency (ω , cm^{-1}) according to Eq. (4) for three values of the critical vibration of the reactant; $\nu = 355 \text{ cm}^{-1}$ (filled squares), $\nu = 400 \text{ cm}^{-1}$ (open squares) and $\nu = 680 \text{ cm}^{-1}$ (circles).

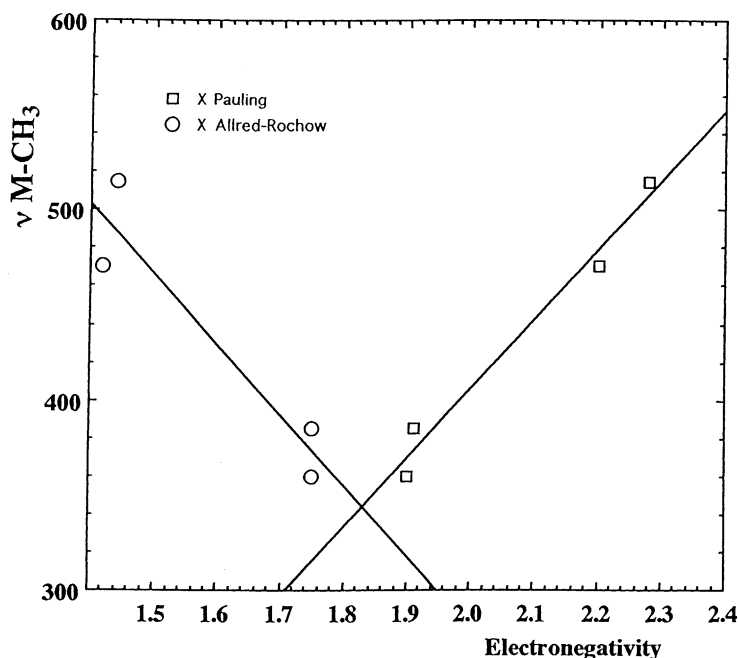


Fig. 6. The relation between ν M-CH₃ and electronegativity. The two lines representing Pauling ($R^2 = 0.977$) and Allred-Rochow ($R^2 = 0.893$) electronegativities are cut at the appropriate value for Co (1.88 and 1.70).

of $T_{\text{iso}} = 490$ K is read if $\omega \approx 620$ cm⁻¹ for the $\nu = 400$ cm⁻¹ curve and, also, if $\omega \approx 600$ cm⁻¹ for the $\nu = 355$ cm⁻¹ curve.

It thus seems that both mechanisms might work if an energy source of about 600–700 cm⁻¹ is available. In analogy with our previous investigation on supported metal catalysts [16] we suggest that vibration modes of the silica support might supply this energy. For many of the different silica forms, one finds strong to medium IR bands in this region [17]. It may seem strange that, e.g. a vibration with $\omega \approx 620$ cm⁻¹ should resonate with a vibration at 400 cm⁻¹. One can observe however that $600:400 = 3:2$; this relation means that two quanta of the energy source will activate three quanta of the reacting molecule. Such a many-quanta effect has been found previously [18], e.g. in the case of formic acid decomposition.

4.2. Activation energies

Returning now to the order of the activity of different cobalt catalysts: Sinfelt [12] \geq Haddad and

Goodwin [7] > present work > Babernics et al. [13], one might surmise that the size of cobalt particles is causing this trend. The influence of metal particle size on reactivity has been thoroughly discussed by Che and Bennett [19]. Using nickel as an example, these authors found that metal dispersions (=fraction exposed) at the order of magnitude met in the present report gave a rapid decrease of activity with decreasing dispersion (increasing particle size).

Of course, both pre-exponential factors and activation energies determine the magnitude of reactivity. It might be difficult to distinguish between the two parameters. It is a corollary to the SET model that activation energies are determined by geometric factors and will change stepwise [20] with increments made up by the vibrational quanta of that vibrational mode that we call ν in this context. Such geometric factors can very well be determined by the size of the particles.

In Table 6 we have collected the activation energies reported by Sinfelt et al., Babernics et al. and Haddad and Goodwin, as well as obtained in this work. We

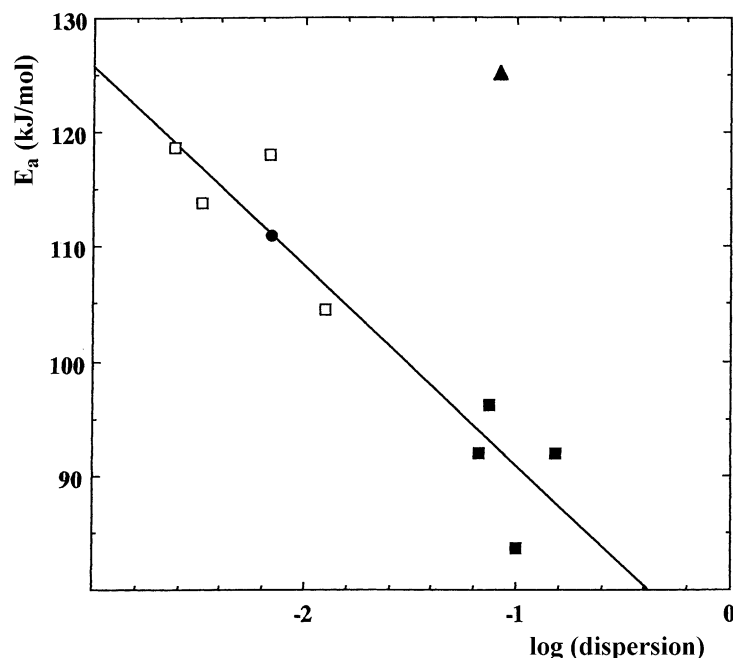


Fig. 7. The effect of particle size (metal dispersion) on the experimental activation energies: Haddad and Goodwin [7] (filled squares), Sinfelt et al. [13] (triangle), Babernics et al. [13] (circle), present work (open squares). A good correlation ($R^2 = 0.89$) is observed if Sinfelt et al. data are omitted.

have also tried to estimate ² the dispersions of the various catalysts used. It appears that there is a fairly good correlation between activation energies and (decreasing) dispersions (Fig. 7). In Table 6 we have also performed a type of calculation that has been used before [21,22] based on the above-mentioned stepwise change of activation energies. The successive differences between consecutive E_a data in the table have been calculated. From the procedure described in the comments of Table 6 we find a common increment of about 4.25 kJ/mol. This would correspond to $\nu = 355 \text{ cm}^{-1}$ in good agreement with the extrapolation in Fig. 6 using the Pauling scale of electronegativities. As the differences in experimental temperatures are not very large between the different investigations we have neglected the correction with the term RT so as not to complicate the presentation. Actually, the same value of ν is obtained if such a calculation is performed. It is

from this result we have constructed one of the curves in Fig. 5, which indicates that the requirement $T_{\text{iso}} = 490 \text{ K}$ is fulfilled for $\omega = 600 \text{ cm}^{-1}$. Obviously, we do not have a perfect resonance condition, but one can note that $600:355 = 1.69$, i.e. almost exactly 5:3.

5. Conclusions

Above we found that a value of $\nu = 680 \text{ cm}^{-1}$ fulfills the experimental criterion of isokinetic temperature with full resonance. We also found that $\nu = 355$ or 400 cm^{-1} reproduced the isokinetic temperature if the driving frequency ω is 600 or 620 cm^{-1} , respectively. From the analysis of activation energies it seems most likely that the reacting vibration is $\nu = 355 \text{ cm}^{-1}$. The above analysis strongly indicates that the rate determining step is one of breaking one (or possibly two) carbon–metal bond, not one of breaking the carbon–carbon bond of ethane. This conclusion is in full agreement with the proposal of Sinfelt [2].

² See footnote 1. Estimation of cobalt dispersion in cobalt powder based on data presented in Ref. [13] ($4.5 \text{ m}^2/\text{g}$ BET surface area, $6.5 \text{ \AA}^2/\text{Co atom}$).

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