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Kinetic study on carbon dioxide hydrogenation over Ru/γ-Al_2O_3 catalysts

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ABSTRACT

Set of Ru/γ-Al_2O_3 catalysts prepared by the DIM method was examined in reaction of carbon dioxide hydrogenation. Overall apparent activation energy reaches a minimum at ruthenium dispersion equal 0.5. Reaction order with respect to hydrogen decreases with H/Ru, whilst reaction order with respect to CO_2 changes slightly within examined dispersion range. Two interpretations of observed isokinetic effect, calculated T_{iso} and corresponding wavenumber are presented.

1. Introduction

Carbon dioxide is one of the main greenhouse gases being emitted into the atmosphere due to human activity. Its growing concentration increases global warming [1–3]. Very recently Global Research Technology in cooperation with Klaus Lackner from Columbia University have successfully demonstrated “a bold new technology to capture CO_2 from the air” [4], but the question “what to do with sequestered carbon dioxide?” remains open. Long known Sabatier reaction [5] may offer a way of converting CO_2 into valuable chemical compounds. Simultaneously, it may help to resolve problems with hydrogen storage [6], which is considered to be a clean fuel of the future.

Ruthenium is the most active methanation catalyst [7]. The reaction selectivity depends on support type and addition of modifiers. Silica supported ruthenium catalysts show the highest selectivities towards methane [8,9]. Supporting Ru on oxides that interact with active metallic phase (i.e. Al_2O_3) or use of modifiers increases the selectivity towards other products [10–13]. However, the reaction is considered to be structure insensitive [14,15] it can be found in literature data that metal/oxide interface may have an influence on its course [16–18]. The aim of this study was to determine kinetic parameters of the reaction for ruthenium/alumina systems characterized with different dispersion of metallic phase: rates, activation energies, selectivities and reaction orders with respect to hydrogen and carbon dioxide.

2. Experimental

2.1. Catalysts preparation

A set of ruthenium catalysts was prepared using double impregnation method (DIM) [19,20]. Thus, the alumina support (high purity Cyanamid, 84.4 m^2/g) was initially impregnated with a 0.1 M aqueous solution of disodium salt of EDTA (ethylenediaminetetraacetic acid) at 345 K for 0.5 h. This form of support was dried at 393 K for 1 h and divided into five samples. The samples were then impregnated with a 1 wt.% (calculated on the basis of the pure metal) ruthenium red solution (treated with NH_4OH to yield a pH of 12) for 1, 2, 3, 4 and 5 min, respectively. To avoid generating of volatile ruthenium oxychlorides [21] a calcination was omitted: solids were dried and prereduced in hydrogen (5 cm^3/s) at 773 K for 1 h. Reduction process was repeated *in situ*, just before measurements.

2.2. Catalysts characterization

Ruthenium loadings were measured using the X-ray fluorescence method (XRF). The active surface areas were determined from hydrogen chemisorption at 373 K using a volumetric apparatus, which ensured that a vacuum of at least 1.33×10^{-5} kPa kPa was maintained. It was also assumed that the hydrogen/ruthenium stechiometry was 1:1 [22,23].

2.3. Kinetic tests

Hydrogenation of carbon dioxide ($H_2/CO_2 = 4.2$) was studied using a gradientless reactor described in paper [24]: an *iso-x* tests were performed, i.e. all the results were calculated for CO_2 conversion equal 5% (0.05). A Chrompack CP9001 gas chromatograph with a PC computer as an integrator was used to analyse the

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products. Activation energies were measured within temperature range 573–653 K. Reaction orders with respect to hydrogen and carbon dioxide were determined by varying reagents partial pressures from 0.373 to 0.802 and from 0.091 to 0.176 (respectively) at 583 K.

3. Results and discussion

3.1. Catalysts parameters

Physicochemical properties of investigated catalysts are listed in Table 1. Ruthenium loading varied from 0.575% to 0.815%. As it was expected it increased with the time of second impregnation step. According to literature data [25–27] increasing metal content decreases its dispersion. The opposite phenomenon was observed: ruthenium loading and H/Ru ratio were positively correlated.

In IR study [28] Ryczkowski showed, that adsorbed EDTA may interact with ruthenium ions in ruthenium red via carboxyl groups, and that this interaction is stronger, if the time of the second impregnation step increases. His observation suggests, that with increasing duration of this stage larger amounts of the precursor are deposited on support via EDTA. It has been shown that similar phenomena facilitates high dispersion of catalyst metallic phase after reduction [19,20]: it seems that in this case similar mechanism operated, what explains increase in H/Ru with Ru loading.

Table 1
Physicochemical properties of Ru/γ-Al_2O_3 catalysts

Catalyst[a]	C_{Ru}	V_{H_2}	H/Ru
Ru-01	0.575	0.23	0.36
Ru-02	0.607	0.23	0.34
Ru-03	0.699	0.33	0.42
Ru-04	0.766	0.43	0.50
Ru-05	0.815	0.52	0.58

C_{Ru}—ruthenium loading (%), V_{H_2}—hydrogen chemisorption (cm^3/g_{cat}), and H/Ru—metallic phase dispersion.

[a] Numeral denotes duration of the second impregnation step, e.g. Ru-05 corresponds to 5 min.

3.2. Kinetic parameters

Ruthenium catalysts are highly selective towards methane, even if supported on Al_2O_3 [29]. The main products of the reaction were CH_4 and water. Traces of carbon monoxide were present among products, too, but a methanol was completely absent. No influence of any of the physicochemical properties on the selectivity was observed.

Measured apparent activation energies were within range 82–106 kJ/mol, and are in agreement with literature data. Similar values were reported by Takeishi and Aika (81 kJ/mol) [17], and Li et al. (86–104 kJ/mol) [11]. Slightly lower activation energies were measured by Weatherbee (72 kJ/mol) [8]. The results of this study are presented in Table 2, which also lists respective reaction orders and rates.

Fig. 1a shows a relationship between overall apparent activation energy and dispersion of the metallic phase: clear minimum is attained at dispersion of ruthenium equal 0.5. It is known that enthalpies of substrates adsorption, activation energies and reaction orders are connected by the following equation [30]:

$$E_a = E_t + \sum n_i \Delta H_i \tag{1}$$

Studying ruthenium, ruthenium–silver and ruthenium–copper systems by means of microcalorimetry Narayan and King have shown [31] that low coordination sites (such as corners and edges) do not have significantly different heats of hydrogen adsorption than basal planes. Consequently, changes in population of those sites due to variation of dispersion should not have influence on average enthalpy of hydrogen adsorption and apparent activation energy.

Table 2
Measured kinetic parameters

Catalyst	E_a	n_{H_2}	m_{CO_2}	TOF
Ru-01	96.5 ± 3.9	0.68 ± 0.06	0.22 ± 0.02	2.36 ± 0.39
Ru-02	105.2 ± 3.1	0.87 ± 0.05	0.26 ± 0.04	2.48 ± 0.48
Ru-03	87.7 ± 3.1	0.53 ± 0.03	0.14 ± 0.03	1.73 ± 0.26
Ru-04	82.6 ± 1.1	0.46 ± 0.05	0.18 ± 0.02	1.38 ± 0.21
Ru-05	102.3 ± 2.0	0.53 ± 0.04	0.28 ± 0.03	1.23 ± 0.18

E_a—apparent activation energy (kJ/mol), n_{H_2}—reaction order with respect to hydrogen, m_{CO_2}—reaction order with respect to carbon dioxide, TOF at 608 K (s^{-1}).

In the same paper Narayan and King have shown that this enthalpy strongly depends on surface coverage with hydrogen (θ_H), being the highest (≈95 kJ/mol) for low θ_H. Simultaneously, according to Marwood et al. [18] metal/support interface plays special role in generating of surface CO* species. Observed decrease in apparent activation energy may be explained as follows: higher ruthenium dispersion increases the amount of metal/oxide border, consequently, generating of surface CO* is easier. As a result surface coverage with CO* increases, whilst θ_H decreases, and heat of hydrogen adsorption increases. Since true activation energy E_t remains constant, higher, negative ΔH_{ads} lowers apparent activation energy (Eq. (1)).

Decrease in reaction order with respect to hydrogen from 0.9 to 0.5 (Fig. 2a) can be explained in terms of "portal mediated hydrogen adsorption" proposed by Vanderwiel et al. [23]. According to them highly reactive surface hydrogen species are generated due to H_2 adsorption on edges and corners of ruthenium crystallites. The population of those sites increases with dispersion, what facilitates hydrogen adsorption and lowers reaction order with respect to this substrate. Low and only slightly changing with H/Ru reaction order with respect to carbon dioxide suggest, that CO_2 adsorbs on different parts of catalyst surface.

Measured kinetic parameters and Eq. (1) may be used to estimate the true value of activation energy E_t. The estimation is based on an extrapolation of the dependence $E_a = f(n)$ to zero order: products of reaction orders and adsorption enthalpies disappear from the right side of Eq. (1), thus $E_a = E_t$. It should be emphasized that the results of this procedure should be treated with special care, because apparent activation energy may change with reactants partial pressures, and reaction orders may change with temperature during E_a measurements. According to Bond [30] such results should be considered qualitative.

Results of estimation made under the foregoing limitations are presented in Fig. 1b. Estimated true activation energy is 60 ± 12 kJ/mol. However, this value is quite close to activation energy of hydrogenation surface carbon species measured by authors of publication [18] (75 kJ/mol), taking into account apparent activation energies, positive reaction orders (Table 1) and exothermicity of the adsorption this value is far too low to satisfy Eq. (1), and the above estimation should be considered unsuccessful.

Compensation phenomenon was observed. Linear relationship between preexponential factors and apparent activation energies is presented in Fig. 3a. Many explanations of this effect have been proposed in literature [32–34]. Authors of papers [35–37] have pointed out, that distinction should be made between compensation and isokinetic effect. The latter is defined by the existence of a common intersection point of lines describing activation energies (on Arrhenius plots) in similar catalytic systems [37]. This intersection point describes so called isokinetic temperature T_{iso}. According to theory of selective energy transfer this temperature

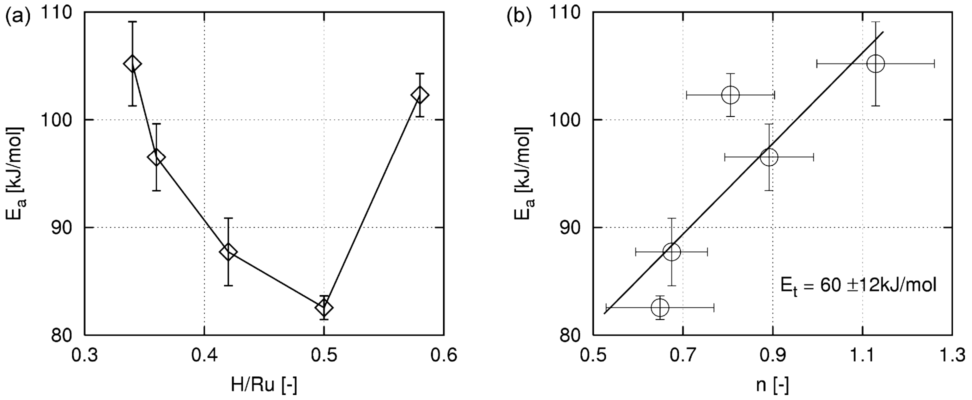

Fig. 1. Apparent activation energy E_a as a function of metal dispersion H/Ru (a) and total reaction order n (b).

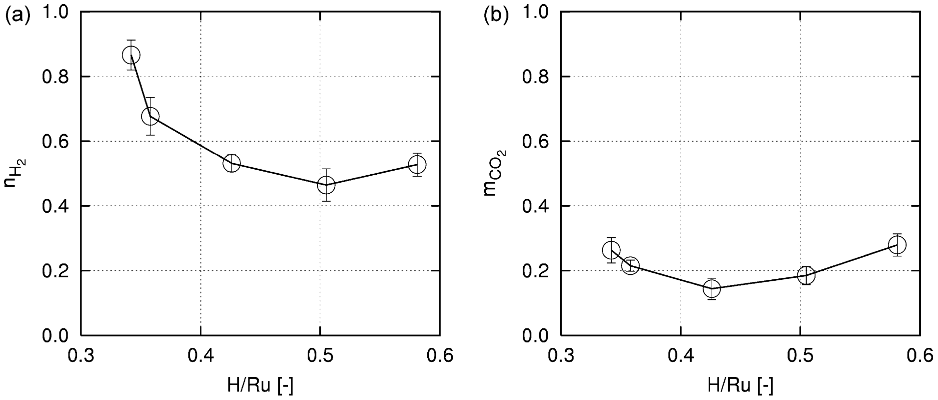

Fig. 2. Relationship between metal dispersion (H/Ru) and reaction order with respect to hydrogen (a) and carbon dioxide (b).

corresponds to those vibrations ν of reacting species, which perturb the structure of an intermediate towards its activated state [38]. The two parameters are connected via Eq. (2) [37,38]:

$$T_{\mathrm{iso}} = 0.715 \cdot \nu \qquad (2)$$

Calculated isokinetic temperature $T_i = 549 \pm 14$ K (Fig. 3b) corresponds to wavenumber $\nu = 770$ cm^{-1}. The latter value may be associated with vibrations of at least two reacting species. In first interpretation $\nu = 770$ cm^{-1} is attributed to vibrations of formates adsorbed on ruthenium/alumina border [39]. According to the reaction mechanism proposed by Marwood et al. [18] those species are precursors of surface carbon monoxide and thus play an important role in the process. Consequently, the results indicate, that reaction pathway described in [18] may be valid for higher temperatures and ruthenium systems supported on alumina.

Second explanation assumes that vibrations at 770 cm^{-1} are attributed to coordinated surface carbon dioxide. In publication [40] Larsson and Mascetti analysed data collected by Grabke [41] and observed an isokinetic effect with $\nu = 780$ cm^{-1} in systems where hydrogen was completely absent (only supported metals and carbon dioxide were present). The authors related obtained wavenumber to bending vibrations of adsorbed CO_2. Consequently, according to this interpretation, value calculated in this study

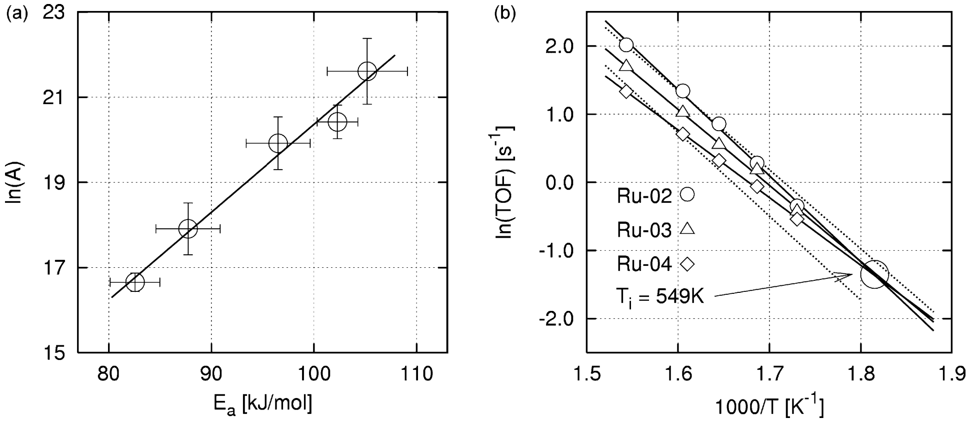

Fig. 3. Linear relationship between apparent activation energies and preexponential factors (a), isokinetic effect (b).

($770 \pm 20\,\mathrm{cm}^{-1}$) indicates, that adsorbed carbon dioxide is a key intermediate, which play role in energy transfer.

4. Conclusions

Obtained results indicate that optimal dispersion of metallic phase exist, at which apparent activation energy reaches a clear minimum. Observed decrease in E_a across catalysts set may be attributed to changes in heat of hydrogen adsorption, which are due to increase in population of low coordination sites.

Calculated isokinetic temperature and corresponding wavenumber do not allow to explicitly indicate, if reaction of carbon dioxide hydrogenation proceeds via mechanism proposed by Marwood et al. [18] at higher temperatures and when supports other than TiO_2 are utilized.

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