

# Дослідження каталітичної дії VO<sub>x</sub>/SBA-15 у процесі дегідрогенації пропану CO<sub>2</sub>

Каміла Зеньчак, Пьотр Міхорчик,  
Ян Огоновські

Факультет хімічної інженерії та технологій  
Краківський технологічний університет імені Тадеуша  
Костюшка, ПОЛЬЩА, Краків, вул. Варшавська, 24,  
E-mail: zenczak@indy.chemia.pk.edu.pl

У даній роботі було досліджено каталітичну дію мезопористих каталізаторів із V-вмістом у процесі дегідрогенації пропану до пропіну з допомогою CO<sub>2</sub>. Даний гексагональний діоксид кремнію, SBA-15, було використано в якості підготовки високо диспергованих V-навантажених каталізаторів (VO<sub>x</sub>/SBA-15). З допомогою насичення SBA-15 з використанням водних розчинів NH<sub>4</sub>VO<sub>3</sub> було підготовлено зразки з різним вмістом V (1, 3, 5, 10 and 20 wt. %). Каталізатори були категоризовані фізико-хімічними методами (H<sub>2</sub>-TPR, UV-Vis DRS, XRD та низькотемпературною фізичною адсорбцією N<sub>2</sub>) для того щоб порівняти каталітичні властивості зі структурою поверхні. Аналіз каталітичної дії у процесі дегідрогенації пропану CO<sub>2</sub> було проведено у кварцовому реакторі потокового типу з допомогою неперервного методу. Було відкрито, що ванадієвий каталізатор показує відносно високу каталітичну активність та селективність до пропіну. Найвищу активність показав зразок, що містив 5 Вт. % V. при температурі 823 K, конверсія пропану становила 26,7%, при чому селективність пропіну перевищувала 70 %. Крім того, було сімлібно вивчено стабільність більшості активних каталізаторів 5V/SBA-15 при різних температурах (723, 823 та 923 K). Також було вивчено вплив складу газу, який подавався, на конверсію пропану, селективність до пропіну, та стабільність каталізаторів 5V/SBA-15.

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# Investigations of VO<sub>x</sub>/SBA-15 catalytic performance in propane dehydrogenation with CO<sub>2</sub>

Kamila Zeńczak, Piotr Michorczyk,  
Jan Ogonowski

Faculty of Chemical Engineering and Technology  
Tadeusz Kościuszko Cracow University of Technology  
POLAND, Cracow, Warszawska street 24,  
E-mail: zenczak@indy.chemia.pk.edu.pl

*The catalytic activity of V-containing SBA-15 materials were prepared by incipient wetness method and tested in propane dehydrogenation with carbon dioxide. It has been found that vanadium catalysts show relatively high catalytic activity and selectivity to propene. The highest activity exhibits the sample containing 5 wt. % of V. At temperature 823 K, propane conversion and propene selectivity were 26,7%, while 70 %, respectively.*

**Keywords** — Mesoporous materials, SBA-15, vanadium-based catalyst, propene, dehydrogenation with CO<sub>2</sub>

## I. Introduction

Propane dehydrogenation in the presence of carbon dioxide (DH-CO<sub>2</sub>) has been investigated as an alternative method for propene synthesis with simultaneous conversion of CO<sub>2</sub> into CO, which is more valuable feedstock for a number of chemical processes.

In DH-CO<sub>2</sub> the catalytic behavior of various materials like pure oxides (e.g. Ga<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>), mixed oxides (Al-Ga-O, In-Al-O) and oxides of Ga, Zn, Cr, Fe, Mo or V supported on active carbon, alumina, titania, zirconia and silica have been studied [1-4]. The best activity from among mentioned catalytic systems exhibit materials containing chromium or gallium oxides.

The catalytic performance of V-based materials are less explored in the dehydrogenation of propane with CO<sub>2</sub>. Supported vanadium containing catalysts indicate that these materials exhibit moderate activity and quite high selectivity.

It has been recognized that the catalytic performances are strongly controlled by vanadium dispersion on oxide support. The isolated tetrahedral V-species with terminal V=O groups was claimed for high activity and selectivity in many processes including oxidative dehydrogenation of light alkanes and methane to formaldehyde by molecular oxygen [5, 6]. While agglomerated V species and crystalline V<sub>2</sub>O<sub>5</sub> were found to be less active and selective.

Taking to assume above it could be conclude that in order to obtain more active vanadium oxide-based catalyst for the dehydrogenation of propane with and without of CO<sub>2</sub> a high dispersion of the vanadium species at V lodgings as high as possible should be achieve. From those reason, in this work, more attention has been dedicated toward high surface area mesoporous material (SBA-15) as the supports for dispersing of V species.

## II. Experimental

The synthesis of SBA-15 material was carried out under acidic conditions using Pluronic P123 (Aldrich) triblock copolymer as a template and tetraethyl orthosilicate (TEOS, 98% Aldrich) as a source of Si according to preparation procedure described elsewhere [7]. Supported vanadium catalysts on SBA-15 (nV/SBA-15, where: n denotes V content) were prepared by wet impregnation using ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) – a source of vanadium. The vanadium loading was varied in order to achieve 1-20 wt. % of V (1, 3, 5, 10 and 20 wt.%) in the calcined materials

The dehydrogenation of propane (99.6 %, Linde) in the presence of  $\text{CO}_2$  (99.96 %, Linde) was carried out in a flow-type quartz reactor provided with coaxial thermocouple. The amount of catalyst for each test was 200 mg (grain size 0.2-0.3 mm). The gas reaction mixture consisted of  $\text{C}_3\text{H}_8$  and  $\text{CO}_2$  at the molar ratio 1:5. The total flow rate of substrates was  $30 \text{ cm}^3 \cdot \text{min}^{-1}$ . The experiments were performed at atmospheric pressure in the temperature range 823-923 K. The products and unreacted substrates were analysed on-line using a gas chromatograph [7].

## III. Results and discussion

First, the catalytic performance of catalysts with different V content were investigated at 823 K. It was found that conversion of propane and yield of propene rise with the increase of V content up to 5 wt. %, and then decrease slightly over the catalysts with higher V loadings. The negative effect of V loading can be caused by pores blocking and partial destruction of hexagonal rearrangement of SBA-15. These conclusions confirm the low temperature adsorption and XRD results. It was found that the specific surface area and intensity of the XRD lines (characteristic for hexagonal structure) decrease rapidly above 5 wt.% of V that confirms degradation of SBA-15.

Next, the stability of 5V/SBA-15 catalyst during the dehydrogenation of propane with  $\text{CO}_2$  was investigated. The variation in the propane conversion and in the selectivity to propene were investigated with the time-on-stream (Fig.1.). In all temperatures, the conversion of propane decreases gradually with TOS, while the selectivity to propene varies in the reverse direction. The highest  $\text{C}_3\text{H}_8$  conversion is in 923 K. however, the selectivity to the desirable product – propene is the lowest. It is caused by the increase of side reactions (i.e. cracking, hydrocracking) participation. Moreover, increasing temperature increase rate of catalyst deactivation that is caused probably by coke deposition on catalyst surface and partial ( $\text{VO}_4$ ) species reduction.

The 5V/SBA-15 catalyst behavior at different feed gas mixtures with TOS was also investigated. The increase of  $\text{O}_2$  content in the substrates composition gives a possibility to

enlarge  $\text{C}_3\text{H}_8$  conversion. Unfortunately, in the same time, the selectivity to propene rapidly decreases.

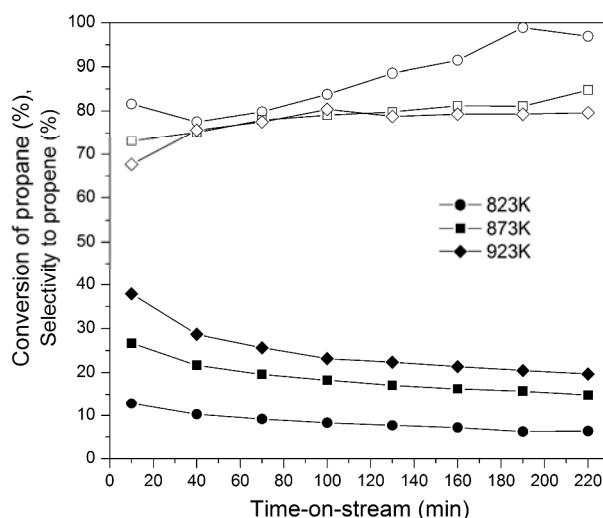


Fig. 1. Variation of propane conversion (solid symbols) and selectivity to propene (empty symbols) with time-on-stream at 823, 873 and 923 K over 5V/SBA-15

## Conclusion

$\text{VO}_x/\text{SBA-15}$  possesses high catalytic activity and selectivity in DH- $\text{CO}_2$ . At 650°C, 34,1% of propane conversion was obtained with 64,3% selectivity to propene.

Oxygen addition causes the increase in propane conversion, however the decrease in selectivity to propene is observed,

During the dehydrogenation of propane with  $\text{CO}_2$ , the catalyst undergoes two types of deactivation processes – reversible and irreversible.

## References

- [1] S. Wang, Z. Zhu, Energy & Fuels 2004, 18, 1126-1139.
- [2] O. Krylov, A. Mamedov, S. Mirzabekova. Ind. Eng. Chem. Res. 34 (1995) 474-482.
- [3] M. Chen, J. Xu, Y.M. Liu, Y. Cao, H.Y. He, J.H. Zhuang, K.N. Fan, Catal. Lett. 124 (2008) 369.
- [4] M. Chen, J. Xu, Y. Cao, H.-Y. He, K.-N. Fan, J.-H. Zhuang, J. Catal., 272 (2010) 101.
- [5] Fornes, C. Lopez, H. Lopez, A. Martinez Appl. Catal. A: General 249 (2003) 345-354.
- [6] Y-M. Liu, Y. Cao, N. Yi, W-L. Feng, W-L Dai, S-R. Yan, H-Y. He, K-N. Fan, J. Catal. 224 (2004) 417-428.
- [7] K. Zeńczak, P. Michorczyk, R. Rachwalik, J. Ogonowski, Czasopismo Techniczne, 1Ch (2010) 353-360.