Effect of Zn-BEA zeolites dealumination on their catalytic perfomance in propane dehydrogenation to propylene with CO₂



Orlyk S.M.¹, Chedryk V.I.¹, Kyriienko P.I.¹, <u>Kapran A.Yu</u>.¹, Balakin D.Yu.², Dzwigaj S.³

¹L.V. Pisarzhevskii Institute of Physical Chemistry, NAS of Ukraine, 31 Prosp. Nauky, 03028 Kyiv, Ukraine ²Institute of Physics, NAS of Ukraine, 46 Prosp. Nauky, 03028 Kyiv, Ukraine

³Laboratoire de Réactivité de Surface, Sorbonne Université-CNRS, UMR 7197, 4 place Jussieu, Paris, F-75005, France Corresponding author: Andriy Kapran, E-mail address: ayukapran@ukr.net

Introduction

Oxidative dehydrogenation of alkanes, in particular, propane to propylene assisted with CO₂ (PDH-CO₂: C₃H₈ + CO₂ \leftrightarrow C₃H₆ + CO + H₂O), is considered a promising alternative to the oil-based cracking processes of olefins production [1, 2].

► The formation of propene during PDH-CO₂ on catalysts that exhibit redox properties (Cr-, V-, Fe-containing, etc.) proceeds according to the Mars-Van Krevelen (MvK) mechanism [3]. In the presence of catalysts, which do not undergo redox transitions under the conditions of the target process (in particular Ga, Zn-based), propylene is formed mainly due to direct alkane dehydrogenation (1), the equilibrium of which is shifted to alkene production owing to the consumption of hydrogen in the reverse water-gas shift reaction (2) [4]:

$$C_{3}H_{8} \leftrightarrow C_{3}H_{6} + H_{2}$$
(1)
$$C_{2} + H_{2} \leftrightarrow CO + H_{2}O$$
(2)

▶ Promising catalysts for the PDH-CO₂ process include compositions based on BEA zeolites which are characterized by high thermal, hydrolytic and acid resistance, with a porous system formed by intersecting channels shaped by rings of 12 silicon-oxygen tetrahedra [5].

Experimental

► Preparation of the catalysts Catalyst samples were synthesized based on templated tetraethylammonium BEA zeolite (TEABEA, Si/Al=17). To prepare dealuminated specimens, the starting zeolite was treated with a solution of HNO₃ at a temperature of 353 K [5]. 1 wt % of Zn was introduced from aqueous solutions of zinc nitrate into AlBEA (detemplated starting zeolite, Si/Al=17), AlSiBEA (partially dealuminated, Si/Al=100) and SiBEA (fully dealuminated, Si/Al=1000) specimens.

Characterization Low-temperature (77 K) N₂ ad(de)sorption (Sorptomatic-1990), XRD (Bruker AXS GmbH D8 Advance (series II)), FTIRS-Py (Spectrum One FTIR spectrometer (Perkin Elmer)) and TPD-NH₃(CO₂) techniques were used to determine texture, structure and acid-base characteristics of synthesized Zn-BEA samples.

Catalytic runs were performed in a flow-type reactor at atmospheric pressure with gas chromatography control. Testing the catalytic properties of ZnSi(Al)BEA zeolites was performed under the temperature range of 823–923 K with inter-step regeneration of the catalyst sample carried out by calcination in air at 873 K to remove the coke particles. The target catalytic process PDH-CO₂ was characterized by calculated indices of propane conversion (X_{C3H8}), selectivity (S_{C3H6}) and yield (Y_{C3H6}) with respect to propylene, averaged in time on stream (TOS).

► In this work, the results of studying the influence of preliminary dealumination of BEA zeolite followed by the incorporation of zinc cations in the T-positions of the zeolite framework on the acid-base characteristics of the Zn-BEA samples and their catalytic properties regarding the PDH-CO₂ process, are presented.

Results

As follows from the data presented in Table 1, the complete pre-dealumination provides the formation of mesopores with the largest diameter/surface ~60 nm/80 m²/g and a specific surface area (BET) of 605 m^2/g .

Table 1 Texture characteristics of zeolite Zn-BEA samples

Sample	Microp	ores	Mesopores			S _{BET} ,	Adsorption
	Volume	Diameter,	Voume,	Diameter,	(S _{me} +	m²/g	volume
	V _{mi} , cm³/g	d _{mi} , nm	V _{me} , cm ³ /g	d _{me} , nm	S _{outer}), m²/g		at p/p ₀ , cm³/g
ZnAlBEA	0.19	1.00	0.37	32±5	70	535	0.58
ZnSiAlBEA	0.18	1.01	0.32	50±15	60	505	0.52
ZnSiBEA	0.21	1.05	0.33	~60	80	605	0.56

According to XRD data, dealumination of the starting TEABEA sample with nitric acid followed by the incorporation of zinc cations into the SiBEA framework does not affect the crystallinity of the structure.

The fully dealuminated ZnSiBEA sample is characterized by half the total acidity and basicity compared to ZnAlBEA (Table 2).

Table 2 Acid-base characteristics of zeolite samples Zn-BEA according to TPD-NH₃(CO₂) profiles

Sample		Concentr	ation of acidic sites, rel. un. ¹		Concentration of basic sites, rel. un. ¹			
	Weak (293- 423 K) ²	Medium strength (423- 673 K) ²	Strong (>673 K) ²	Total	Weak (293- 423 K) ²	Medium strength (423-673 K) ²	Total	
ZnAlBEA	0.26	0.36	0.38	1.00	0.78	0.10	0.88	
ZnAlSiBEA	0.14	0.38	0.08	0.60	0.89	0.11	1.00	
ZnSiBEA	0.04	0.31	0.08	0.43	0.22	0.26	0.48	

According to the FTIRS-Py data (Fig. 1), the ZnSiBEA surface is characterized by the presence of Lewis acid sites (LAS – Zn^{2+} cations, probably associated with silanol groups). At the same time, on the surface of ZnAIBEA and ZnAISiBEA, in addition to LAS, there are Brønsted acid sites (BAS) – probably bridging OH groups bound to aluminum cations in the T-positions of the zeolite framework.



Figure 1 Normalized FTIR absorption spectra of pyridine adsorbed at 423 K on ZnAlBEA (a), ZnAlSiBEA (b), and ZnSiBEA (c) after heat treatment at 873 K, followed by evacuation at different temperatures.

At temperatures of 873–923 K, the higher selectivity (86–94%) and yield (16–33%) with respect to propene are achieved for the fully dealuminated ZnSiBEA catalyst sample. For ZnAlSiBEA and ZnAlBEA specimens at temperatures of 873 and 923 K, the conversion of propane decreases quite rapidly with increasing TOS (Table 3).

Table 3 Indices of PDH-CO₂ process on Zn-BEA catalysts

Catalyst	Т, К	Х _{сзн8} , %	S _{сзн6} , %	Ү _{сзн6} , %	TOS, min
	873	36–31	37–42	13	
ΖΠΑΙΒΕΑ	973	64–35	17–27	11–9.5	
7.0.415:05.0	873	45–31	40–33	18–13	20 120
ΖΠΑΙΣΙΔΕΑ	973	58–29	21–33	12–10	30-120
7xC;DEA	873	20	90–94	16–18	
ΖΠΣΙΒΕΑ	973	38–32	86–94	33–30	

¹rel. un. – a ratio of the peak (peaks) area in a certain temperature range to the peak area under the curve corresponding to the sample with the maximum acidity/basicity ²desorption temperatures of NH₃ and CO₂

On the surface of both ZnAIBEA and ZnAISiBEA samples, predominantly weak basic sites are present, while the surface of a completely dealuminated ZnSiBEA specimen is characterized by a higher fraction of basic sites of medium strength – probably oxygen anions/vacancies of [Zn-O-Si] structures or those of ZnO particles, dispersed on the SiBEA surface.

Conclusions

- ▶ Fully dealuminated ZnSiBEA zeolite, prepared by a two-step post-synthesis procedure, is characterized by:
- more developed mesoporous nanostructure and specific surface area BET
- (in comparison with ZnAlBEA and ZnAlSiBEA samples);
- half the total acidity and basicity compared to ZnAIBEA;
- the highest fraction of acidic (Zn²⁺ as LAS) and basic (O²⁻ as Brønsted base and oxygen vacancies) sites of medium strength as well as an absence of BAS.
- ► On the ZnSiBEA catalyst, the achieved selectivity of 94% and yield of 30% propene formation in the target PDH-CO₂ process exceed thereof for ZnAIBEA and ZnAISiBEA specimens.
- ► The effect of full dealumination is attributed foremost to the absence of Brønsted acid sites on the surface of ZnSiBEA, which are capable of intensifying the further course of side processes.

P = 0.1 MPa, RM (vol %): $2.5C_3H_8 - 15CO_2 - He$, GHSV = 6000 h⁻¹

Achievement of higher propene production indices on ZnSiBEA can be explained by the absence of Brønsted acid sites on the ZnSiBEA surface, which are capable (in the case of ZnAlBEA and ZnAlSiBEA) of protonating produced olefin at the π -bond, intensifying thereby the further course of side processes of polymerization, cracking (CH_4, C_2H_4, C_2H_6) were detected among the products) followed by carbonization of catalyst surface [6].

References

1. Atanga M.A., Rezaei F., Jawad A., Fitch M., Rownaghi A.A., Appl Catal B Environ. 220(2018)429.

2. Otroshchenko T., Jiang G., Kondratenko V.A., Rodemerck U., Kondratenko E.V., Chem Soc Rev. 50(2021)473.

- 3. Ansari M.B., Park S.-E., Energy Environ. Sci. 5(2012)9419.
- 4. Michorczyk P., Ogonowski J., Zeńczak K., J Mol Catal A. 349(2011)1.
- 5. Michorczyk P., Zeńczak-Tomera K., Michorczyk B., Węgrzyniak A., Basta M., Millot Y., Valentin L., Dzwigaj S., J CO₂ Util. 36(2020)54.
- 6. Gambo Y., Adamu S., Abdulrasheed A.A., Lucky R.A., Ba-Shammakh M.S., Hossain M.M., Appl Catal A Gen 8(2021) https://doi.org/10.1016/j.apcata.2020.117914