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Investigation of catalytic activity of CrSBA-1 materials obtained by direct method in the dehydrogenation of propane with $\rm CO_2$

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ABSTRACT

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Keywords: Dehydrogenation with CO₂ Propene Chromium catalysts SBA-1 A series of the Cr-containing SBA-1 (xCrSBA1) cubic mesoporous catalysts with various Cr/Si molar ratios have been prepared by direct method using cetyltriethylammonium bromide, ammonium dichromate, tetraethyl orthosilicate and hydrochloric acid. The obtained materials have been characterized by different physicochemical techniques including ICP, XRD, UV-vis DRS, H₂-TPR and N₂-adsorption. XRD and N2-adsorption results have revealed that xCrSBA1 materials possess well organized threedimensional pore structure. However, incorporation of Cr into the SBA-1 framework leads to small perturbation of the structural order. ICP results have shown that the amount of Cr incorporation in SBA-1 can be controlled by adjustment of the molar ratio of $(NH_4)_2Cr_2O_7$ to Si $(C_2H_5O)_4$ in the gel. Finally, the catalytic activity of pure SBA-1 and Cr-containing SBA-1 materials were investigated in the dehydrogenation of propane with CO₂. In the case of the most active, 0.04CrSBA1 catalyst, the effect of various reaction parameters such as, reaction temperature, reaction time and feed gas composition on the conversion of propane, yield and selectivity to propene as well as on molar ratio of CO/H₂ has been evaluated. Moreover, stability of the catalyst during the dehydrogenation/regeneration conditions was studied as well. It has been found that during the fourth consecutive cycle the catalyst undergoes two types of deactivation processes - reversible and irreversible. The former is caused mainly by the coke deposition, which can easily overcome by air treatment of the catalyst at 550 °C. The latter one, insignificant, is due to partial collapse of mesoporous structure of the catalysts.

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1. Introduction

Dehydrogenation of propane in the presence of CO₂ has been investigated recently as a new way for obtaining propene from its low cost and poorly reactive saturated analogue, propane. In this process, propene can be obtained with higher yield than in the non-oxidative dehydrogenation of propane. This positive effect of CO₂ is explained by its participation in direct oxidation of propane to propene ($C_3H_8 + CO_2 = C_3H_6 + CO + H_2O$) and hydrogen consumption by reverse water-gas shift reaction ($CO_2 + H_2 = CO + H_2O$), which shifts propane dehydrogenation equilibrium. Moreover, the side benefit of the new process is utilization of CO₂ that is converted to useful co-product, carbon monoxide.

In the dehydrogenation of propane with CO₂, different oxide materials were investigated as catalysts [1–23]. Among them, much attention has been dedicated to chromium and gallium oxide-based catalysts, which are the most active, selective and stable in the process with CO₂ [1,4–7,9–22]. Furthermore, it has

been found that the over the latter mentioned catalysts positive effect exerted by CO_2 is different. In the case of gallium oxidebased catalysts, CO_2 suppresses partially deactivation by coke formation and enhances the yield of propene by removal of H₂ that is formed in the dehydrogenation reaction [17–19]. The experimental data has been confirmed recently by DFT study, which revealed that over Ga_2O_3 , in the presence of CO_2 , the main route of propene formation is the dehydrogenation of propane, while oxidative dehydrogenation is energetically less workable [24]. In contrast, in the case of chromium oxide-based catalysts, promoting effect of CO_2 on the yield of propene is due to its oxidative abilities. It has been suggested that CO_2 acts as an oxidant in the oxidative dehydrogenation of propane to propene [5,10,13].

The redox mechanism, proposed in the case of chromium oxidebased catalysts, needs the redox Cr species (Cr^{6+} , Cr^{5+} or Cr^{3+}), whose concentration depends mainly on the chromium loading, the preparation conditions, the precursor compound of chromium and nature of support. In the case of SiO₂-supported chromium oxide catalysts, the redox Cr species (mainly Cr^{6+} in form of chromates or polychromates) are dominant at low Cr loadings, where a high degree of Cr dispersion is expect, while at higher Cr loadings and low dispersion nonredox polymeric Cr^{3+} species as well as crystalline Cr_2O_3 are also present.

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Taking to assume above it could be conclude that in order to obtain more active chromium oxide-based catalyst for the dehydrogenation of propane with CO_2 a high dispersion of the chromium oxide species at Cr lodgings as high as possible should be achieved. From those reasons, more attention has been dedicated recently toward mesoporous sieves. A large surface area (>1000 m² g⁻¹) of the mesoporous materials makes it possible to create much higher number of the redox Cr species in compare with traditional SiO₂-supports. Several recent investigations have shown that Cr-containing mesoporous sieves have an excellent catalytic activity in the dehydrogenation of propane to propene with and without CO_2 [5,11,13–15].

The newly discovered SBA-1 mesoporous silica material has high potential to be applied as a catalyst support, because of its unique textural properties. In particular, it has a three-dimensional channels (Pm3n) ranging from 2.1 to 2.6 nm and specific surface area in the range 1200–1450 m² g⁻¹. Such three-dimensional pore network is more resistant to pore blocking, they provide more adsorption sites due to their high surface area and the pores can be easily accessible to reactant molecules [25]. Moreover, cubic mesoporous phase is mechanically more stable compared to hexagonal mesoporous materials, such as: SBA-15 and MCM-41 [26]. The latter feature is important for industrial applications where the catalyst powders are subjected to shaping process.

Although SBA-1 materials possess interesting structural properties the studies concerning their application in catalysis are limited, compared with other mesoporous materials such as hexagonal MCM-41 or SBA-15. Up to now, only a few efforts have been made to incorporate Cr [27] or other heteroatoms like Ga [25], Ti [28–30], V [31,32], Co [33], Al [34,35] Mo [36] and Fe [28,37–39], Pd [40] into the SBA-1 for catalytic purpose. The main reasons for that is difficulty with preparation of template with large headgroups (e.g. alkyltriethylammonium bromide) and incorporation of heteroatoms (mainly in cationic form) into the SBA-1 frameworks under strong acidic conditions.

In this work we investigated the catalytic activity of Crcontaining SBA-1 catalysts (*x*CrSBA1) with different Cr loadings, prepared by the direct method. All the *x*CrSBA1 catalysts were characterized by various techniques such as X-ray diffraction (XRD), diffusion reflectance, N₂-adsorption and temperatureprogrammed reduction experiments (H₂-TPR). Finally, the catalytic performance of the *x*CrSBA1 catalysts in the dehydrogenation of propane to propene with CO₂ was evaluated.

2. Experimental

2.1. Surfactant preparation

Hexadecyltriethylammonium bromide (HTEABr) was synthesized by reaction of 1-bromohexadecane (97%, Aldrich) with an equimolar amount of triethylamine (98%, Fluka) in ethanol (99.8%, Chempur) under reflux for 72 h. The surfactant cetyltriethylammonium bromide (CTEABr) was purified by recrystallization from chloroform/ethyl acetate mixture [41].

2.2. Synthesis of mesoporous CrSBA-1 catalysts

The catalysts were prepared under acidic conditions using cetyltriethylammonium bromide as the surfactant, tetraethyl orthosilicate (TEOS) as the silica source and ammonium dichromate as the chromium source according to the modified procedure described in [27]. In a typical synthesis, 10 g of CTEABr, 1157 cm³ of distilled water and 566 cm³ of hydrochloric acid (37%, Chempur) were combined with 0.158–1.58 g of ammonium dichromate (99%, Chempur) to form a homogeneous solution, which was cooled to 0 °C and stirred for 30 min. Then 27.90 cm³ of TEOS (98% Aldrich),

precooled to 0 °C was added, while vigorous stirring. The molar composition of the reaction mixture was TEOS:CTEABr:HCl:- $H_2O:(NH_4)_2Cr_2O_7 = 1:0.2:56:700:(0.005-0.05)$. Stirring was continued for 6 h until the precipitation of the silica-chromium-surfactant assemblies was completed. The resultant precipitate was filtered off and dried (without washing) at 60 °C overnight. The dried material was then calcined in air by rising temperature from ambient to 550 °C over 9 h and keeping it at 550 °C for another 12 h. The samples were labeled xCrSBA1 where x denotes the Cr/Si ratio in the gel (x = 0.01, 0.02, 0.04, 0.06 and 0.1).

2.3. Catalyst characterization

XRD patterns were recorded in two ranges of $0.5-10^{\circ}$ and $10-70^{\circ}$ (2 θ) at room temperature, using a Panalytical X'Pert Pro instrument operated at 40 kV and 30 mA, equipped with a Cu K α X-ray source. The crystals size of Cr₂O₃ was calculated based on Scherrer formula using the Rietveld method in the TOPAS R2.1 program.

Nitrogen adsorption–desorption isotherms were measured at -196 °C using a Quantachrome Autosorb-1 instrument. The samples were degassed at 250 °C before measurements. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method within the relative pressure range $P/P_0 = 0.05-0.15$. Pore size distributions were calculated from the branch of the desorption curve using the Barrett–Joyner–Halenda (BJH) model. Pore volumes were obtained from the volumes of nitrogen adsorbed at $P/P_0 = 0.95$ or vicinity.

Diffusion reflectance UV–vis spectra (UV–vis DRS) were taken on an Ocean Optics HR2000+ instrument (integration time 400 ms, 100 scans) equipped with an Ocean Optics DH-2000 BAL halogendeuterium light source and optical fiber probe (FCR-7UV400A-2ME-HTX) at room temperature. The spectra were recorded within the wavelength range of 220–800 nm using BaSO₄ as a standard.

Temperature-programmed reduction, using H₂ as the reducing agent was carried out in a modified gas chromatograph with a thermal conductivity detector (TCD). Purified mixture of N₂/H₂ (95/5 vol.%, Air Liquide) served as a combined carrier and reducing gas at a total flow rate 30 cm³ min⁻¹. Before experiment the catalyst sample (100 mg) was preheated in a dry He stream at 550 °C for 30 min, and then cooled to room temperature. The sample was heated at 10 °C min⁻¹ to the final temperature of 650 °C. The H₂ consumption was measured by a thermal conductivity detector and NiO (99.998%, Aldrich) was used as a reference for the calibration of H₂ consumption.

ICP spectrometry (Perkin Elmer ELAN 6100) was applied for quantitative determination of chromium content. The samples were dissolved in a mixture of HF and HNO₃.

2.4. Catalytic tests

The dehydrogenation of propane (Linde, 99.6 vol.%) in the presence of CO₂ (Linde, 99.96 vol.%) was carried out in flow-type quartz reactor packed with 200 mg of the catalyst (grain size 0.2-0.3 mm). The dehydrogenation feed consisted of a mixture of CO₂:C₃H₈:He = 10:1:4, 5:1:9, 1:1:13 and 0:1:14. The total flow rate was 30 cm³ min⁻¹. The catalyst was preheated in a stream of dry argon (Linde, 99.999 vol.%) for 0.5 h at 550 °C before the catalytic tests. The reaction was started in the 500-650 °C temperature range at atmospheric pressure. The reactants and products were analyzed on-line using a gas chromatograph (Agilent 6890N) equipped with two columns (Hayesep Q and molecular sieve 5A) and a thermal conductivity detector. The column packed with Hayesep Q was used for the quantification of H₂, CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈. The molecular sieve 5A was used for the quantification of CH₄ and CO. The conversion of propane, yield of propene and selectivity to all hydrocarbon products were calculated as described previously [13].



Fig. 1. XRD patterns of pure SBA-1 and fresh xCrSBA1 catalysts.

Coke amounts were estimated from the amounts of CO₂ and CO evolved during oxidative regeneration of the catalysts at 600 $^\circ\text{C}$ in air.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1A and B display the XRD patterns recorded for pure and Crcontaining SBA-1 materials in two different regions of 2θ angles. In the 2θ range of $1-10^{\circ}$ three diffraction lines are observed (Fig. 1A). These lines are indexed to the (2 0 0), (2 1 0) and (2 1 1) reflections, characteristic of the cubic *Pm3n* mesostructure [26,39]. The intensity of the diffraction lines for the xCrSBA1 catalysts decreases as the Cr-containing materials increases. However, even in the case of the 0.1CrSBA1 catalyst the diffraction lines characteristic for the cubic structure are still observed.

In the 2θ range of $10-70^{\circ}$, the diffraction lines, corresponding to the crystal phase of α -Cr₂O₃ are detected for the catalysts with the Cr/Si atomic ratio 0.04, 0.06 and 0.1 (Fig. 1B). The crystallite size of α -Cr₂O₃ calculated from Scherrer formula (the last column in Table 1) is in the range between 17 and 31 nm. These values are much higher than mesopore size of Cr-containing SBA-1 materials indicating that in all cases the particles of α -Cr₂O₃ are formed outside of mesochannels. The absence of the diffraction line in the samples with lower Cr/Si atomic ratio may be explained either by Cr dispersion or smaller size of the Cr₂O₃ crystals.

Textural properties of the calcined catalysts were characterized
by low temperature adsorption of nitrogen. The calculated specific
surface area, pore volume and average pore size are summarized in
Table 1.
Meconorous SBA_1 and the $vCrSBA1$ catalysts show uniform pore

Mesoporous SBA-1 and the *x*CrSBA1 catalysts show uniform pore size with the pore diameter within the narrow range between 2.4 and 2.6 nm, as calculated by the BJH method. The specific surface area and pore volume decrease with increase in the Cr/Si atomic ratio. The monotonic decrease of the textural parameters and the XRD lines intensity drop suggest small destruction of the structural regularity of the mesoporous structure with increase of the Cr content.

Furthermore, diffuse reflectance spectroscopy in UV–vis range was applied for the investigation of oxidation state of chromium species in the calcined samples (Fig. 2).

The range 200–800 nm is useful for diagnostic of Cr^{6+} in tetrahedral and Cr^{3+} in octahedral symmetry [42]. Two main absorption bands at 270 and 365 nm appear for all the samples. These bands were assigned to $Cr^{6+}-O^{2-}$ charge transfer transition of chromate species [42,43]. A shoulder at around 460 nm is also shown, ascribed to dichromate or polychromates arrangement in a contact with the support [43]. The spectra of the 0.04CrSBA1, 0.06CrSBA1 and 0.1CrSBA1 catalysts show additionally band at around 600 nm due to the $A_{2g} \rightarrow T_{2g}$ transition of Cr^{3+} in octahedral symmetry. Specifically, the band at 600 nm is assigned to a d–d charge transfer transition in a strongly distorted octahedral crystal field [44]. This absorption band does not appear in the spectra of

Table 1			
Characteristics	of pure SBA-1	and xCrSBA1	catalysts.

Sample	Cr _{ICP} (wt.%)	Cr/Si in gel	Texture			H ₂ -TPR ^a			Cr ₂ O ₃ crystal
		$(mol mol^{-1})$	$S_{\rm BET}(m^2{\rm g}^{-1})$	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	H_2 uptake $(\mu mol g^{-1})$	$H_2/Cr_{ICP} (mol mol^{-1})$	$L_{Cr^{6+}}/H_{Cr^{6+}}$ (%)	size (nm)
SBA-1	-	-	1279	0.71	2.4	-	-	-	-
0.01CrSBA1	0.7	0.01	1202	0.71	2.4	215	1.53	-	-
0.02CrSBA1	1.8	0.02	1106	0.66	2.4	377	1.09	-	-
0.04CrSBA1	3.5	0.04	1025	0.61	2.6	663	0.99	-	20
0.06CrSBA1	4.3	0.06	932	0.61	2.6	650	0.79	9	17
0.1CrSBA1	9.8	0.10	824	-	-	388	0.21	23	31

^a H₂ uptake – the total hydrogen consumption in µmol g⁻¹. L_{G⁶⁺}/H_{G⁶⁺} – ratio of the low temperature maxima (L_{G⁶⁺}) to that of the high temperature maximum (H_{G⁶⁺}).



Fig. 2. UV-vis DR spectra of fresh xCrSBA1 catalysts.

the calcined 0.01CrSBA1 and 0.02CrSBA1 samples, indicating that Cr^{6+} species are predominant in the case of the catalysts with a low Cr content, while in the 0.04CrSBA1, 0.06CrSBA1 and 0.1CrSBA1 catalysts both Cr^{6+} and Cr^{3+} coexist. Moreover, the intensity of the band at 600 nm increases with the increase of Cr content indicating that the concentration of Cr^{3+} species increase with the rise of Cr content. The UV–vis results reflect in the colour of the catalyst that turns from bright yellow in the case of 0.01CrSBA1 to dark green for the 0.1CrSBA1 catalyst.

Fig. 3 displays temperature-programmed reduction profiles of the fresh *x*CrSBA1 catalysts.



Fig. 3. H₂-TPR curves of fresh *x*CrSBA1 catalysts.

The reduction effects depend on the Cr content. The H₂-TPR profiles of the 0.01CrSBA1 and 0.02CrSBA1 catalysts show single reduction maximum at ca. 466 and 445 °C, respectively, while the profiles of the catalysts with higher Cr content (0.04CrSBA1, 0.06CrSBA1 and 0.1CrSBA1) exhibit an additional low temperature reduction maximum at around 276 °C with a shoulder ca. at 320 °C. These H₂-TPR results are in agreement with those reported earlier. Zhao and Wang [27] have observed also only one reduction maximum in the case of CrSBA-1 catalysts with the Cr content below 2 wt.% and two maxima (high and low temperature) for the samples with the higher Cr content. In the presented work the additional very weak shoulder of low temperature maximum was found. It is clearly seen after $4 \times$ magnification in the TPR curve for sample with the highest Cr content. This small difference in the redox behaviour could be caused by distinct preparation conditions, e.g. by the calcination temperature (550 °C instead 600 °C). The intensity of the low temperature maxima increases with increase of the Cr content in the catalysts, whereas the high temperature maximum at ca. 445 °C gradually decreases. The location of the low temperature maxima coincided well with the reduction maximum observed for α -Cr₂O₃, which are assigned to the reduction of Cr^{6+} to Cr^{3+} [45] or Cr^{2+} [46] species dispersed on α -Cr₂O₃. The high temperature maximum that is observed for all of the xCrSBA1 catalysts is assigned to the reduction of Cr^{6+} to Cr^{3+} species directly attached to the silica materials (Cr⁶⁺/SBA-1) [46]. Moreover, the latter maximum shifted to lower values as the Cr content in the catalyst increased from 0.7 to 1.8. This T_{max} shifting can be attributed to the change in the polymerization degree of Cr^{6+} species with rise of Cr concentration in the catalysts.

Results of the calculation of hydrogen consumption and the molar ratio of H₂/Cr_{ICP} for each catalyst sample, on the basis of the total area under TPR peaks and the amount of Cr_{ICP} are summarized in Table 1. The amounts of Cr⁶⁺ species directly bonded with SBA-1 to those attached to α -Cr₂O₃ (L_{Cr⁶⁺}/H_{Cr⁶⁺}) are presented as well (the last column in Table 1). The values of L_{Cr⁶⁺}/H_{Cr⁶⁺} were estimated on the basis of mathematical deconvolution of the experimental H₂-TPR curves. The total H₂ consumption increases with the increase of Cr content up to 3.5 wt.% and then declines, while the ratio of H₂/Cr_{ICP} drops from 1.60 to 0.21 as the Cr content is increased from 0.7 to 0.9 wt.% of Cr. This drop of the H₂/Cr_{ICP} ratio with the increase of Cr content is due to formation of crystalline α -Cr₂O₃. Similar drop of the H₂/Cr_{ICP} ratio with the increase of Cr loading we observed previously [13] in the case of MCM-41 supported chromium oxide catalysts.

Taking into account the H₂-TPR results, it can be concluded that in the *x*CrSBA-1 catalysts obtained by the direct method two types of the Cr⁶⁺ species with different reducibility are presented. The Cr⁶⁺/SBA-1 species are harder to reduce compared to Cr⁶⁺/ α -Cr₂O₃ species. At low loadings the Cr⁶⁺ species directly attached to the silica supports (Cr⁶⁺/SBA-1) dominate, whereas at higher Cr contents both Cr⁶⁺/SBA-1 and Cr⁶⁺/ α -Cr₂O₃ species coexist. Moreover, the presence of low temperature maxima confirms the existence of Cr₂O₃ in the catalysts 0.04CrSBA1, 0.06CrSBA1 and 0.1CrSBA1, which stays in agreement with the XRD and UV-vis DRS results.

The formation of crystalline α -Cr₂O₃ and polychromates (see Fig. 2, the bands at 460 nm) in the fresh catalysts indicates that the part of chromium precursor is weekly dispersed in the SBA-1 matrix. Zhao and Wang [27] have suggested the reason of that is tendency of Cr₂O₇^{2–} anions to polymerization under strong acid conditions (pH < 2). Moreover, it is known that not only decreasing of the pH but also increasing the chromium species concentration results in the formation of more polymerized chromium species like tri- (Cr₃O₁₀^{2–}) and tetrachromates (Cr₄O₁₃^{2–}) [44]. Such polychromates interact weakly with the SBA-1 support and during thermal treatment they are decompose to α -Cr₂O₃.



Fig. 4. Variation of propane conversion (\triangle) and selectivity to propene (\blacklozenge) with Cr content (A) and yield of propene with the number of Cr_{red} species (B). Reaction conditions: T = 550 °C; catalysts weight 200 mg; feed gas composition C₃H₈:CO₂:H = 1:5:9; The results after 10 min on-stream.

3.2. Dehydrogenation activity

The catalytic performance of pure and Cr-containing SBA-1 materials was investigated in the dehydrogenation of propane with CO_2 at 550 °C. The variation of the initial conversion of propane and selectivity to propene with the Cr content is displayed in Fig. 4A.

Pure siliceous SBA-1 is inactive in the dehydrogenation of propane with CO₂. In the series of *x*CrSBA1 catalysts the conversion of propane increased with the increase of Cr content up to 4.3 wt.% and for the sample with the highest Cr content declined. The lower catalytic activity of the 0.1CrSBA1 catalyst can be explained by its lower cubic regularity caused by incorporation of the high amount of Cr. Moreover, selectivity to propene over pure SBA-1 is very low, while increasing dramatically after incorporation of Cr into the SBA-1 framework.

In accordance with earlier observation [17,22,45–47], the dehydrogenating activity of chromium oxide-based materials in the presence and absence of CO_2 are strongly affected by the redox Cr species (Cr_{red}). It has been proposed that the Cr^{6+} and Cr^{5+} species

present on the surface of calcined supported chromium oxide catalysts are precursors for redox Cr³⁺ species, which are very active in dehydrogenation of alkanes [46,47]. Contrary to the simple dehydrogenation, in the presence of CO₂ oxidative dehydrogenation/hydrogenation pathways are activated over Cr_{red}. So far, several different redox cycles including Cr^{6+}/Cr^{3+} [10,48], Cr^{5+}/Cr^{3+} [49] or Cr^{3+}/Cr^{2+} [50], have been proposed for explanation of CO₂ effect in the dehydrogenation of hydrocarbons. Taking that into account, the variation of the yield of propene with the number of Cr_{red} in the xCrSBA1 catalysts was investigated (Fig. 4B). The number of Cr_{red} species was calculated from hydrogen consumption (see Table 1, H₂-TPR results) by assuming that hydrogen is consumed only in the reduction of Cr^{6+} (2CrO₃ + 3H₂ = Cr₂O₃ + 3H₂O, 1.5 mmol H₂/mol Cr⁶⁺), and that the reduction of both Cr⁶⁺/SBA-1 and Cr⁶⁺/Cr₂O₃/SBA-1 species yields selectively Cr³⁺. The increase of propene yield with the number of Cr_{red} species is consistent with the previous results [13]. However, there is no fully linear correlation, which indicates that the dehydrogenating properties are attributed not only to the redox but also to nonredox Cr species.



Fig. 5. Variation of propene yield, selectivity to propene and molar ratio of H_2/CO at different feed gas composition with TOS over 0.04CrSBA1 catalyst. Molar ratio of C_3H_8 :CO₂:He = 1:10:4 (\blacktriangle), 1:5:9 (\blacksquare), 1:1:13 (\bigstar) and 1:0:14 (\square). Reaction conditions: T = 550 °C; catalysts weight 200 mg; total flow rate 30 cm³ min⁻¹.

Temperature (°C)	Conversio	on (%)	Yield (%)	Selectivity (%)			Molar ratio (mol m	ol ⁻¹)	
	C ₃ H ₈	CO ₂	C ₃ H ₆	C ₃ H ₆	C_2H_6	C_2H_4	CH ₄	$(CO + H_2)/C_3H_6$	CO/H ₂
500	12.9	1.3	11.8 (7.4) ^b	91.7	1.8	2.3	4.1	1.3 (1.1)	0.77 (0.6)
550	26.7	3.4	24.1 (15.2)	90.2	2.0	3.5	4.3	1.4 (1.2)	0.90 (0.7)
550 ^c	24.4	-	21.7 (10.8)	88.9	2.6	4.3	4.2	1.1 (1.0)	0.03 (0.01)
600	39.4	6.2	34.1 (21.6)	86.6	2.3	6.0	5.1	1.7 (1.3)	1.03 (0.8)
650	55.2	9.9	42.3 (23.2)	76.7	2.8	12.8	7.7	2.2 (1.5)	1.09 (0.7)

 Table 2

 Initial catalytic performance of 0.04CrSBA1 at different temperature^a.

^a Reaction conditions: molar ratio of $CO_2:C_3H_8:He=5:1:9$, total flow rate = 30 cm³ min⁻¹, catalyst weight = 200 mg, reaction time = 10 min.

^b The values in the brackets are calculated after 220 min on-stream.

^c Reaction without CO₂: C₃H₈:Ar:He = 1:5:9, V_{total} = 30 cm³ min⁻¹, 550 °C, reaction time = 10 min.

Fig. 5 presents the variation of the catalytic performance at different feed gas compositions with time-on-stream (TOS) at 550 $^{\circ}$ C.

With the increase of molar ratio of CO_2/C_3H_8 yield of propene, selectivity to propene and molar ratio of H₂/CO increase. As it has been pointed in the introduction, CO₂ enhances the yield of propene by two ways (i) direct oxidation of propane to propene $(C_3H_8 + CO_2 = C_3H_6 + CO + H_2O)$ and (ii) hydrogen consumption by reverse water-gas shift reaction $(CO_2 + H_2 = CO + H_2O)$, which shifts propane dehydrogenation equilibrium. Thus, in the dehydrogenation process with CO₂ beside propene, the main useful by-products are CO and H₂ are produced, which separately or together (as synthesis gas) find many applications in chemical synthesis. From Fig. 5 it can be seen that the regulation of feed gas composition (i.e., CO₂/propane molar ratio) gives a possibility to control the molar ratio of H_2/CO . The mixture rich in CO is obtained at high initial molar ratio of CO_2/C_3H_8 , while at the low ratio of CO_2/C_3H_8 the gas pure with CO is formed. It should be pointed out that synthesis gas with the ratio of H₂/CO between 1:1 and 3:1 or higher is widely applied in chemical industry. The high H₂/CO ratios of the order of 2-3 are suitable for Fischer-Tropsch synthesis, production of methanol and dimethyl ether, while the synthesis gas with lower H_2/CO ratios (around 1:1) is useful for OXO process.

Furthermore, in the case of 0.04CrSBA1 catalyst, the effect of reaction temperature on the catalyst performances was investigated. The initial conversion, yield of propene, and selectivity to all hydrocarbon products are summarized in Table 2.

Both the conversion of propane and the yield of propene increase with the rise of the reaction temperature while the selectivity to propene gradually drops. In the same time, the selectivity to by-products (i.e. methane, ethene and ethane) rise as the temperature increase, indicating facilitation of side reactions, like cracking and hydrocracking, at high temperatures. Moreover, the rise of the reaction temperature enhances the molar ratio of useful by-products, H_2/CO .

Fig. 6 shows the variation of propane and carbon dioxide conversion with time-on-stream (TOS) at 500, 550, 600 and 650 $^{\circ}$ C over the 0.04CrSBA1 catalyst.

In all the reaction temperatures the conversion of propane and carbon dioxide drops with the TOS. This unfavorable phenomenon is caused mainly by the coke deposition, which is accelerated at high temperatures. The deactivation data for the 0.04CrSBA1 catalyst at different temperature are summarized in Table 3. The results obtained for that catalyst in the absence of CO_2 at 550 °C are summarized as well.

A % activity loss, represented by the difference between the initial and the final conversion of propane, rises as the reaction



Fig. 6. Variation of propane (\triangle , Δ) and carbon dioxide (\bigcirc) conversion with temperature over 0.04CrSBA1 catalyst. Solid symbols – dehydrogenation with CO₂; empty symbol – dehydrogenation without CO₂. Dehydrogenation conditions: catalysts weight 200 mg; feed gas composition C₃H₈:CO₂:He = 1:5:9; total flow rate 30 cm³ min⁻¹.

Table 3 The effect of temperature on deactivation of 0.04CrSBA1 catalyst.							
Temperature (°C)	Activity loss ^a	Coke					
	(%)	$(mgC g_{cat.}^{-1})^{b}$	$n_{\rm coke}/n_{ m propane}$ (%) ^c				
500	2.9	3.4	0.13				
550	10.1	6.9	0.27				
550 ^d	12.7	3.7	0.14				
600	15.6	17.1	0.66				
650	22.8	32.9	1 28				

^a Difference between initial (after 10 min on-stream) and final (after 240 min onstream) conversion of propane.

 b Coke amount estimated on the basis of CO_x amounts determined during oxidative regeneration of used 0.04CrSBA1 catalyst in air at 600 °C.

^c Number of carbon atoms in the deposited coke per number of carbon atoms in the propane injected into the reactor during 240 min on-stream.

^d After process without CO₂: C₃H₈:Ar:He = 1:5:9, $V_{total} = 30 \text{ cm}^3 \text{ min}^{-1}$, 550 °C, after 240 min on-stream.

temperature increases. Similarly, the increase of the reaction temperature enhances the amount of coke deposited on the catalyst surface and the number of propane molecules converted to coke. Moreover, after the dehydrogenation of propane with CO₂ over 0.04CrSBA1 catalyst, the coke amount is higher then after the process without CO₂ (third column of Table 3). The latter result is consistent with the results of previous investigations concerning different silica-supported chromium oxide catalysts [10]. Larger coke amount observed in atmosphere of CO₂ than in inert gas atmosphere can be explained by higher reactivity of propene compared to propane. As suggested by Takehira et al. [10] coke is produced more intensely on the catalyst from propene than from propane, thus the enhanced formation of propene results in a larger amount of coke. This also indicates that CO₂ is not an effective gasification agent. Hence, under the dehydrogenation process conditions CO₂ cannot suppress the catalyst deactivation by Boudouard reaction $(CO_2 + C = 2CO)$.

Furthermore, the comparison of the deactivation data obtained for processes in the presence and absence of CO_2 at 550 °C reveals that despite of lower amount of coke, in the inert gas atmosphere the catalyst is deactivated faster than in the presence of CO_2 (see also Fig. 6). Such behaviour suggests that the additional reason for



Fig. 7. Variation of propane (\blacktriangle) and carbon dioxide (\odot) conversion as well as selectivity to propene (\diamondsuit) in consecutive dehydrogenation cycles. DH – dehydrogenation of propane with CO₂; R – regeneration by air at 550 °C; P – purification by helium at 550 °C. Dehydrogenation conditions: *T* = 550 °C; catalysts weight 200 mg; feed gas composition C₃H₈:CO₂:He = 1:5:9; total flow rate 30 cm³ min⁻¹.



Fig. 8. Adsorption-desorption isotherms and BJH pore distributions for fresh (a) and regenerated (b) 0.04CrSBA1 catalyst.

the deactivation is reduction of active sites of 0.04CrSBA1 catalyst. Such reduction is slower in the presence of CO₂ that helps maintain higher oxidation state of the chromium catalysts during the process.

Fig. 7 presents the catalytic performance of 0.04CrSBA1 catalyst in consecutive dehydrogenation–regeneration–purification cycles.

In the dehydrogenation step, the conversion of propane drops gradually with the TOS due to coke deposition and the reduction of active sites on the catalysts surface. This unfavorable phenomenon can be removed by treatment of the catalyst with air in the short regeneration step at 550 °C. However, after fourth cycle a small drop of the catalytic performance is observed. The initial (10 min on-stream) and final (240 min on-stream) conversion of propane drops from 26.7 and 16.6% in the first dehydrogenation step to 23.5 and 14.4% in the fourth step, respectively.

N₂-adsorption–desorption isotherms and BJH pore distributions of fresh and regenerated 0.04CrSBA1 catalyst after four cycles are displayed in Fig. 8.

There is no significant difference in the N₂-isotherms shape and pore size distributions, however specific surface area calculated by BET (S_{BET}) method as well as total pore volumes (V_{total}) drop from $S_{BET} = 1025 \text{ m}^2 \text{ g}^{-1}$, $V_{total} = 0.61 \text{ cm}^3 \text{ g}^{-1}$ for fresh catalysts to $S_{BET} = 787 \text{ m}^2 \text{ g}^{-1}$, $V_{total} = 0.49$ for the regenerated catalyst after four cycles. In summary, these results reveal that the irreversible deactivation of 0.04CrSBA1 material is due to loss of textural parameters. Lattice oxygen consumption during dehydrogenation of propane with CO₂ would have an impact on the corruption of 0.04CrSBA1 catalyst.

4. Conclusions

CrSBA-1 catalysts with the highly ordered cubic structure and high specific surface area ($S_{BET} > 900 \text{ m}^2 \text{ g}^{-1}$) are obtained by direct method up to Cr/Si = 0.06 atomic ratio in the gel. All Crcontaining SBA-1 materials possess good catalytic activity and selectivity in the dehydrogenation of propane with CO₂. The dehydrogenation activity is proportional to the number of redox chromium species. During the dehydrogenation of propane with CO₂, the catalysts undergo two types of deactivation processes – reversible and irreversible. The former is caused mainly by the coke deposition. The latter is due to partial collapse of mesoporous structure of the catalysts.

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