

Effect of dealumination on the catalytic performance of Cr-containing Beta zeolite in carbon dioxide assisted propane dehydrogenation

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ABSTRACT

New active and selective catalysts for propane to propene dehydrogenation in assistance of CO₂ (CO₂-PDH) were prepared by chromium incorporation in siliceous SiBeta. The Cr-containing SiBeta zeolite catalysts were obtained by two-step postsynthesis preparation procedure which consist, in the first step, removal of aluminum from TEABeta zeolite with Si/Al of 17 by treatment with nitric acid solution to obtain an aluminium-free Si-Beta support with Si/Al ratio of 1000 and, in the second step, various amounts of Cr were introduced into the siliceous SiBeta zeolite structure by wet impregnation. The well correlation between the number of redox Cr sites and propene yield up to 2 wt % of Cr has been determined. Comparing of catalytic activity of Cr-containing Beta zeolite catalysts with the identical Cr content (2 wt % of Cr) supported on SiBeta and AlBeta revealed that the dealumination has great impact on catalytic properties. Low acidity of SiBeta is suitable for achieving high selectivity to propene (above 80 %) while high acidity of starting AlBeta promotes propane cracking to lighter hydrocarbons. Moreover, in switch operation mode between propane dehydrogenation in presence and absence of CO₂ the formation rate of propene raises in mode with CO₂ only over Cr-containing SiBeta zeolite catalyst, while over Cr-containing AlBeta zeolite catalyst a negative effect on the rate of propene formation was observed.

1. Introduction

Nowadays unsaturated hydrocarbons are basic and most important intermediates for chemical industry. Particularly, the demand for propene has been growing since it has found an assured position on the chemical raw material and monomers market due to its numerous uses. Worldwide demand for propene currently reaches 90 million tonnes per year and at an estimated growth rate of about 5 % annually, will reach a value of around 130 million tonnes by 2023 [1]. It is estimated that such high demand for propene won't be satisfied by its current two most important sources, that is, steam cracking and catalytic cracking, in which propene is obtained as co-products. Attempts at increasing propene production, e.g. through optimisation of conditions of these processes, will negatively influence the production of other important co-products. Thus, selective processes dedicated solely to

propene synthesis, such as propane dehydrogenation, olefin metathesis, and propene synthesis using methanol (e.g. MTP - methanol-to-propene), will gain significance with time.

Concerns connected to meeting demand for propene without simultaneously decreasing production of remaining valuable products also favour intensification of fundamental research. One of the crucial research directions is the development of a new selective process of obtaining propene from propane that could replace propane dehydrogenation process (PDH) currently used for industrial needs. However, this process has disadvantages such as reversibility and endothermality. An attractive alternative for the traditional PDH is propane oxidative dehydrogenation in the presence of O₂ (ODH) or propane dehydrogenation in the presence of CO₂ (CO₂-PDH). A shared characteristic of all the aforementioned processes is utilising a co-reagent that either removes PDH thermodynamic limits or increases production through hydrogen binding in consecutive reactions. Typically in this process per-

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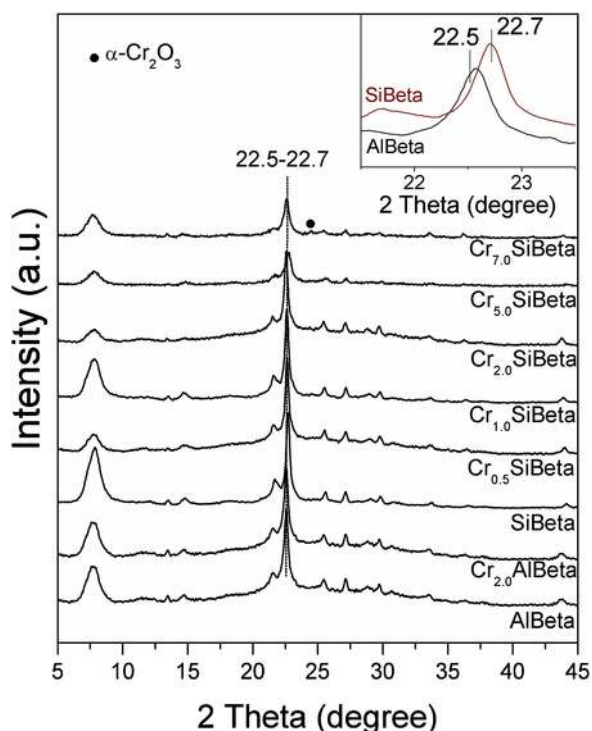


Fig. 1. XRD of AlBeta, SiBeta, Cr_{0.5}SiBeta, Cr_{1.0}SiBeta, Cr_{2.0}SiBeta, Cr_{5.0}SiBeta and Cr_{7.0}SiBeta recorded at room temperature and ambient atmosphere.

pass conversion of propane and yield of propene are higher than in commercial non-oxidative dehydrogenation. Moreover, due to large scale propene production the process can be attractive way for chemical CO₂ utilisation, because in addition to propene, hydrogen and carbon monoxide (syngas) are produced as the main products. Some possibility of CO₂-PDH integration with syngas or propene required processes are proposed previously [2].

Many different catalysts were investigated in CO₂-PDH containing Pt [3], Ni-Fe [4] Cr [5–16], Ga [17–20], In-Al [21–23], Fe [24] or V

[25,26]. Among them, the chromium oxide-based materials are considered as a very promising for CO₂-PDH due to high activity and selectivity. The mechanism of propane dehydrogenation in presence of CO₂ is complex. Various possible scenarios of the CO₂-PDH in which propene is produced either by non-oxidative dehydrogenation with participation of Cr(II) or/and Cr(III) species or by various redox mechanisms with participation of carbon dioxide as a mild oxidant in an oxidative dehydrogenation pathway have been proposed [10,27–31]. In the oxidative pathway various redox cycles between the oxidised/reduced forms of Cr sites, such as Cr(III)/Cr(II), Cr(VI)/Cr(III) or Cr(V)/Cr(III) has been suggested. It has been recognized that high dispersion and presence of redox chromium species are important factors for achieving high catalytic performance in CO₂-PDH [18,27,28]. From above reasons chromium is typically dispersed on a support. Very good support ensuring high chromium dispersion is silica, particularly of ordered mesoporous structure. Due to large specific surface area (in the most cases above 1000 m² g⁻¹) of mesoporous materials like MCM-41, SBA-1, SBA-15 or MSU_x a high dispersion and concentration of chromium oxide species can be obtained in comparison to unordered silica support [6,9,10,14,18,27,28]. Others tested support, for instance γ -Al₂O₃, which is commercially used for chromium dispersion in PDH catalyst (CATOFIN Process) or active carbon are less useful. Over γ -Al₂O₃ supported chromium oxide catalysts CO₂ addition exerts poisoning effect while in the case of active carbon supported catalyst an application in CO₂-PDH is limited by period regeneration with air [5,11,32].

In this work Cr-containing Beta zeolites were investigated as a catalysts for propane dehydrogenation in the presence of carbon dioxide. Beta zeolite was applied due to a three-dimensional structure, the pores larger than those of ZSM-5 with 12-membered ring openings (0.75 by 0.57 nm for linear and 0.65 by 0.56 nm for tortuous channels), a high thermal and acid stability and a large specific surface area needed for high chromium species dispersion [33–35]. We have shown that dealumination of Beta and subsequently chromium dispersion by simple impregnation procedure give excellent catalysts for CO₂-PDH.

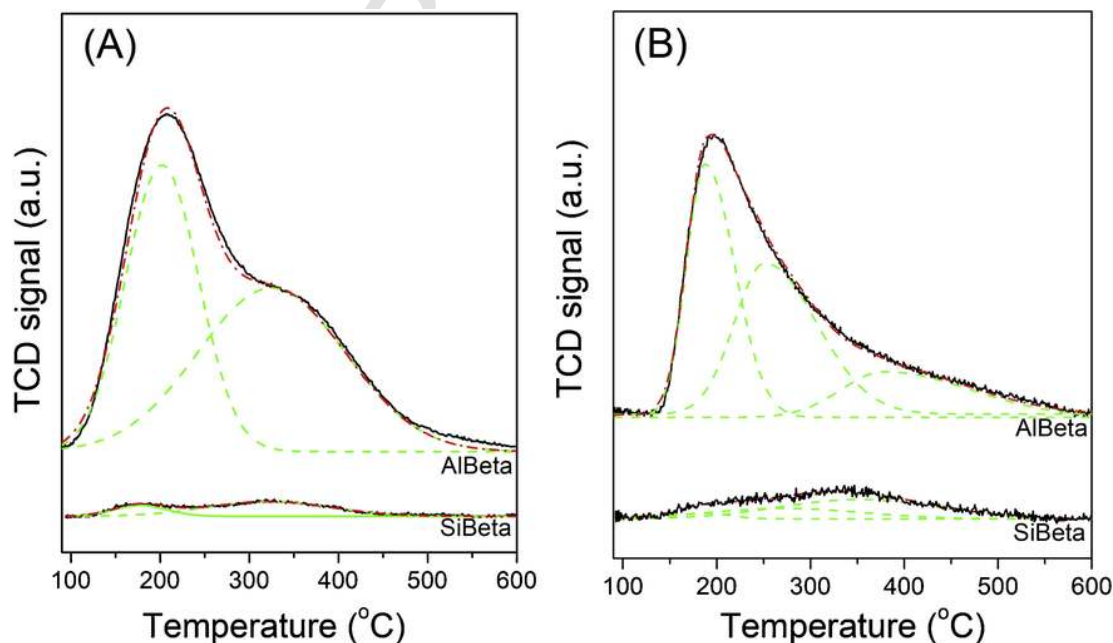


Fig. 2. Thermodesorption profiles of ammonia (A) and carbon dioxide (B) for AlBeta and SiBeta.

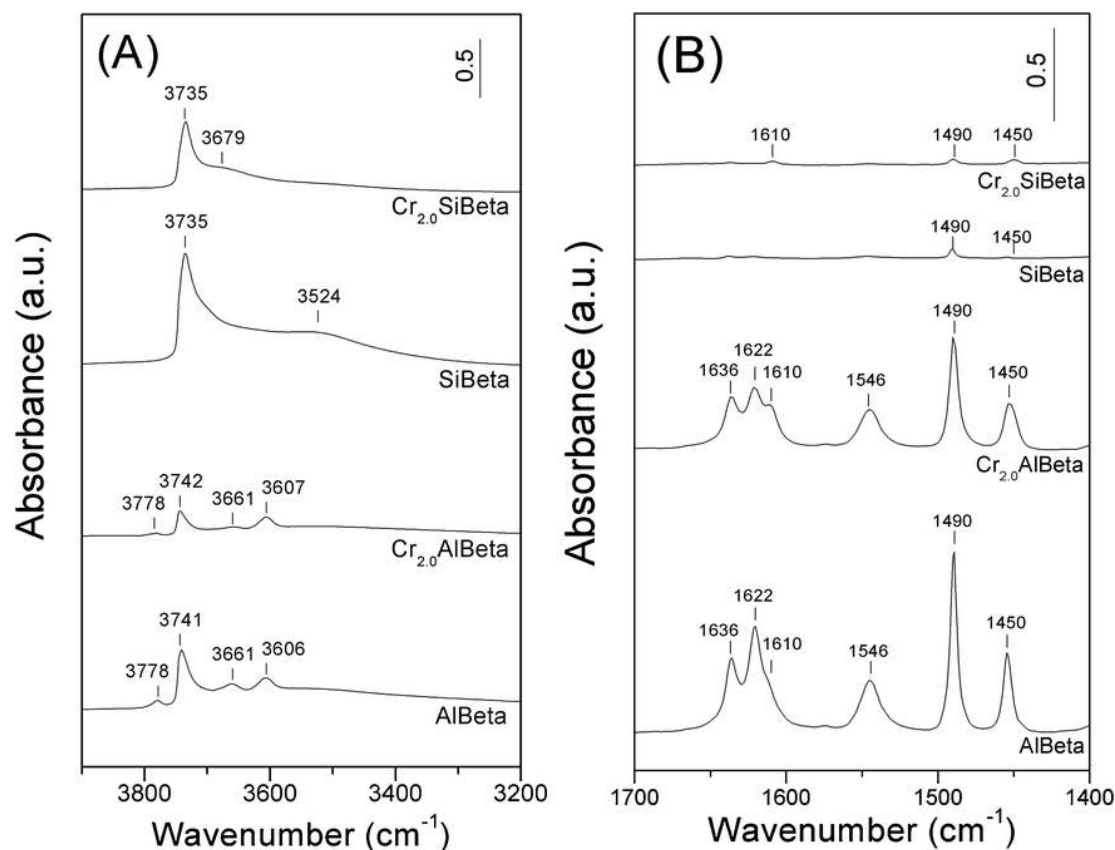


Fig. 3. FTIR spectra recorded at room temperature of AlBeta, Cr_{2.0}AlBeta, SiBeta and Cr_{2.0}SiBeta for activated (calcined at 723K for 3h in O₂ (1.6 · 10⁴Pa) and then outgassed at 573K (10⁻³Pa) for 1h) (Fig. 3A) and after adsorption of pyridine (133Pa) for 1h at room temperature and desorption at 423K for 1 (Fig. 3B).

Table 1
Acid-base properties of AlBeta and SiBeta determined by NH₃-TPD, pyridine adsorption and CO₂-TPD.

Sample	Acidity			Basicity				
	NH ₃ -TPD (mmol NH ₃ · g ⁻¹)			Pyridine adsorption and desorption at 150 °C - FTIR		CO ₂ -TPD (mmol CO ₂ · g ⁻¹)		
	LT	HT	Total	PyH ⁺ 1545 cm ⁻¹ [μmol · g ⁻¹]	PyL 1445–1455 cm ⁻¹ [μmol · g ⁻¹]	LT	HT	Total
SiBeta	0.01	0.04	0.06	12	10	0.01	0.01	0.02
AlBeta	0.60	0.69	1.29	235.6	134.9	0.13	0.03	0.16

2. Experimental

2.1. Materials preparation

The AlBeta support with a Si/Al atomic ratio of 17 was obtained by calcination of tetraethylammonium Beta (TEABeta) parent zeolite in air at 550 °C for 15h. The SiBeta support with a Si/Al atomic ratio of 1000 was obtained by a treatment of TEABeta with 13 mol L⁻¹ HNO₃ solution at 80 °C for 4h, washed with distilled water and dried at 95 °C overnight.

Chromium-containing SiBeta catalysts were obtained by two-step postsynthesis method wet impregnation. In typical procedure, the SiBeta was contacted with an aqueous chromium nitrate solutions containing from 0.8 to 15.2 · 10⁻³ mol L⁻¹ Cr(NO₃)₃ · 9H₂O and AlBeta was contacted with solution containing 3.2 · 10⁻³ mol L⁻¹ Cr(NO₃)₃ · 9H₂O. Then, the separation of the solids from the suspensions were done in evaporator under vacuum of a membrane pump for 2h in air at 60 °C. Finally, all materials were calcined at 550 °C for 6h. The sample with

SiBeta contained 0.5, 1, 2, 5 and 7 wt % of Cr were labelled as Cr_{0.5}SiBeta, Cr_{1.0}SiBeta, Cr_{2.0}SiBeta, Cr_{5.0}SiBeta and Cr_{7.0}SiBeta and this with AlBeta, containing 2 wt % of Cr was labelled as Cr_{2.0}AlBeta.

2.2. Materials characterization

Textural properties of supports and catalysts were determined from the low-temperature adsorption/desorption isotherms using the Micromeritics (ASAP 2020). Prior to measurements the samples were degassed under vacuum at 350 °C for 12h. Total pore volume were measured for the value of p/p₀ = 0,98 and the surface area of the samples were calculated from nitrogen isotherm data using BET and Langmuir models. The micropore volume was determined using the t-plot method.

Powder X-ray diffraction (XRD) analysis of supports and catalysts were performed on a Bruker D8 ADVANCE using Cu K_α radiation (λ = 154,05 pm) in 2θ range of 5–45°.

Analysis of the acidic properties of samples was performed by adsorption of pyridine (Py) followed by infrared spectroscopy. Before analysis, the samples were pressed at ~1 ton cm⁻² into thin wafers of

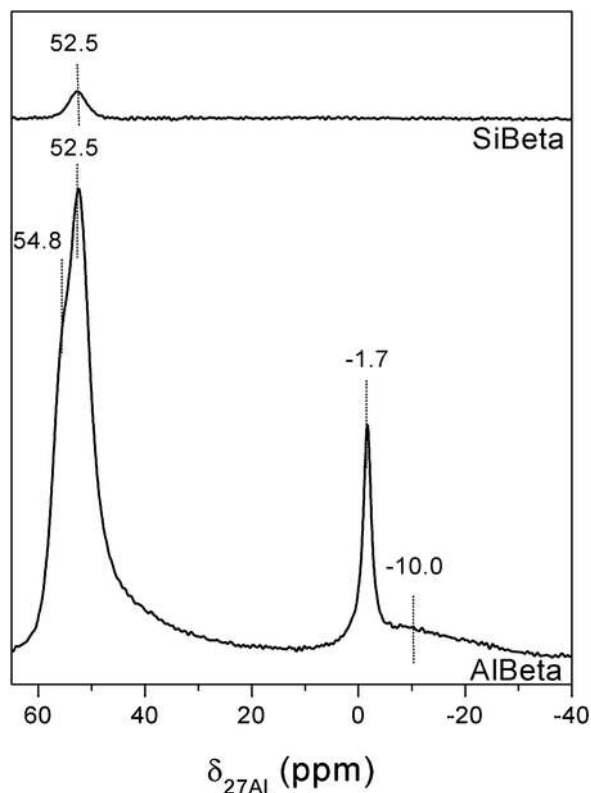


Fig. 4. ^{27}Al MAS NMR recorded at room temperature of AlBeta and SiBeta supports in 4 mm (external diameter) zirconia rotor.

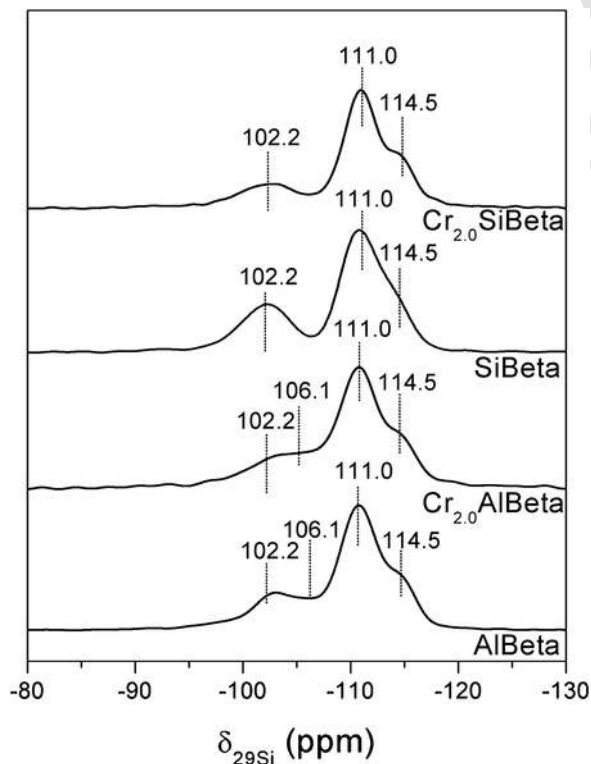


Fig. 5. ^{29}Si MAS NMR recorded at room temperature of AlBeta, $\text{Cr}_{2.0}\text{AlBeta}$, SiBeta and $\text{Cr}_{2.0}\text{SiBeta}$.

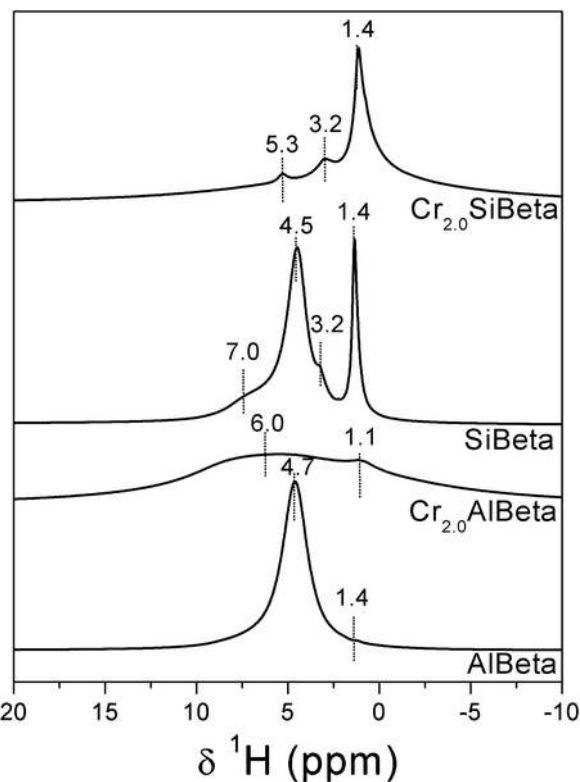


Fig. 6. ^1H MAS NMR recorded at room temperature of AlBeta, $\text{Cr}_{2.0}\text{AlBeta}$, SiBeta and $\text{Cr}_{2.0}\text{SiBeta}$.

ca. 10 mg cm^{-2} and placed inside the IR cell. Then, the wafers were activated by calcination in static conditions at 723K for 3h in O_2 ($1.6 \cdot 10^4\text{ Pa}$) and outgassed at 573K (10^{-3} Pa) for 1h. After the wafers were contacted at room temperature with gaseous Py (133 Pa). The IR spectra were recorded after desorption at room temperature and 423K for 1h with a Bruker Vector 22 spectrometer (resolution 2 cm^{-1} , 128 scans). The reported spectra were obtained after subtraction of the spectrum recorded before Py adsorption.

^{29}Si MAS NMR spectra were recorded at 99.3MHz with Bruker AVANCE 500 spectrometer and 7 mm zirconia rotors spinning at 5kHz. Tetramethylsilane was used as reference. ^{29}Si MAS NMR spectra were recorded with a $4.2\mu\text{s}$ excitation pulse and a 10s recycle delay.

^{27}Al and ^1H MAS NMR experiments were performed using a 4 mm zirconia rotors spinning at 12kHz. The resonance frequency of 500.16MHz and 130.33MHz were used for recording of ^1H and ^{27}Al , respectively. An aqueous $\text{Al}(\text{NO}_3)_3$ 1N solution was used as second reference to determine chemical shifts. ^1H MAS NMR was recorded with a 90° pulse duration of $2.9\mu\text{s}$ and a recycle delay of 5s and 16 accumulations. A small-flip-angle technique with a pulse of $1.2\mu\text{s}$ ($\pi/8$), 0.5s for the recycle delay and 2048 accumulations was used for recorded ^{27}Al MAS NMR.

The total Cr content (Cr_{ICP}) in the samples was determined using an Optima 2100 DV (Perkin-Elmer, USA) ICP-OES instrument, equipped with axially viewed plasma. In the typical mineralization procedure, a sample (ca. 50mg) was crashed and mixed with 2g of NaNO_3 (POCh-Polish Chemical Reagents) and 2g of NaOH (POCh-Polish Chemical Reagents) in a melting pot. Then, the mixture was heated to 600°C in air. The mineralization mixture was cooled to RT, dissolved in deionized water and filtered. Cr_{ICP} was determined in a dissolved solution.

Temperature-programmed desorption of ammonia ($\text{NH}_3\text{-TPD}$) and reduction with hydrogen ($\text{H}_2\text{-TPR}$) experiments were carried out using microreactor connected on-line with a GC equipped with a thermal conductivity detector. In $\text{NH}_3\text{-TPD}$ measurements about 0.1g sample

Table 2
Cr content, specific surface area, porosity and redox properties of Cr_xSiBeta catalysts.

Sample	Cr _{ICP} content (wt %)	S _{BET} (m ² g ⁻¹)	S _{Langmuir} (m ² g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{total} (cm ³ g ⁻¹)	H ₂ -TPR	
						H ₂ consumption (mmol g _{cat} ⁻¹)	H ₂ /Cr _{ICP} (mol/mol)
Cr _{0.5} SiBeta	0.55	627	724	0.22	0.42	0.13	1.46
Cr _{1.0} SiBeta	1.15	621	713	0.20	0.41	0.23	1.34
Cr _{2.0} SiBeta	2.14	554	644	0.16	0.34	0.42	1.14
Cr _{5.0} SiBeta	4.96	552	640	0.19	0.37	0.73	0.84
Cr _{7.0} SiBeta	6.40	517	597	0.17	0.35	1.18	0.81
Cr _{2.0} AlBeta	2.20	618	713	0.20	0.41	0.46	1.18

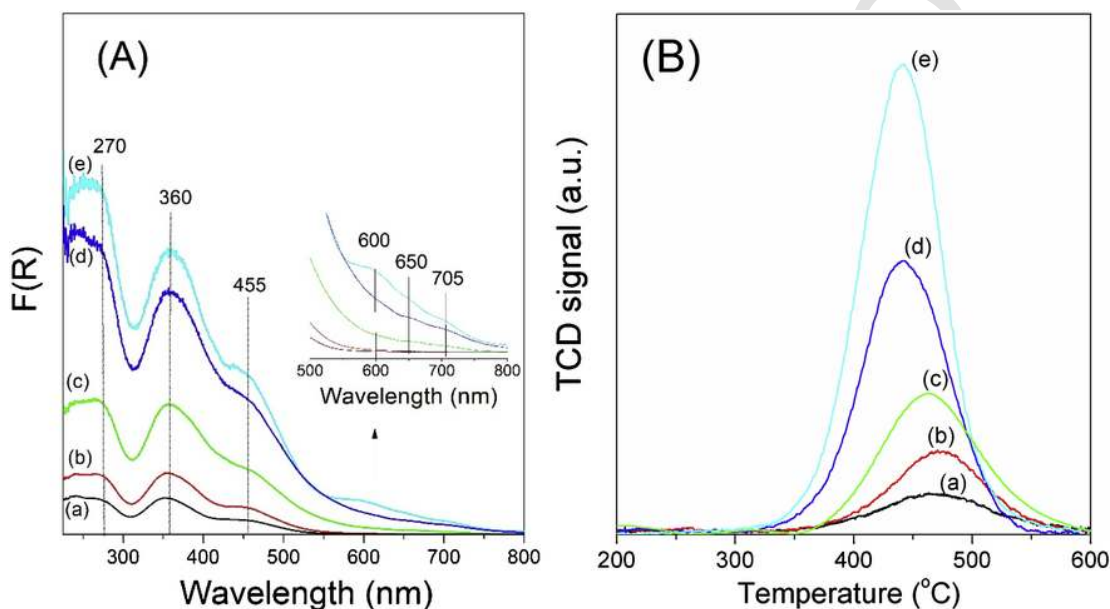


Fig. 7. UV-vis DRS spectra recorded at room temperature and H₂-TPR profiles of (a) Cr_{0.5}SiBEA, (b) Cr_{1.0}SiBEA, (c) Cr_{2.0}SiBEA, (d) Cr_{5.0}SiBEA and (e) Cr_{7.0}SiBEA zeolite catalysts.

Table 3
Catalytic performance of chromium-containing Beta catalysts and other supported chromium oxide-based catalysts in CO₂-PDH process.

Sample	Reaction temperature	Specific activity × 10 ⁶ (mol s ⁻¹ g _{cat} ⁻¹)	Conversion (%)		Yield (%)			Selectivity (%)		References
			C ₃ H ₈	CO ₂	C ₃ H ₆	C ₃ H ₆	C ₂ H ₆	C ₂ H ₄	CH ₄	
Cr _{0.5} SiBeta	550	0.82	11.0	0.6	10.1	94.7	1.5	3.6	2.8	This work ^a
Cr _{1.0} SiBeta	550	1.31	17.6	1.2	16.0	90.8	1.4	4.5	3.3	
Cr _{2.0} SiBeta	550	1.85	24.8	4.0	21.6	87.1	2.4	4.2	6.2	
Cr _{5.0} SiBeta	550	2.05	27.6	5.5	23.3	84.4	2.8	4.0	8.8	
Cr _{7.0} SiBeta	550	2.48	33.3	7.0	27.2	81.6	3.7	4.0	10.7	
Cr _{2.0} AlBeta	550	0.33	4.5	0.8	2.0	45.1	8.0	25	21.9	
Cr _{5.0} /AC ^b	550	n.r. ^c	39.8	n.r.	34.5	86.7	1.6	2.8	7.5	[32]
Cr _{3.4} /D ^d	600	n.r.	19.7	n.r.	11.8	59.6	7.3 ^e		5.4	[7]
Cr _{3.4} /Al ₂ O ₃	550	n.r.	3.3	n.r.	3.3	92.9	0.5	1.6	5.0	[5]
Cr _{3.4} /SiO ₂	550	1.6	15.4	1.3	14.3	92.6	1.3	2.5	3.6	[28]
Cr _{5.0} /ZrO ₂	550	n.r.	58	42	30	n.r.				[60]
Cr _{3.4} /MCM-41	600	n.r.	39.4	6.7	34.9	88.5	2.9	2.5	6.1	[14]
Cr _x /ZSM-5-S	550	n.r.	48.3	n.r.	41.5	86.0	2.0	4.8	7.2	[61]
Cr _{3.4} /SBA-1	550	2.60	33.2	4.6	29.2	87.9	2.9	3.3	5.9	[28]
Cr _{3.4} /SBA-15	550	2.20	27.2	3.4	24.3	89.3	2.4	3.5	4.7	[28]
Cr _{5.0} /MSUx	600	n.r.	28.0	n.r.	26.6	95.0	n.r.	n.r.	n.r.	[15]

^a Reaction conditions: C₃H₈:CO₂:He molar ratio = 1:5:9; Total flow rate = 30 cm³ min⁻¹; Catalyst weight = 200 mg; WHSV = 1.2 h⁻¹; Catalytic test results summarized after 10 min.

^b AC- activated carbon.

^c n.r.- not reported.

^d D- diamond.

^e Sum of ethane and ethene selectivity.

(mixed with SiC to constant volume 1,5 mL) was preheated under helium (99.999 vol %, Linde) with heating rate 10 °C min⁻¹ to 550 °C, kept for 2 h, and then cooled to 100 °C under the same atmosphere.

Subsequently, ammonia (99.98 vol %, Linde) at flow rate 20 mL min⁻¹ for 30 min were adsorbed at 100 °C. The sample was then flashed by helium at a flow rate 30 mL min⁻¹ for 2 h. The NH₃-TPD measurement

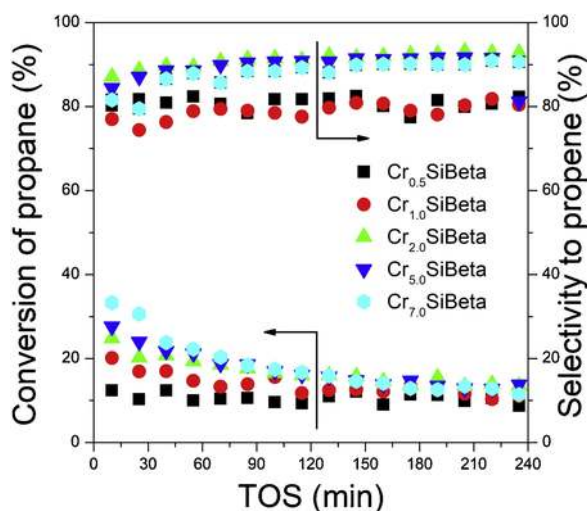


Fig. 8. Conversion of propane and selectivity to propene vs. TOS in CO₂-PDH process over Cr_xSiBeta series. Reaction conditions: T = 550 °C; C₃H₈:CO₂:He molar ratio = 1:5:9; Total flow rate = 30 cm³min⁻¹; Catalyst weight = 200 mg; WHSV = 1.2 h⁻¹.

was conducted by heating the sample from 100 °C to 800 °C with the heating rate of 10 °Cmin⁻¹.

In H₂-TPR experiments 0.1 g of sample dilute with SiC was first preheated in air flow for 30 min at 550 °C and then in dry He (99.999 vol. %, Linde,) stream for next 30 min. After that the sample was cooled down in the He stream to 100 °C. The H₂-TPR analysis was then performed using mixture of N₂/H₂ (95/5 vol. %, Air Liquide) environment at a total flow rate 30 mLmin⁻¹ and ramped from 100 to 650 °C with heating rate of 10 °Cmin⁻¹. The H₂ consumption was mea-

sured using TCD and NiO (99.999 %, Aldrich) was used as a reference for the calibration of H₂ consumption.

Diffuse reflectance UV-vis analysis was conducted using an Ocean Optics HR2000+ spectrometer (integration time 50 ms, 50 scans) equipped with an DH-2000 BAL halogen-deuterium light source. The spectra were recorded between 225 to 800 nm and barium sulfate (99% Sigma-Aldrich) was use as a standard.

During selected catalytic tests carried out at 550 °C experiments with the oxidation state of chromium species was monitored using UV-vis equipment mentioned above (integration time 25 ms, 25 scans) and a high temperature reflection probe (FCR-7UV400-2-ME-HTX, 7 × 400 μm fibers). The probe was attached at the top of quartz microreactor within the distance of 2–3 mm from catalyst bed.

2.3. Catalyst evaluation

CO₂-PDH reaction was carried out in a flow-type quartz reactor. Typically, 0.2 g of the catalyst (grain size 0.2–0.3 mm) was preheated in a stream of dry helium (99.999 vol. %, Linde) for 30 min at 550 °C before each catalytic measurements, and then the reaction was started at 550 °C under atmospheric pressure. The feed consisted of a mixture of propane (99.96 vol. %, Linde) and CO₂ (99.996 vol. %, Linde) diluted with helium. The volumetric ratio of CO₂/C₃H₈/He = 5/1/9 was introduced into the reactor at a flow rate of 30 mLmin⁻¹. In reference catalytic test without CO₂ (non-oxidative dehydrogenation) the volumetric ratio of C₃H₈/He = 1/14 was used.

The composition of the reactor exhaust was analyzed by gas chromatograph (Agilent 6890N) which was equipped with a thermal conductivity detector, Hayesep Q and molecular sieve 5A columns. H₂, CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ were separated by Hayesep Q column

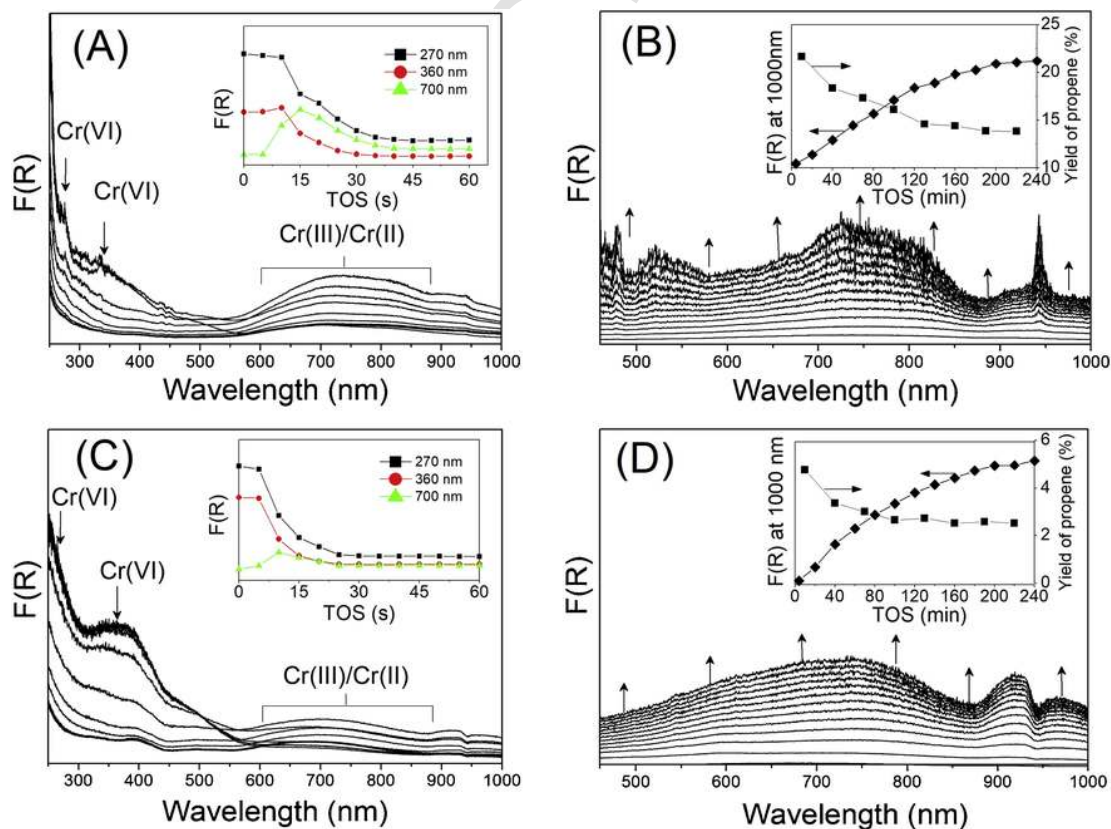


Fig. 9. UV-vis DRS spectra recorded during CO₂-PDH at 550 °C over Cr_{2.0}SiBeta (A and B) and Cr_{2.0}AlBeta (C and D). Spectra show in region between 0–1 min (A and C) and between 1–240 min (B and D) in interval 5 s. and 10 min, respectively.

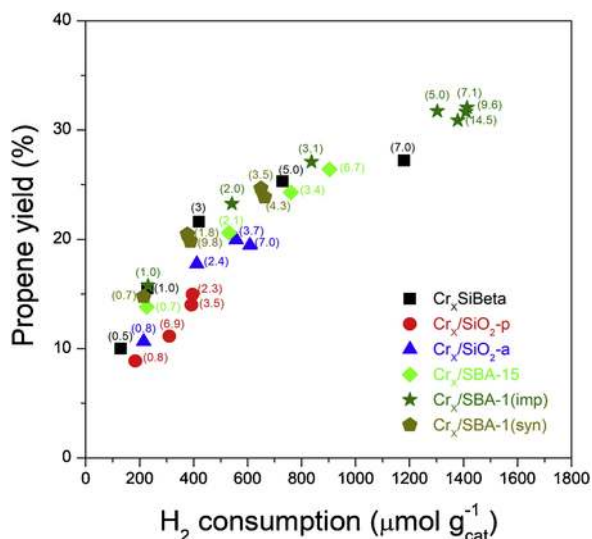


Fig. 10. The variation of propene yield with hydrogen consumption (proportional to number of Cr redox species) for several different chromium oxide based catalysts. Hydrogen consumption was calculated per catalysts weight based on H₂-TPR experiments. Sample notations: Cr_x/SBA-1(imp), Cr_x/SBA-15, Cr_x/SiO₂-a (silica support from Aldrich) and Cr_x/SiO₂-p (silica support from Polish Chemical Reagents) catalysts obtained by impregnation [28]; Cr_x/SBA-1(syn) catalyst prepared by Cr incorporation during SBA-1 synthesis [65]; The values in the brackets indicates total Cr content in the catalysts.

while CH₄ and CO were separated using column with molecular sieve 5A.

Activity normalized per catalyst weight (1), conversion of propane (2) and carbon dioxide (3), yield of propene (4) and selectivity to hydrocarbon products (5) were calculated as:

$$\text{Specific activity (mmol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{cat}}^{-1}) = F_{\text{C}_3\text{H}_8} \cdot C_{\text{C}_3\text{H}_8} \quad (1)$$

$$\text{Yield of propene (\%)} = \frac{n_{\text{C}_3\text{H}_6,\text{outlet}}}{n_{\text{C}_3\text{H}_8,\text{inlet}}} \cdot 100\% \quad (2)$$

$$\begin{aligned} \text{Conversion of propane (\%)} \\ = \frac{n_{\text{C}_3\text{H}_8,\text{inlet}} - n_{\text{C}_3\text{H}_8,\text{outlet}}}{n_{\text{C}_3\text{H}_8,\text{inlet}}} \cdot 100\% \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Conversion of carbon dioxide (\%)} \\ = \frac{n_{\text{CO}_2,\text{inlet}} - n_{\text{CO}_2,\text{outlet}}}{n_{\text{CO}_2,\text{inlet}}} \cdot 100\% \end{aligned} \quad (4)$$

$$\text{Selectivity (\%)} = \frac{\frac{a_i}{3} \cdot n_i}{n_{\text{C}_3\text{H}_8,\text{inlet}} - n_{\text{C}_3\text{H}_8,\text{outlet}}} \cdot 100\% \quad (5)$$

where: $F_{\text{C}_3\text{H}_8}$ is a number of propane moles per second, $C_{\text{C}_3\text{H}_8}$ is conversion of propane per gram of a catalyst $n_{\text{C}_3\text{H}_8,\text{inlet}}$, $n_{\text{CO}_2,\text{inlet}}$ and $n_{\text{C}_3\text{H}_8,\text{outlet}}$, $n_{\text{CO}_2,\text{outlet}}$ are numbers of propane and carbon dioxide moles in the reactor inlet and outlet, respectively, $n_{\text{C}_3\text{H}_6,\text{outlet}}$ is a number of propene moles in the reactor outlet, a_i is a number of carbon atoms in a product, and n_i is a number of moles of "i" product.

3. Results and discussion

3.1. Support characterization

Initially, AlBeta (Si/Al = 17) and SiBeta (Si/Al = 1000) were characterized for clarify dealumination effect on structure, texture and acid-base properties. As shown in Fig. 1, the crystallinity of Beta zeolite is preserved after dealumination and in the SiBeta support any extra lattice crystalline compounds and long range amorphization do not occur. The increase of 2 theta value of the main diffraction line after dealumination from 22.5 (AlBeta) to 22.7° (SiBeta) indicates contraction of the Beta matrix, in line with earlier investigations (Fig. 1 inset) [36,37].

Moreover, the dealumination leads to small change in porosity and specific surface area. After HNO₃ treatment the BET specific surface area (S_{BET}) increases from 642 m² g⁻¹ (AlBeta) to 724 m² g⁻¹ (SiBeta) while the total pore volume from 0.52 cm³ g⁻¹ (AlBeta) to 0.72 cm³ g⁻¹ (SiBeta) [38]. In contrary to structure and texture changes the dea-

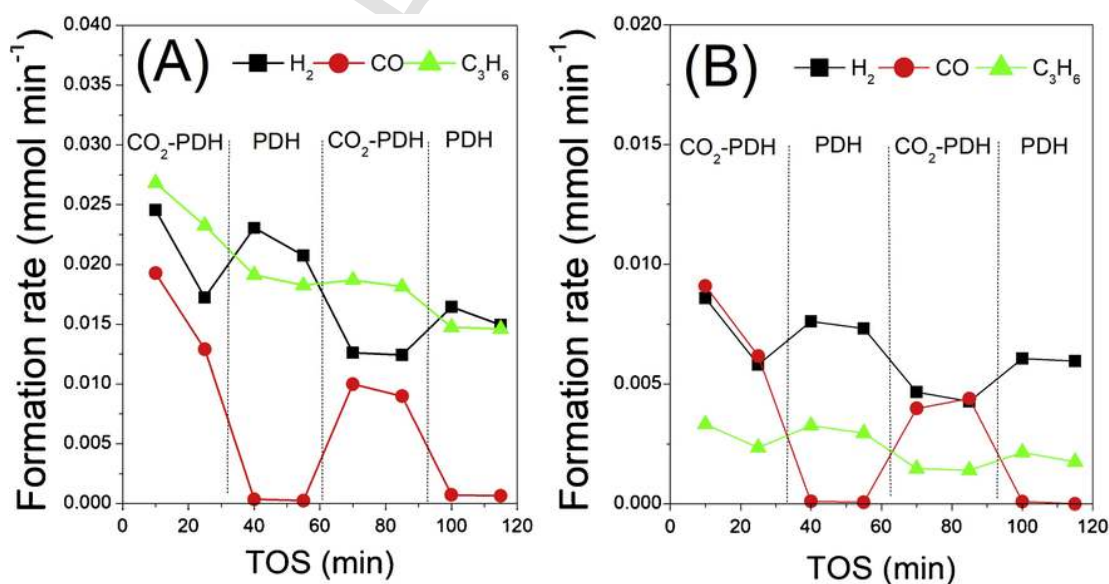
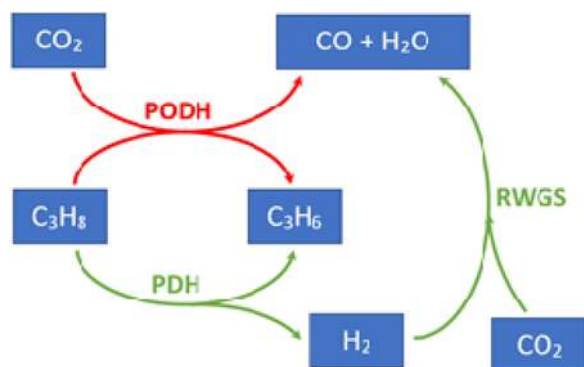


Fig. 11. Rate of propene formation (▲), hydrogen (■) and carbon monoxide (●) in dehydrogenation of propane to propene in the presence (CO₂-PDH) and absence (PDH) of CO₂ at 550 °C over (A) Cr_{2.0}SiBeta and (B) Cr_{2.0}AlBeta catalysts.



Scheme 1. Possible pathways of propene generation in assistance of CO₂ over Cr-containing SiBeta zeolite catalyst. Red arrows - propane oxidative dehydrogenation (PODH); Green arrows: propane dehydrogenation (PDH) coupling with reverse water-gas shift (RWGS).

dealumination has much significant impact on acidity. The NH₃-TPD profiles for AlBeta and SiBeta are compared on Fig. 2A. In both cases two maxima at 200 °C and 370 °C are observed on the NH₃-TPD profiles suggesting the presence of two type of acid sites, such as Lewis acid sites related to the presence in zeolite structure of Al³⁺ ions (maximum at around of 200 °C) and Brønsted acid sites related to the acidic proton of Si—O(H)—Al groups (maximum at around of 370 °C), in agreement with earlier reports [39,40].

However, the intensity of these two peaks on SiBeta profile is much lower than on AlBeta profile indicating clearly that dealumination leads to significant reduction of acid sites number.

Presence of both type acidic sites is confirmed by FTIR investigation with pyridine as probe molecule Fig. 3.

The treatment of AlBeta zeolite with HNO₃ solution involve of elimination of Al atoms from the framework evidenced by disappearance of IR bands at 3778, 3661 and 3606 cm⁻¹ related to AlO—H groups (Fig. 3A), in agreement with our earlier investigation [41–43]. The appearance of narrow band at 3735 and shoulder at 3710 cm⁻¹ related to isolated silanol groups and of a broad band at 3524 cm⁻¹ due to H-bonded SiOH groups in SiBeta reveals the presence of vacant T-atom sites [41,44]. As shown in Table 1, the number of Brønsted and Lewis acid sites decrease strongly when AlBeta zeolite is dealuminated and only traces of Brønsted and Lewis acid sites are detected in SiBeta.

To determine the nature and strength of acidic centres in AlBeta, Cr_{2.0}AlBeta, SiBeta and Cr_{2.0}SiBeta zeolite samples, the adsorption of pyridine as probe molecules has been performed. Fig. 3B presents the FTIR spectra of AlBeta, Cr_{2.0}AlBeta, SiBeta and Cr_{2.0}SiBeta after adsorption of pyridine at room temperature and after that desorption by outgassing 1 h under vacuum of 10⁻³ Pa at 150 °C. The several IR bands at 1637, 1622, 1610, 1546, 1490, and 1450 cm⁻¹ are observed for AlBeta related to Brønsted acidic centres (the bands at 1637 and 1546 cm⁻¹), Lewis acidic centres (the bands at 1622, 1610 and 1450 cm⁻¹), Brønsted and Lewis acidic centres (the band at 1490 cm⁻¹). The bands typical of pyridinium cations are seen at 1545 and 1637 cm⁻¹, indicating the presence of Brønsted acidic centres related to the acidic proton of Al—O(H)—Si groups, in line with earlier data [45]. The bands at 1450 cm⁻¹ correspond to pyridine interacting with strong Lewis acidic centres (Al³⁺). The band at 1490 cm⁻¹ corresponds to pyridine interacting with both Brønsted and Lewis acidic centres.

The ²⁷Al MAS NMR of AlBeta zeolite possesses 4 resonances (Fig. 4). The signals at 54.8 and 52.5 ppm associated to aluminum atoms present in two types of the tetrahedral environment of the framework. The signals at -1.7 and -10 ppm correspond to aluminum atoms in two types of octahedral environment. The first narrow peak, could be attributed to aluminum atoms in a tetrahedral environment near water molecules and the second a large peak could be attributed to ex-

traframework species. Due to dealumination, the ²⁷Al NMR spectrum of SiBeta zeolite (Fig. 4) present only one a small signal at -52.5 ppm corresponding to aluminum atoms in the framework of zeolite [46,47].

The ²⁹Si MAS NMR spectrum of AlBeta (Fig. 5) shows two peaks at -114.5 and -111.0 ppm related to two crystallographic sites of the framework, Si atom in a Si(OSi)₄ (Q⁴) environment. The signals at -102.2 and -106.1 ppm correspond to two Q³ species, (OSi)₃Si(OH) and (OSi)₃Si(Al) groups, respectively. ²⁹Si MAS NMR spectrum of SiBeta (Fig. 5) is very similar to that of AlBeta. Only the signal at -106.1 ppm disappeared as a result of dealumination [48].

The ¹H MAS NMR of the AlBeta zeolite (Fig. 6) shows a broad signal at 4.7 ppm due to bridging hydroxyl protons (Si(OH)Al). The small signal at 1.37 corresponds to proton of SiOH groups. In the ¹H MAS NMR spectrum of SiBeta (Fig. 6) two main signals at 4.5 and 1.37 ppm, related to the protons of hydrogen bonded Si—OH groups present at vacant T-atom sites and to the protons of isolated Si—OH groups respectively [49,50]. Two peaks at 7 and 3.22 ppm are attributed to protons of water molecules and of hydrogen bonded Si—OH groups located in a second type of crystallographic site [51].

Moreover, dealumination leads also to significant reduction of basic sites number. The CO₂-TPD profiles for both materials are reported on Fig. 2B. In the case of AlBeta one intensive and a broad maximum ca. 200 °C with high temperature shoulder appeared, confirming presence of weak and medium basic sites which can be assigned to desorption weakly adsorbed CO₂ (physisorbed) and decomposition of carbonates like species. In contrast, the amount of CO₂ adsorbed on dealuminated support (SiBeta) is much lower than that on parent AlBeta support. Two maxima with very low intensity at about 200 and 350 °C appear. The quantitative calculation reported in Table 1 indicates that the total amount of CO₂ adsorbed on SiBeta is more than 8 times lower than on AlBeta.

3.2. Catalysts characterization

Using SiBeta support the series of Cr-containing SiBeta catalysts was prepared by wet impregnation. Based on AlBeta support the Cr_{2.0}AlBeta reference catalyst was prepared as well. Base characterization results of SiBeta series are summarized in Table 2.

Chemical analysis confirms good reproducibility of Cr incorporation into the Beta zeolite. Both BET and Langmuir specific surface areas as well as total pore volume drops gradually with the total Cr content indicating that chromium deposition on SiBeta leads to porosity and surface area reduction, simultaneously.

The decrease of the 2θ value of the narrow main diffraction line around 2θ of 22.60° after introduction of Cr ions (Fig. 1) indicates some expansion of the Beta structure and suggests that the latter are incorporated into lattice sites. The 2θ value of this diffraction line decreases from 22.71 (SiBeta) to 22.64 (Cr_{0.5}SiBeta), 22.61 (Cr_{1.0}SiBeta) and 22.56° (Cr_{2.0}SiBeta) which indicates expansion of the matrix after incorporation of chromium ions into framework of SiBeta support. For higher Cr content, the decreasing of the 2θ value of this diffraction line is not observed (Fig. 1), so it suggests that for higher amount than 2 Cr wt % the Cr ions are introduced in the extra-framework position of the zeolite structure.

In contrast, the same 2θ value of the main diffraction line at 22.55 for AlBeta and Cr_{2.0}AlBeta suggests that upon wet impregnation of AlBeta support with Cr(NO₃)₃ precursor expansion of zeolite matrix do not occurred. It indicates that Cr ions are introduced in the extra-framework position of Beta structure.

The incorporation of Cr leading to Cr_{0.5}SiBeta, Cr_{1.0}SiBeta and Cr_{2.0}SiBeta induces a reduction of intensity of the bands of silanol groups, isolated and hydrogen bonded at 3735 and 3524 cm⁻¹ respectively (Fig. 3). Similar change has been observed for incorporation of vanadium and cobalt ions into SiBeta suggesting that silanol groups are

consumed in the reaction with chromium nitrate and Cr ions are simultaneously incorporated into framework of Beta zeolite, in agreement with later reports [41,44]. In addition, introduction of Cr ions in the AlBeta support leads to decreasing of Brønsted acid sites from 235.6 $\mu\text{mol g}^{-1}$ for AlBeta to 227.3 $\mu\text{mol g}^{-1}$ for Cr_{2.0}AlBeta and Lewis acid sites from 134.8 $\mu\text{mol g}^{-1}$ for AlBeta to 126.4 $\mu\text{mol g}^{-1}$ for Cr_{2.0}AlBeta. For SiBeta and Cr_{2.0}SiBeta only traces of Brønsted and Lewis acid sites are observed.

The incorporation of chromium in SiBeta and AlBeta causes a decrease in the signal corresponding to the (OSi)₃Si(OH) group (−102.2 ppm), which suggests an interaction between the chromium and the silanols of the zeolite (Fig. 5). The effect is much more important on Cr_{2.0}SiBeta than on Cr_{2.0}AlBeta.

In presence of chromium, the signals of bridging hydroxyl protons in AlBeta (4.7 ppm) and the signal of H-bonded Si—OH groups present at vacant T-atom sites in SiBeta (4.5 ppm) are very disturbed (Fig. 6). These modifications are due to the paramagnetic properties of chromium, which indicates a proximity between the species.

Furthermore, an oxidation state of chromium species in fresh samples was monitored using UV–vis diffuse reflectance spectroscopy (UV–vis DRS). Fig. 7A summarizes the spectra recorded in the range of 225–800 nm that is characteristic for charge transfer (CT) and d-d transition of chromium species. In all cases, in the CT transition region two peaks at 270 nm and 360 nm are detected. These peaks are assigned to CT of Cr⁶⁺-O²⁻ transition in monochromate species attached with support [52,53]. In the case of catalysts with 5 or higher wt % of Cr an additional bands with low intensity in d-d region appeared (Fig. 7A). These two bands are characteristic for spin-allowed d-d transitions of Cr³⁺ [52–55]. Moreover, the band at 600 nm is asymmetric and has two low energy shoulders ca. 650 nm and 705 nm, which are assigned to spin-forbidden transition of Cr(III) (inset to Fig. 7A) [43]. The UV–vis DRS results indicate that below 5 wt % of Cr_{total} on SiBeta surface predominate Cr(VI) species while at and above this content Cr(VI) and Cr(III) species coexists.

Presence of Cr(VI) species in fresh samples is confirmed by H₂-TPR experiments (Fig. 7B). In all cases a single reduction maximum between 450 to 470 °C was observed. This maximum is assigned to reduction of Cr(VI) to Cr(III) species [54–56]. However, over ordered and unordered silica supports a deeper reduction of Cr(VI) to Cr(II) may also occur [27,28,56–58].

Quantitative results of H₂-TPR (Table 2) reveal that the hydrogen consumption rises with the Cr_{total} content indicating systematic rises of redox Cr(VI) species concentration. However, the ratio of H₂/Cr_{total} drops from 1.46 to 0.81 as Cr content rise from 0.5 to 7 wt % suggesting that with Cr_{total} content rises faster contribution of non redox Cr species (mainly Cr₂O₃ amorphous and crystalline) than redox ones. UV–vis DRS results (Fig. 6A) confirm that above 2 wt % rise the intensity of the d-d transition bands characteristic of Cr(III) species which are non-redox in nature while XRD indicates α -Cr₂O₃ formation above 5 wt % of Cr (Fig. 1).

3.3. Catalytic performance

Initially, the catalytic performances of all materials was investigated in CO₂-PDH process at 550 °C. Table 3 summarized initial specific activity, propane and carbon dioxide conversion as well as propene yield and selectivity to hydrocarbon products. The catalytic results for reference Cr_{2.0}AlBeta catalyst and several others Cr-based materials reported in literature are summarized as well.

It is clear from Table 3 that Cr_xSiBeta exhibits high catalytic performance, similar to other well know chromium oxide-based system supported on mesoporous silica supports (SBA-1, SBA-15, MCM-41, MSU-x) or active carbon. In Cr_xSiBeta series maximum initial yield 27.2 % was obtained on the sample with 7 wt % of Cr.

Moreover, it is clear that dealumination significantly improve both activity and selectivity. In the case of Cr_{2.0}AlBeta reference catalyst, the low selectivity to propylene is due to high concentration of strong acid sites over AlBeta support which prefer cracking of propane. Thus, over Cr_{2.0}AlBeta in product predominates methane, ethane and ethene produced in cracking reaction.

The variation of propane conversion and selectivity to propene vs. time-on-stream (TOS) are summarized in Fig. 8. Over all materials investigated conversion of propane drops with TOS, slightly for Cr-containing SiBeta zeolite with low Cr content (Cr_{0.5}SiBeta and Cr_{1.0}SiBeta) and much significantly for Cr-containing SiBeta zeolite with higher Cr content (higher than 2 Cr wt %). The selectivity to propene variation has opposite trend than propane conversion. It is also clear that in all cases the deactivation has not monotonic trend. It is faster at the beginning of the process and slow down with TOS.

To clarify deactivation process the catalysts was investigated upon catalytic test by UV–vis DRS. During the CO₂-PDH process over Cr_{2.0}SiBeta and Cr_{2.0}AlBeta the spectra were collected in two time period. The first period between 0–1 min and second ones between 1–240 min on stream. The Fig. 9 summarizes the spectra collected in these two periods.

In both cases, spectra of degassed in helium samples (fresh catalysts before CO₂-PDH process) have two main maxima at 270 nm and 360 nm characteristic for CT transitions of Cr(VI) species. These maxima are reduced rapidly during first minute in contact with CO₂-C₃H₈ mixture (Fig. 9A and C). Simultaneously, new broad bands between 650–700 nm appear indicating reduction of Cr(VI) to Cr(III)/Cr(II) species. The latter species were found to be catalytically active in non-oxidative dehydrogenation of hydrocarbons [56]. Their also involve in the dehydrogenation with CO₂ [10,27,28]. Ohisih et al. [59] have proposed redox cycle between Cr(II) and Cr(III) species in which CO₂ acts as a mild oxidant. However, CO₂ is very weak oxidant. As we found previously Cr(VI) species reduced with CO selectively to Cr(II) species are very slowly re-oxidized by ultrapure CO₂ (additionally deoxygenated and dry) [62]. This may suggest that in the case of chromium-containing SiBeta catalyst an oxidation role of CO₂ cannot be responsible alone for observed promoting effect.

In the second time period (between 1–240 min on stream) continuous rise of the intensity in whole range was observed that confirms a darkening of the sample due to coke formation. Tracking of the intensity variation at 1000 nm indicates that darkening of the catalysts is faster at the beginning of the process and slow down with TOS unlike to propylene yield (inset to Fig. 9B and D). This variation of coke formation rate with TOS can be explained based on higher reactivity of propylene than propane. Because coke is produced more easily from propene its high yield leads to faster deactivation. Similar effect was observed in propane dehydrogenation over CrO_x/Al₂O₃ [63,64].

Fig. 10 shows variation between initial propene yield (after 10 min on stream) and hydrogen consumption (from H₂-TPR) that is proportional to number of redox Cr species for several various supported chromium oxide based catalysts including also Cr_xSiBeta.

Over different Cr-containing Beta materials the yield of propene rise with the number of redox Cr species which on various silicas depend on their pore structure and specific surface area of method of Cr incorporation/deposition as well as total Cr content. Typically, the yield rises with the increase of total Cr content up to the maximum value (monolayer coverage). After exceeding the monolayer coverage of support the redox Cr species are no longer stabilized (attached directly with support) and during the preparation there are decompose to less active and non-redox Cr₂O₃ particles. In Cr_xSiBeta series linear proportion between formation rate and number of redox species is observed up to 2 wt % of Cr. After exceeding this content catalytic performance did not correlate further with number of redox sites. In this respect the Cr_xSiBeta catalysts exhibits quite different behavior than chromium ox-

ide-based catalysts supported on ordered mesoporous silica (SBA-1 or SB-15). In the latter case propane rate was proportional to redox Cr species in wide range (between 0.7–13.6 wt % of Cr) while in Cr_xSiBeta series the yield of propene remains constant at and above 5 wt % of Cr.

Finally, the effect of CO₂ on catalytic performance was investigated. Fig. 11 shows the variation of formation rate of propene, carbon monoxide and hydrogen with TOS in the dehydrogenation of propane in the presence and absence of CO₂, respectively. The switching process was carried out over Cr_{2.0}SiBeta and Cr_{2.0}AlBeta catalysts.

Promoting effect of CO₂ on formation rate of propene was observed over Cr_{2.0}SiBeta catalyst. In each cycle with CO₂ addition, the formation rate of propene was higher than in the cycles without it. Similar promoting effect was observed over chromium oxide-based catalysts supported on different pure siliceous supports, such as non-ordered SiO₂ or ordered MCM-41, SBA-15, SBA-1, MSU-x [5,9–11,14,15,27,28]. Typically, CO₂ addition enhances propene formation in comparison with PDH carried out using dilution with inert gas only [5,27,28]. Over Cr_{2.0}SiBeta, in CO₂ presence, rises formation rate of propene and carbon monoxide while at the same time decreases formation rate of hydrogen. It should be pointed out that addition of CO₂ never stops formation of hydrogen. Changes of formation rate of propene and hydrogen in cycles with and without CO₂ are similar suggesting that positive effect of CO₂ on propene production is due mainly to shifting propane dehydrogenation equilibria via RWGS reaction. A good catalytic performance of Cr-containing catalysts in RWGS reaction was confirmed previously [13,27]. The equilibria calculations for two-step pathway of CO₂-PDH process i.e. for PDH reaction coupling with RWGS reaction and for single PDH confirm that CO₂ addition enhances significantly equilibrium conversion of propane [66]. Under reaction conditions applied in this work (p = 1 atm, t = 550 °C and feed with molar ratio C₃H₈:CO₂:Inert = 1:5:9 or C₃H₈:Inert = 1:14) the equilibrium conversion of propane rises from 70 % in PDH process to 89 % in CO₂-PDH process [2].

Taking into account above and considering very weak oxidative abilities of CO₂ against reduced Cr species it can be concluded that over chromium-containing SiBeta catalysts propene is produced mainly by PDH pathways facilitated by hydrogen removing in RWGS. Propane oxidative dehydrogenation (PODH) pathway has small contribution because CO₂ reoxidizes very slowly reduced Cr species. Scheme 1 summarizes both possible pathways responsible for CO₂ promoting effect on formation rate of propene.

It should be pointed out that the promoting effect observed in the case of Cr_{2.0}SiBeta is similar to those observed on Cr-based catalysts supported on ordered or unordered mesoporous silicas. Over all these catalysts CO₂ addition enhances only partially propene formation (10–25 %). Comparing to other catalytic systems, for instance palladium supported on Ce-based supports the promoting effect of CO₂ on Cr-based systems is moderate [3]. This variation of CO₂ effect with catalyst can be explained by different contribution of PODH and PDH pathways. In the case of Pd/Ce-based catalysts a dissociation of CO₂ to active O species and CO over ceria-based support facilitated both PODH and RWGS reactions, while over Cr/Silica based (or Si rich supports) catalysts such dissociation is not pronounced thus propene is produced mainly in PDH reaction.

In contrast, over Cr_{2.0}AlBeta reference catalyst CO₂ exerts negative effect, e.g. the formation rate of propene drops in the process carried out with CO₂. In this respect the Cr_{2.0}AlBeta exhibits similar catalytic behavior to CrO_x/γ-Al₂O₃ catalyst [2,5,11]. In the latter case the poisoning effect of CO₂ was assigned to strong CO₂ adsorption on the surface of γ-Al₂O₃. FTIR investigation with CO₂ as a probe molecule has revealed that on the surface of CrO_x/γ-Al₂O₃ carbon dioxide is strongly adsorbed in form of carbonates which may limit dehydrogenation of propane [2]. The quantitative CO₂-TPD measurements show that amount CO₂ adsorption on AlBeta is much higher than over dealu-

minated form (SiBeta) (Table 1). This confirms stronger interaction of CO₂ with AlBeta which may explain poisoning effect observed over the Cr_{2.0}AlBeta zeolite catalyst.

4. Conclusions

Catalytic performance of chromium-containing SiBeta catalysts was investigated in the dehydrogenation of propane to propene in CO₂ assistance. Dealumination with acid nitrate leads to significant reduction of Si/Al molar ratio from 17 to 1000. This has great impact on catalytic performance in CO₂-PDH process. A comparative catalytic results indicate that the promoting effect of CO₂ on propene formation was observed on Cr_{2.0}SiBeta. On this dealuminated form of Beta zeolite both the yield and selectivity to propene rise in the presence of CO₂. In contrast, on Cr_{2.0}AlBeta zeolite catalyst CO₂ exerts negative effect similar to poisoning effect observed over γ-Al₂O₃ based chromium oxide catalyst. Moreover, in series of Cr_xSiBeta catalysts a correlation between number of redox Cr species and catalytic performance was found.

Declaration of Competing Interest

None.

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