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Oxidative Dehydrogenation of Propane over Pentasil Ring Co-Zeolites

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The activity of Co-zeolites with MFI, BEA, MOR and FER topologies was studied in propane oxidative dehydrogenation. The products of oxidative dehydrogenation of propane were propene, CO, CO_2 and a very small amount of ethene and methane as products of cracking, which play only a minor role. The sequence in ODH activity of Co-zeolites is CoH-BEA > CoH-MFI > CoH-MOR > CoH-FER. The difference in activity of various zeolite matrices is ascribed to the differences of channel diameter and architecture of Co-β sites in the pentasil zeolites. Rate limiting step of propene formation is not the reaction of propane or adsorbed species of propane with oxygen but desorption of propene.

Key words: oxidative dehydrogenation of propane, cobalt, zeolite, propene

Zeolites with ion exchanged cobalt ions seem to be promising catalysts for several selective redox reactions. Recently, Li and Armor [1–5] reported a high activity of zeolites of BEA and MFI structure with ion exchanged Co ions in ethane ammoxidation, which had much higher catalytic activity than oxide-based catalysts for this reaction (Cr-Nb-Mo-O catalyst) [6]. Mechanism of ethane ammoxidation suggested by Li and Armor consists of ethane dehydrogenation to ethylene in the first step, which is subsequently added to strongly adsorbed ammonia, resulting in formation of ethylamine, subsequently, followed by dehydrogenation to acetonitrile [2]. This view was confirmed by study of ethene ammoxidation over Co-MFI catalyst, which led to a very high rate of ethene consumption and formation of acetonitrile with a high selectivity. In our previous studies we dealt with ammoxidation of propane over Co-zeolites [7,8]. We reported the formation of substantial amount of propene and acetonitrile in ammoxidation of propane over Co-zeolites. Our results indicate that ammoxidation of propane proceeds *via* propene as a product of oxidative dehydrogenation of propane, which takes place largely over Co-zeolites under these reaction conditions. Formation of acetonitrile proceeds during addition of ammonia either to propene molecule (Markovnikov rule) or to ethene, which is formed as a result of cracking of propane. In virtue of these facts it seems that activity and selectivity to nitriles in ammoxidation of light alkanes over Co-zeolites depend on activity and selectivity of these materials in the oxidative dehydrogenation of corresponding alkanes. Therefore, it is advisable to attend of catalytic activity studying of Co-zeolites in oxidative dehydrogenation reactions as an initial step of ammoxidation.

Numerous experimental data have been reported on oxidative dehydrogenation of propane and they have been recently reviewed [9–12]. Catalysts tested in oxidative dehydrogenation of propane are mainly mixed oxides, based on vanadium oxide as the main component, which are combined with Mg or Nb. In the last decade, metal containing zeolites or zeolite-like materials were tested in this reaction too [13–21]. The main advantage of zeolitic materials is the possibility of generated isolated oxidizing sites inside the catalytic inert matrices. The greatest attention was paid to the catalytic behaviour of vanadium ions supported in zeolitic materials. Vanadium ions in V-silicalite [13,21], V-MCM-41 [16,20] or VAPO-5 [19] exhibit relatively high yields of propene. Catalytic activity of some other metal ions like Sb, Ga, In [17,18] or Ti [15] in zeolites was investigated.

In the current study, catalytic activities of cobalt containing zeolites are compared in propane oxidative dehydrogenation. CoH-BEA zeolite, which showed the best catalytic results, was investigated in more detail, varying the concentration of reactants and contact time. TPD experiments of propene from CoH-BEA and CoH-FER zeolites were performed in order to obtained information about the activation energy of the propene displacement from zeolite.

EXPERIMENTAL

Catalysts. Na-MFI zeolite was kindly provided by the Institute of Oil and Hydrocarbon Gases, Slovnaft, Slovakia. Na,K-FER and NH_4-MOR were purchased from TOSOH Co., Japan. NH_4-MFI was prepared from Na-MFI by repeated ion exchange with 1 M NH_4NO_3 solution (10 g of a zeolite per 150 cm^3 of solution at 353 K stirring overnight). NH_4-FER was prepared from Na,K-FER by the repeated exchange with 1 M NH_4NO_3 solution at 343 K (1000 cm^3 of solution per 20 g of a zeolite). After ion exchange were both zeolites washed several times with distilled water, filtered and dried in air at room temperature. NH_4-BEA zeolite with Si/Al ratio 12.4 was purchased from PQ Corp., USA. Cobalt ions were introduced into zeolites by ion exchange of the NH_4-forms of MFI, BEA, MOR and FER zeolites with cobalt(II) nitrate or cobalt(II) acetate solutions. After ion exchange, the solids were thoroughly washed with distilled water, filtered and dried in air at RT. The chemical composition of zeolites was determined by Wavelength-disperse X-Ray Fluorescence Spectroscopy (WD XRF) and by Atomic Absorption Spectrometry after zeolites' dissolution. The method of calibration of WD XRF is described elsewhere [22]. Conditions of preparation of zeolites and their chemical composition are given in Table 1.

Catalytic activity measurements. The reaction runs were made by using plug-flow reactor in a steady-state at atmospheric pressure. Comparative study was performed at a total flow rate of 100 cm^3/min, a catalyst weight of 0.2 g (0.25–0.5 mm particle size) mixed with 1.5 cm^3 of inert silicon carbide, and helium was used as an inert carrier gas. A feed composition was 5 vol. % of propane, 6.5 vol. % of O_2 in helium. The catalysts were pretreated in a stream of mixture containing 6.5 vol. % of O_2 in He at 723 K 1 h before each reaction run. The conversion and selectivity were measured in the temperature range from 653 to 773 K, using step by step increasing temperature. Steady-state conditions for each temperature were reached within one hour. A composition of reaction products was analyzed by a gas chromatograph CHROM 5, equipped with thermal conductivity detector and packed column (length 250 cm, 2/3 Carboxen 1000 and 1/3 Porapak Q). Blank runs showed that under the experimental conditions used, the contribution of the homogenous reaction could be neglected. Conversions, yields and selectivity were measured repeatedly (minimally threefold) and their values presented in the paper are arithmetic means. Experimental error of measured data was ±5 relative percents. Catalytic activities of Co-zeolites were expressed as values of TOF factor determined at 723 K (number of propane molecules converted over 1 Co atom for 1 hour).

Temperature programmed desorption (TPD) of propene. A 100 mg of sample was first dehydrated at 723 K for 1 h and cooled to ambient temperature in flowing helium. The catalyst was saturated with adsorbate at RT (1 vol. % propene in He) and then was flushed with He at adsorption temperature with the flow rate of 150 cm^3/min for 1 h. TPD experiment was carried out in the temperature range from RT to 973 K at a variable heating rate (5–40 K/min). The concentration of desorbed species in effluent gas was monitored by the quadrupole mass spectrometer OmniStar^{TM} GDS 300. Mass fractions at 28, 29, 39, 40, 41, 42, and 44 were monitored simultaneously during the C_3H_6-TPD experiment. The intensities of the individual mass fractions were registered every 3 s.

Table 1. Chemical composition and conditions of preparation of CoH-zeolites.

Sample	Chemical composition			Ion exchange parameters				
	Si/Al^a	Co/Al^a	w_{Co}^b	solution	$(mol \cdot dm^{-3})$	cm^3 sol./ 1 g zeolite	time/h	T (K)
CoH-BEA	12.4	0.25	1.80	$Co(CH_3COO)_2$	0.01	66.6	8	298
CoH-MFI	12.5	0.23	1.65	$Co(CH_3COO)_2$	0.05	16	2×7	343
CoH-MOR	9.4	0.28	2.11	$Co(NO_3)_2$	0.05	50	2×3	333
CoH-FER	9.4	0.13	1.04	$Co(CH_3COO)_2$	0.10	16	5×10	333

[a] – atomic ratio; [b] – weight percentage of cobalt in hydrated zeolites.

RESULTS AND DISCUSSION

Oxidation of propane over CoH-zeolites led to formation of carbon oxides and propene as a main product under the reaction conditions. No partially oxygenated compounds were observed. Only a very small amount of ethene (selectivity less than 1%) was detected over zeolites MFI, BEA and MOR. CoH-FER zeolite exhibits a considerably higher amount of ethene, accompanied by a comparable amount of methane (13.9% selectivity to ethene and 13.2% selectivity to methane, see Table 2). The amount of the cracking products slightly increases with increasing reaction temperature. The activity of the catalysts studied in oxidative dehydrogenation of propane at 723 K is presented in Table 2. All the zeolitic matrices (H-zeolites) without cobalt exhibited a very low activity (conversion < 1%) and incorporation of Co ions into cationic sites of zeolites enhanced the activity. But the catalytic activity of CoH-zeolites strongly depended on the zeolite structural type. CoH-FER and CoH-MOR zeolites showed a lower activity compared to Co ions in H-MFI and H-BEA zeolites. Similar effect of the structural type of zeolite matrices was reported for ammoxidation and oxidation of ethane [3,7] over Co-zeolites and for total combustion of propane over Cu-zeolites [23].

Fig. 1 shows the dependence of propene yields on propane conversion at various temperatures for different CoH-zeolites. It is clearly seen, that CoH-BEA zeolite exhibits the highest propene selectivity and herewith exhibits the highest catalytic activity (see Tab. 2). The sequence in total catalytic activity of investigated zeolites is CoH-BEA > CoH-MFI > CoH-MOR > CoH-FER and is in accordance with the sequence in ammoxidation activity of investigated catalysts, as was reported in [7]. Fig. 2 shows the dependence of propene selectivity on propane conversion. The highest propene selectivity exhibits the CoH-BEA zeolite and the lowest selectivity the zeolite CoH-FER. Although propene is initially formed, it is rapidly transformed into carbon oxides in the case of all zeolites investigated, which leads to a decrease of propene selectivity with increasing propane conversion. In addition, initial value of propene selectivity (at zero propane conversion) does not reach 100%. It means that only a part of propane is converted to propene and the rest of propane is directly oxidized to carbon oxides. Arrhenius plot was constructed from temperature dependence of propane conversion in oxidative dehydrogenation over all investigated catalysts and the resulted values are summarized in Table 2. Apparent activation energies of reaction on CoH-zeolite catalysts change from 44 to 77 kJ/mol. Rather higher values were estimated by Kubacka *et al.* [18] for oxidative dehydrogenation of propane over In, Ga or Sb doped MFI and USY zeolites (88–103 kJ/mol).

Table 2. Oxidative dehydrogenation of propane over CoH-zeolites. F = 100 cm^3/min, $C_3H_8/O_2/He$ = 5/6.5/88.5, m_{cat} = 0.2 g, T = 723 K.

Sample	$X_{propane}$ (%)	S(propene) (%)	S(CO) (%)	S(CO_2) (%)	S(ethene) (%)	E_{act} [a] (kJ/mol)	TOF [b] (h^{-1})
CoH-BEA	6.4	41.5	31.4	26.2	0.9	51.4±4	14.0
CoH-MFI	5.4	16.7	40.6	42.6	0.1	44.2±3	12.9
CoH-MOR	3.3	23.3	40.3	36.4	not detected	52.1±5	6.2
CoH-FER	1.5	18.8	33.3	20.8	13.9	76.5±7	5.7

[a] – apparent activation energies determined from the Arrhenius plot.
[b] – turn over frequency factor, it means number of propane molecules converted over Co atom at 723 K for 1 hour.

We explain the differences in catalytic activity of Co ions in zeolites by a different level of accessibility and the spaces around the cations, which enable or restrict the reactant adsorption and formation of reaction intermediates in accordance with Dědeček *et al.* [24]. Dědeček *et al.* estimated the coordination and positions of Co ions in pentasil ring zeolites by means of UV-Vis spectroscopy and denoted these sites as α, β and γ site [25]. In all structures, the most populated site of the Co ions is the β-type cationic site (50–70% of cobalt ions). The Co-β site in BEA structure is localized in the very open channels, and in MFI structure it is localized at the intersection of the straight and sinusoidal channel. Localization of cobalt ions in the relatively wide pores (7.6×6.4 Å in the case of BEA zeolite and 5.3×5.5 Å in the case of MFI zeolite) corresponds to a high TOF value (see Table 2). Conversely, the Co-β sites in the mordenite and ferrierite are localized in the narrow eight-member ring channels with diameters 3.5×4.8 Å in the case of ferrierite and 2.6×5.7 Å in the case of mordenite. In addition, our actual studies of UV-Vis spectroscopy of CoH-zeolites with adsorbed reactant, products or intermediates indicate that only β positions of cobalt ions interact with probe molecules, whereas cobalt ions in α and γ positions are inaccessible for the adsorbed molecules.

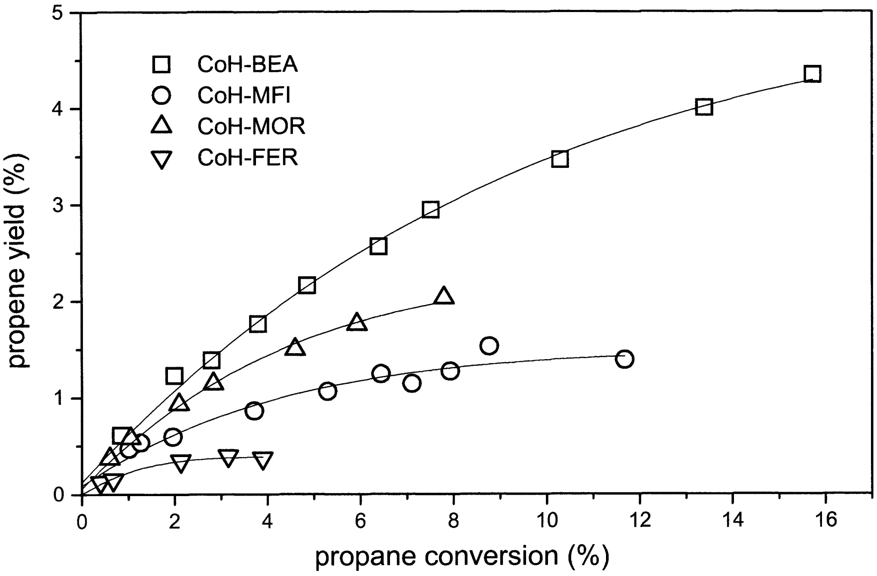

Figure 1. The dependence of propene yield on propane conversion over Co-zeolites obtained by variation of reaction temperature. m_{cat} = 0.2 g, F = 100 cm^3/min, molar ratios $C_3H_8/O_2/He$ = 5/5/90, □ – CoH-BEA, o – CoH-MFI, ▽ – CoH-FER, △ – CoH-MOR.

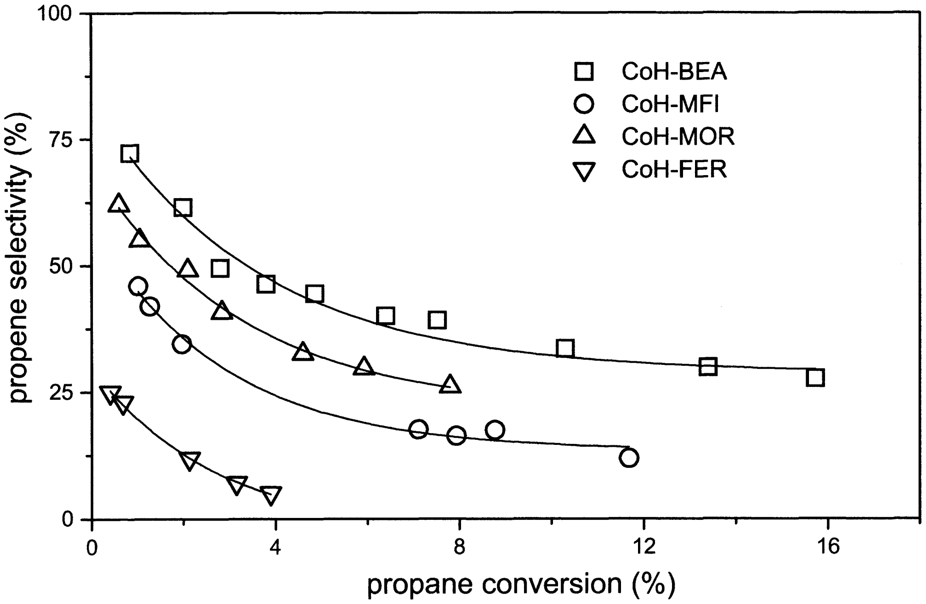

Figure 2. The dependence of propene selectivity on propane conversion over Co-zeolites obtained by variation of reaction temperature. m_{cat} = 0.2 g, F = 100 cm^3/min, molar ratios $C_3H_8/O_2/He$ = 5/5/90, □ – CoH-BEA, o – CoH-MFI, ▽ – CoH-FER, △ – CoH-MOR.

The best catalytic results in the ammoxidation and oxidative dehydrogenation reactions were obtained over CoH-BEA zeolite. CoH-BEA zeolite exhibits comparable catalytic activity in propane oxidative dehydrogenation with other zeolitic catalysts (USY and MFI zeolites with In and Ga ions reported by Kubacka *et al.* [18] or CoAPO catalyst reported by Okamoto *et al.* [19]). Therefore, CoH-BEA zeolite was chosen as a catalyst for investigation of the influence of reaction conditions on the conversion of propane and the yield of products. In Fig. 3, the influence of the W/F ratio, which was varied either by increasing amount of catalyst or by varying the total reaction gas flow rate, keeping the concentration constant, on the conversion and selectivity is presented. The conversion of propane increases with increasing W/F ratio, but the selectivity to propene decreases. The conversion of oxygen reaches maximally 50%. The decrease of propene selectivity and the increase in selectivity to CO and CO_2 show that propene is an intermediate product and the oxidative dehydrogenation of propane has a consecutive character. As may be seen in Fig. 3, an initial propene selectivity (extrapolated to W/F ratio equal to zero) is close to 75% and the initial selectivity to CO and CO_2 is approximately 20% and 5% respectively. It implies that part of the carbon oxides is formed in the parallel reaction directly from propane. The reaction scheme of oxidative dehydrogenation of propane over CoH-BEA zeolite exhibits parallel-consecutive pattern, as is shown in Fig. 4. Concentration of ethene in the reaction mixture is rather constant at about 3% in selectivity. But, ethene was not detected at the very low value of W/F ratio, *e.g.* at very low conversions of propane, and therefore it may be caused by a small amount of ethene, below the detection limit.

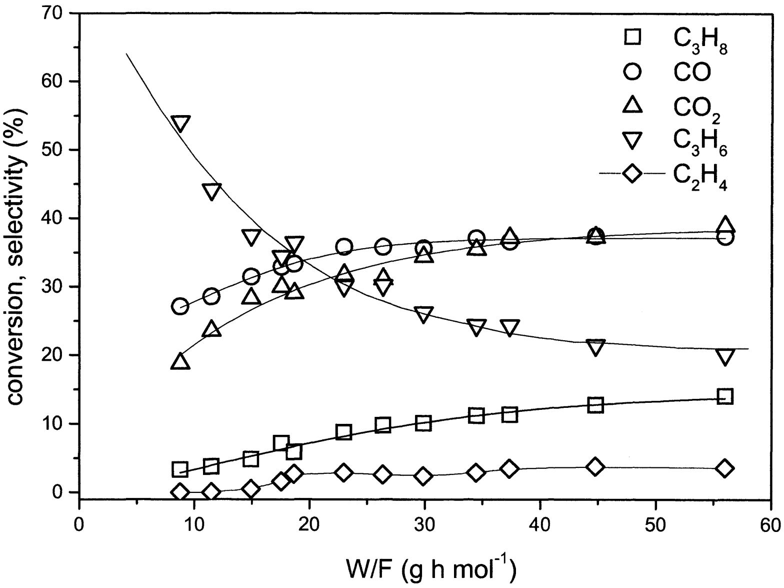

Figure 3. The influence of the W/F ratio on the oxidative dehydrogenation of propane over CoH-BEA. T = 723 K, molar ratios $C_3H_8/O_2/He$ = 5/5/90, □ – conversion of C_3H_8, ▽ – selectivity to C_3H_6, △ – selectivity to CO_2, o – selectivity to CO, ◇ – selectivity to C_2H_4.

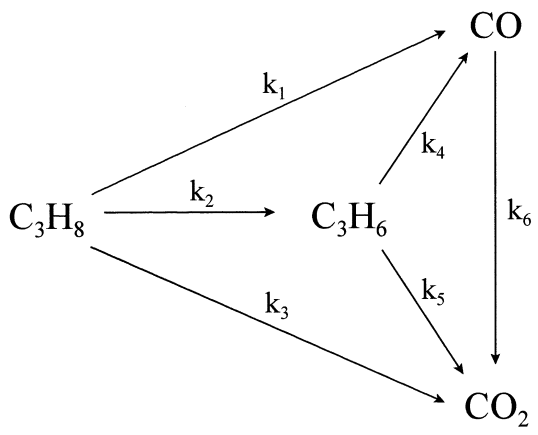

Figure 4. Formal reaction scheme of conversion of propane over CoH-zeolites in the presence of oxygen.

Figure 5 shows the effect of oxygen concentration on the catalytic result at 723 K at constant space velocity and propane concentration. The oxygen/propane molar ratio was varied between 0.2 and 4. There was no complete oxygen consumption, the highest conversion of oxygen was 74% for the lowest concentration of oxygen. The selectivity to propene decreases with increasing oxygen concentration from 55 to 25%. Formation of ethene exhibited a very low rate in the whole range of oxygen concentration and reaches maximally 5% of selectivity. The conversion of propane increases only slowly from 2.5 to 10%. The calculation from a plot of the $r_{(propane)}$ *versus* p_{O_2} indicates that the reaction order for O_2 was the 0.52 ± 0.05. It means that the dissociation of oxygen is slower than the adsorption of oxygen on the surface of the catalyst. The same feature of propane oxidative dehydrogenation was reported on other zeolitic materials with transition metal ions [20,21]. The rate of propene formation depends only slightly on the concentration of oxygen, and the reaction order for oxygen in the formation of propene is very close to zero. It means that the rate limiting step of propene formation is not the reaction of propane or adsorbed species of propane with oxygen, but some other reaction step.

These facts could be an indication for an insufficient amount of active sites or a blockage of the active sites by coke, mass transport limitation or limitation in the adsorption-desorption cycle. Formation of some coke was observed during the reaction. Measurement of conversions and selectivity in dependence on time of reaction run showed that catalytic activity of CoH-BEA zeolite is constant till 24 hours in the reaction mixture. It means that the formation of small amount of coke does not affect significantly the catalytic activity of CoH-BEA catalyst.

Oxidation of propene at the same conditions as the oxidation of propane over CoH-BEA zeolite (it means 5 vol. % of propene and 6.5 vol. % of oxygen) leads to a 6.8% propene conversion at 723 K. This value is very close to the conversion of propane (6.4%) at the same temperature. It means that the propene blockage of active si-

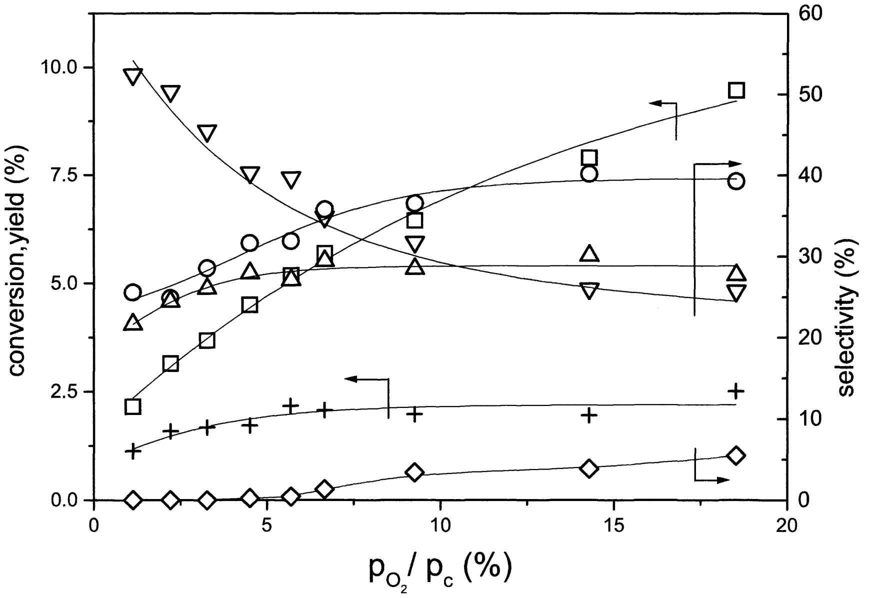

Figure 5. The influence of oxygen concentration on the oxidative dehydrogenation of propane over catalyst CoH-BEA. T = 723 K, m_{cat} = 0.2 g, F = 100 cm^3/min, molar ratios $C_3H_8/O_2/He$ = 5/1-18/94-77, □ – conversion of C_3H_8, ▽ – selectivity to C_3H_6, △ – selectivity to CO_2, o – selectivity to CO, ◇ – selectivity to C_2H_4, + – yield of C_3H_6.

tes and desorption of propene or the consecutive oxidation to CO and CO_2 is the rate limiting step of propane and propene oxidation. Therefore, desorption of propene from Co-zeolites was investigated.

Desorption of propene was investigated by temperature programmed desorption experiments (TPD). For TPD investigation BEA and FER zeolites were selected by reason of their greatest differences in catalytic activity. Desorption of propene takes place between 373–623 K. In order to estimate the desorption energy, series of TPD curves at different heating rates were taken. The desorption energy of propene from CoH-BEA and CoH-FER zeolites from series of TPD experiments was estimated by the heating rate variation method [26] basing on Polanyi-Wigner equation. Fig. 6 shows a plot of the $\ln(\beta/T^2_{max})$ *versus* $1/T_{max}$ (β means here heating rate). The desorption energies were estimated from the slope of the linear dependence. CoH-BEA zeolite exhibits desorption energy at about 54 kJ/mol while CoH-FER zeolite has the desorption energy at about 76 kJ/mol. Estimated values of desorption energy from BEA and FER catalysts correlate very good with values of apparent activation energies of oxidation of propane (see Table 2). It must be noted that the activation energies of oxidation of propane were estimated from the linear part of the Arrhenius plot ln $X_{propane}$ *versus* $1/T_{reaction}$. It can be deduced that the oxidation of propane is limited by the desorption of propene from the surface of the zeolite catalysts.

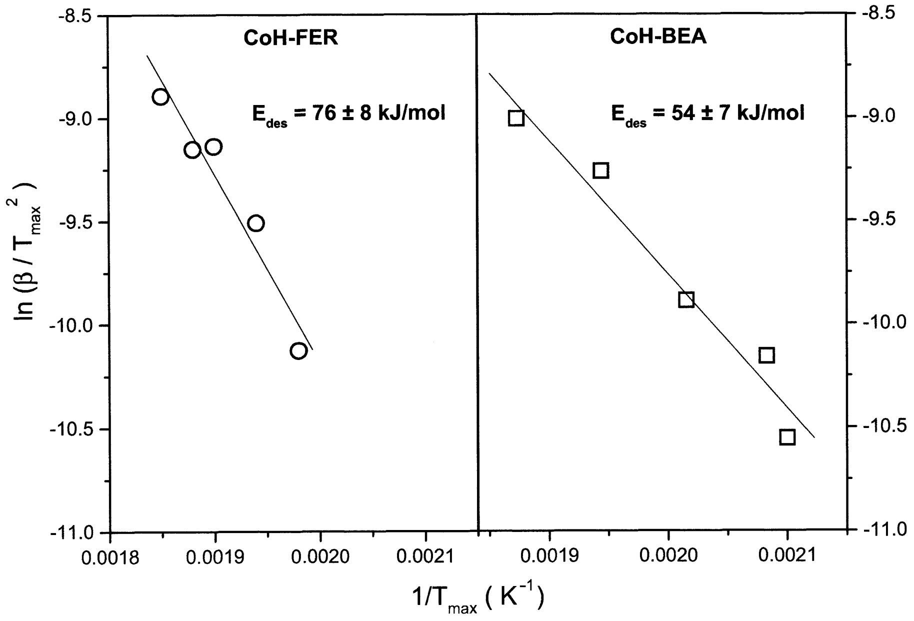

Figure 6. Polanyi-Wigner plot for CoH-FER and CoH-BEA zeolites.

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REFERENCES

1. Li Y. and Armor J.N., *Chem. Commun.*, 2013 (1997).
2. Li Y. and Armor J.N., *J. Catal.*, **176**, 495 (1998).
3. Li Y. and Armor J.N., *J. Catal.*, **173**, 511 (1998).
4. Armor J.N. and Li Y., *Appl. Catal. A-Gen.*, **188**, 211 (1999).
5. Armor J.N. and Li Y., *Appl. Catal. A-Gen.*, **183**, 107 (1999).
6. Aliev S.M., Sokolovskii V.D and Boreskov G.B., USSR Patent SU-738657 (1980).
7. Bulánek R., Novoveská K. and Wichterlová B., *Appl. Catal. A-Gen.*, **235**, 181 (2002).
8. Novoveská K., Bulánek R. and Wichterlová B., *Sci. Pap. Univ. Pardubice Ser. A*, **7**, 175 (2001).
9. Kung H.H., *Adv. Catal.*, **40**, 1 (1994).
10. Cavani F. and Trifiro F., *Catal. Today*, **24**, 307 (1995).
11. Blasco T. and López Nieto J.M., *Appl. Catal. A-Gen.*, **157**, 117 (1997).
12. Mamedov E.A. and Cortés Corberán V., *Appl. Catal. A-Gen.*, **127**, 1 (1995).
13. Conception P., López Nieto J.M. and Peréz Pariente J., *Catal. Lett.*, **19**, 558 (1993).
14. Centi G., Perathoner S., Trifiro F., Aboukais A., Aissi F.C. and Guelton M., *J. Phys. Chem.*, **96**, 2617 (1992).
15. Schuster W., Niederer J.P.M. and Hoelderich W.F., *Appl. Catal. A-Gen.*, **209**, 131 (2001).
16. Pena M.L., Dejoz A., Fornés V., Rey F., Vázquez M.I. and López Nieto J.M., *Appl. Catal. A-Gen.*, **209**, 155 (2001).

17. Cortés Corberán V., Valenzuela R.X., Sulikowski B., Derewiński M., Olejniczak Z. and Kryściak J., *Catal. Today*, **32**, 193 (1996).
18. Kubacka A., Włoch E., Sulikowski B., Valenzuela R.X. and Cortés Corberán V., *Catal. Today*, **61**, 343 (2000).
19. Okamoto M., Luo L., Labinger J.A. and Davis M.E., *J. Catal*., **192**, 128 (2000).
20. Zhang Q., Wang Y., Ohishi Y., Shishido T. and Takehira K., *J. Catal*., **202**, 308 (2001).
21. Centi G. and Trifiro F., *Appl. Catal. A-Gen*., **143**, 3 (1996).
22. Pouzar M., Černohorský T., Bulánek R. and Krejčová A., *Chem. Listy*, **94**, 197 (2000).
23. Bulánek R., Wichterlová B., Sobalík Z. and Tichý J., *Appl. Catal. B-Environ*., **31**, 13 (2001).
24. Dědeček J., Kaucký D. and Wichterlová B., *Top. Catal.*, **18**, 283 (2002).
25. Dědeček J. and Wichterlová B., *J. Phys. Chem. B*, **103**, 1462 (1999).
26. Cvetanovic R.J. and Amenomiya Y., *Adv. Catal*., **17**, 103 (1967).