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VOC COMBUSTION ON CERAMIC FOAM SUPPORTED CATALYST

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Open cellularceramic foam with the Mn-Cu catalyst layered was investigated in the toluene combustion process. Foam morphology was studied using computed microtomography. The results proved satisfactory functioning of the foam supported catalyst, better than the monolith supported one, probably due to more intense mass transfer of the foam-based reactor.

Keywords: catalytic combustion, ceramic foam, solid foam morphology, reaction kinetics

Stała piana ceramiczna o otwartych porach z naniesionym katalizatorem Mn-Cu była badana w procesie dopalania toluenu. Morfologia piany była badana z użyciem mikrotomografii komputerowej. Wyniki wykazały zadowalające funkcjonowania katalizatora naniesionego na pianę, prawdopodobnie wobec intensywniejszego transportu masy.

Słowa kluczowe: dopalanie katalityczne, piana ceramiczna, morfologia pian stałych, kinetyka reakcji

1. INTRODUCTION

Heterogeneous catalytic reactors are commonly applied e.g. in chemical industry and environmental protection. Two essential reactor types include the packed bed [1] and the monolithic reactors [2]. Both designs have well-known positive and negative features. The packed beds display satisfactory heat and mass transfer characteristics between catalyst particles and flowing fluid, but the catalyst efficiency is often week due to strong resistances of internal diffusion within large porous catalyst grains. Moreover, flow resistances are significant. Monolithic reactors, on the other hand, assure low flow resistances, large specific surface area and satisfactory efficiency of

the catalyst deposited as a thin porous layer, thus causing low diffusional resistances. However, week mass transfer rate may limit fast catalytic reactions.

Researchers are still trying to develop alternative reactor structures free of the above mentioned disadvantages. The structures considered are small catalyst grains encapsulated in wire gauzes, wire meshes with the catalyst layers, short monoliths of varying cross section, perforated metallic foils, solid open cellular foams (that should be properly called sponges), and others [3].

From the chemical reaction engineering point of view, the essential features of the heterogeneous catalytic reactor structure are:

- large specific surface area. The contact surface between the catalyst and flowing fluid has to be large enough to enable appropriate mass transfer of reactants. The catalyst has to be deposited as a thin layer at the carrier to give low internal diffusion resistance, thus good catalytic material exploitation,
- large void fraction (or porosity). Generally, structures of high porosity give relatively low flow resistance,
- high intensity of the heat and mass transfer. The mass transfer intensity has to be suitable for the reaction kinetics so as not to lower the process rate. The heat transfer should be appropriate to carry the reaction heat,
- the structure material has to allow for the catalyst layering, thus the structure material should be appropriate,
- the mechanical and thermal resistance should be sufficient.

Amongst other designs, solid foams offer some unique characteristics. Their specific surface is fairly large, while the void fraction is extraordinarily high, reaching even over 90%. Foams are manufactured from various materials including ceramics (cordierite, mullite, alumina, etc.), metals (aluminum, NiCr, nickel, steel, kanthal, etc.), vitreous carbon, glass, and others. The foams show excellent mechanical and thermal properties (light, resistant to temperature and mechanical stretches). Moreover, in comparison to honeycomb monoliths, ceramic foams provide intense radial mixing as well as enhanced mass and heat transfer. Considering the above, solid foams appear to be promising catalyst carriers; the number of researches still grows.

The solid foams were tested in different catalytic reactions like e.g. catalytic oxidation of CO [4-7], Fisher-Tropsch synthesis [8], purification of waste gases and neutralization of automotive emissions [9] or carbon dioxide reforming [10] as well as in processes of partial oxidation of hydrocarbons [11-13], catalytic combustion [14], soot removal reactions [15-17] or selective reduction of NO with ammonia [18, 19]. Many of the foregoing literature reports that the solid foams give very interesting results in comparison to commonly used reactor fillings like packed beds and monoliths: the transfer intensity and the pressure drop decrease in the sequence: particles > foams > honeycombs [9]; thus, foams offer advantageous mass transfer/pressure drop ratio in comparison to other solutions [5, 7]. Moreover, foams ensure better radial mixing and heat transfer than the honeycomb [5]. For fast processes limited by mass transfer,

foams offer conversion similar to honeycombs but accompanied with significant reductions of the reactor size [7].

The aim of this work is to study reactive behavior of ceramic foam covered with active catalyst compared with the standard monolithic reactor. The reaction chosen was the VOC (volatile organic compounds) combustion. The problem of VOC emissions becomes crucial due to development of industrial hydrocarbons processing, especially aromatic ones. Catalytic combustion (or total catalytic oxidation) is perhaps the most successful technology used to control VOC emissions. In this work, VOC was represented by toluene. The possibility of using such catalytic VOC removal in industrial processes requires application of a catalyst displaying low pressure drop due to large flow of pollutants and sufficiently intense mass transfer [20]. The requirements can be met by the use of structured catalyst supports – ceramic monoliths or foams, the former being most suitable where low pressure drop is mandatory. In comparison to honeycomb monoliths, ceramic foams provide intense radial mixing of the reagents and enhanced mass transfer rates. This paper presents the results on the ceramic foam morphology and catalytic activity of the foam supported catalyst in the toluene combustion reaction.

2. EXPERIMENTAL

2.1. THE FOAM STUDIED

The open cell ceramic foam used was Vukopor S 20 PPI. The foam material mainly bases on SiC with alumina admixture and is produced by Lanik s.r.o. and displaying pore density 20 PPI (pores per inch). The morphological parameters of the foam were obtained using microtomography method and are presented in Table 1.

Table 1. Morphological parameters of the foam obtained by microtomography
Tabela 1. Parametry morfologiczne piany uzyskane przy pomocy mikrotomografii

strut diameter, d_s, mm	0.58
pore diameter, d_p, mm	2.3
porosity, ε	0.78
geometric area of foam, S_v, $m^2 \cdot m^{-3}$	1073
PPI[a]/PPI[b]	20/9

Pores per inch: [a] – declared by the manufacturer, [b] – calculated according to pore diameter

2.2. CATALYST PREPARATION AND CATALYTIC TEST CONDITIONS

2.2.1. IMPREGNATION WITH ACTIVE PHASE

45 g of γ-Al_2O_3 (Puralox, Condea) were impregnated with an aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 2H_2O$ (both POCh, Gliwice). The concentration of

manganese and copper salts was calculated to result with 10 wt% coverage (with respect to Al_2O_3Puralox) of Mn/Cu oxides (molar ratio of Mn : Cu was 1:1). Prepared aqueous slurry containing metal salts and Al_2O_3powder was mixed at room temperature until it was to dry, and then additionally dried at 500C for 60 minutes. After impregnation and drying, material was transferred to a quartz container and calcined in a stream of air at 550^oC for 360 minutes.

2.2.2. WASHCOAT PREPARATION

The coating slurry was prepared by adding 5.6 g of boehmite (Disperal S, Sasol), 22.5 g of CuOx-MnOx@Puralox, deionized water and 4.3 ml of acetic acid (POCh, Gliwice, 99.5%). Dry mass content in such prepared mixture was equal to 18%. The slurry was ball-milled at 400 rpm for 48 hours.

2.2.3. CERAMIC FOAM SUPPORTED CATALYST PREPARATION

Commercial, 1.4 cm x 1.4 cm (diameter x height) cylindrical foam pieces (Vukopor S 20 PPI) were used as a catalyst support which was covered by the prepared coating slurry. The foam substrate was immersed for 1 minute into the washcoat containing vessel. Next, the excess of the washcoat was removed by the air stream and the foam elements were left for drying at room temperature for 24 hours. The final step was calcination in air at 550^oC for 360 minutes. The procedure of coating, drying and calcination was repeated 2 times. Similar procedures were also applied for coating the 100 cpsi (channels per square inch) cordierite monolith (1cm x 1cm x 10cm) that was chosen as a reference catalytic structure. The reason was to compare behavior of the same catalyst deposited at alternative carriers to evaluate the carrier impact on the catalytic reaction.

2.2.4. XRD MEASUREMENT

The powder diffractograms were collected and recorded using Panalytical X'PERT PRO MPD diffractometer with CuKα radiation. Investigation and identification of the crystalline phases were performed with PDF-4 data base.

2.2.5. CATALYTIC TESTS

Catalytic tests of toluene combustion were conducted in a quartz tubular reactor equipped with glass saturator, mass flow controllers (Aalborg) and a heating unit (furnace, controller and TC). The catalytic reactor operated under the steady state conditions with toluene concentration equal to 2 $g \cdot m^{-3}$ and GHSV=5000 h^{-1}. Toluene oxidation reaction was investigated by means of GC-FID (Perkin-Elmer Clarus 500, Elite-1 30m column) apparatus. Calibration of the GC signal was performed based on gas mixtures of known composition.

3. RESULTS

3.1. MORPHOLOGICAL PARAMETERS OF THE SOLID FOAMS

Based on the morphological parameters derived from the microtomography, a problem of the PPI definition occurred. The foam studied - Vukopor S 20 PPI - has the pore densities about 20 pores per inch (PPI) according to the manufacturers (Table 1). However, the PPI numbers derived from our own microtomography observations significantly differ from the manufacturer's declaration (cf. Table 1). Perhaps, the definition of the PPI number used by various manufacturers is still not uniform, although the foams have been produced for many years. This may lead to many misunderstandings, like e.g. unexpectedly low (or high) flow resistance and specific surface area.

3.2. CATALYTIC TESTS

3.2.1. CATALYST PREPARATION

The highest stability of a washcoat slurry and, as a result, homogenous distribution of all the slurry components is attained when forces of gravity and Brownian motion are of equal magnitude. The smaller the dimensions of all the solid particles in a slurry are, the lower the input of gravitational component (higher stabilization) is and, consequently, the better the quality of obtained coating. The stability of a slurry can also be improved by electrostatic interaction – it helps preserve Brownian motion when particle dimensions are small and tend to stick. The electrostatic stabilization can be tuned by the value of the *Zeta* potential, i.e. shift from *IEP* (isoelectric point) of the slurry components (for γ-Al_2O_3, IEP = 7.7) by changing the pH value of coating mixture. In a classical work by Agrafiotis et al. [21] the region for highest stability (good dispersion) of the γ-Al_2O_3 based slurry has been achieved for pH lower than 5 or greater than 9. Therefore in our preparation process we decided to stabilize the slurry within one of the highest Zeta potential regions and tune the pH at the level of 4.7 by adding acetic acid. The ball milling process resulted with pseudo-plastic slurry (18% solid content), i.e. viscosity decreased with increasing shear rate.

The apparent viscosity η =35 mPa·s of the obtained washcoat slurry enabled penetration of both the ceramic foam cells and monolith channels. Dynamic Light Scattering (DLS) measurements and particle size analysis performed in aqueous suspensions of the analyzed slurry revealed that washcoat slurry constitute particles predominantly with diameters of 0.1µm and 1 µm (d90 < 5µm) (Fig. 1). Moreover, just two cycles (coating, drying and calcination) resulted with 9-10 wt% of coverage (with respect to the foam support). The SEM and microtomography images of the ceramic foam coated with the layer of active phase are presented in Fig. 2.
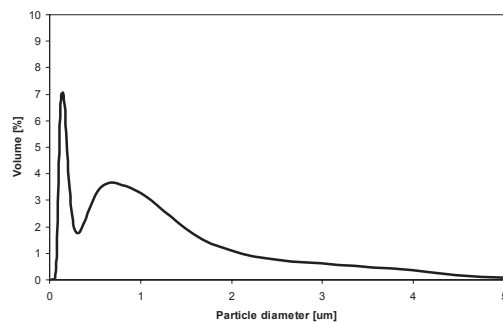
Fig. 1. Particle size distribution in washcoat slurry
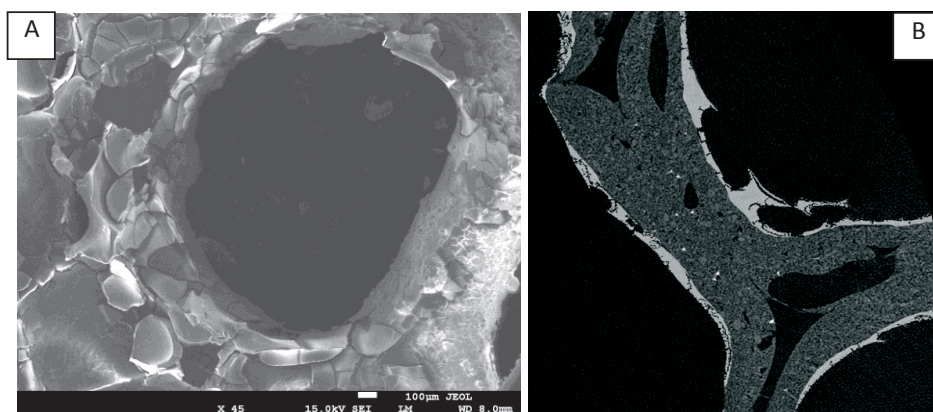Rys. 1. Rozkład średnic cząstek w zawiesinie

Fig. 2. A – SEM and B – microtomography images of ceramic foam coated with catalyst
Rys. 2. Obrazy: A - SEM i B - mikrotomograficzny piany ceramicznej pokrytej katalizatorem
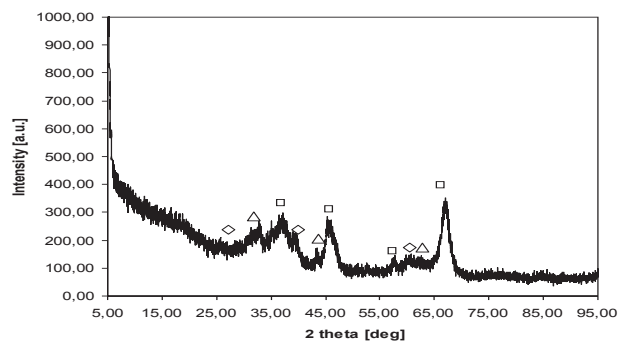

Fig. 3. XRD powder pattern of the calcined wahscoat slurry with essential reflexes: Al_2O_3 (square),
Mn_2O_3 (triangle), CuO (diamond)
Rys. 3. Widmo XRD wyprażonej zawiesiny katalizatora z najważniejszymi refleksami: Al_2O_3 (kwadrat),
Mn_2O_3 (trójkąt), CuO (romb)

The XRD data show the most pronounced presence of Al_2O_3 support phase in the catalyst washcoat prepared (Fig. 3). The analysis of the powder pattern revealed the presence of Mn_2O_3 (cubic, Ia-3) and CuO (monoclinic, C2/c) oxide phases in the calcined washcoat material. The absence of strong X-ray reflexes connected to those crystalline oxides may indicate good dispersion of an active phase in a ceramic support. Presence of the Mn and Cu atoms within the active phase of the catalyst prepared has also been confirmed by SEM-EDX measurement (not shown here) – giving atomic percent ratio of 1 : 1 (Mn:Cu).

3.2.2. CATALYTIC ACTIVITY

Toluene conversion (X_{tol}) was calculated according to the formula typical for differential reactor:

$$X_{tol} = \frac{C_{tol,in} - C_{tol,out}}{C_{tol,out}} \cdot 100\% \tag{1}$$

where $C_{tol,\ in}$ and $C_{tol,\ out}$ are the inlet and outlet concentration of toluene, respectively. Fig. 4 shows the catalytic activity of both foam and monolith supported catalysts in toluene combustion reaction. Differences in toluene conversions for both supported catalyst are clearly visible.
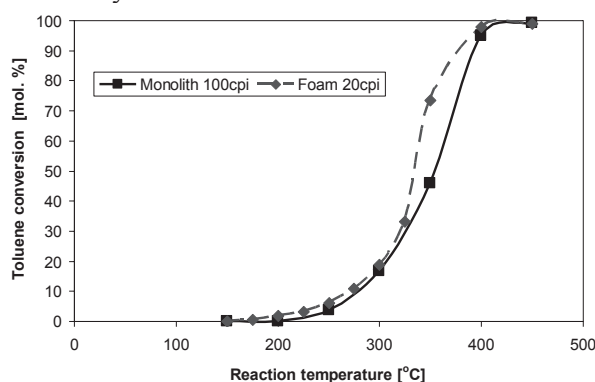

Fig. 4. Catalytic activity of foam and monolith supported catalysts in toluene combustion
Rys. 4. Aktywność katalizatora naniesionego na pianę i monolit w reakcji dopalania toluenu

Up to the reaction temperature of 300^0C both supported catalysts show similar catalytic activity with 18.8% conversion for the foam based catalyst and 16.7% for the monolith based one. However, for reaction temperatures higher than 325^0C the differences are more pronounced. Comparison of both T50 and T 90 values (temperatures recorded for 50% and 90% conversion levels, estimated assuming linear correlation between conversion and reaction temperature in the region analyzed) are given in Table 2.

Table 2. T50 and T90 values for both types of supported catalysts
Tabela 2. Wartości T50 i T90 dla obu badanych katalizatorów

	Foam supported catalyst	Monolith supported catalyst
T50	335.8	346.8
T90	385.4	397.9

It is clearly visible that CuOx-MnOx mixed oxide catalyst supported on ceramic foam exhibits higher catalytic activity, about 11^{0}C lower for both T50 and T90 temperatures, in the oxidation reaction studied. In the catalytic oxidation of toluene, the reaction rate can be based on the simple kinetic model and can be expressed as:

$$r = k \cdot C_{tol}^{n} \cdot C_{O_2}^{m} \qquad (2)$$

In this case (practical application) the concentration (partial pressure) of oxygen is much higher than the concentration of volatile organic compound and can be considered as constant. Thus, the observed rate will depend only on the toluene concentration. For experiments carried out at steady state conditions (i.e. toluene concentration kept at constant level), the apparent activation energies of the investigated reaction are determined from the $ln(r)$ data. The rate of the oxidation reaction was calculated as

$$r = X_{tol} / \left(W_{cat} / F_{tol,in} \right) \qquad (3)$$

where $F_{tol,in}$ is the inlet molar flow rate of toluene and W_{cat} is the weight of the catalyst (weight of the washcoat layer in this case) used in the reactor. Figure 13 presents kinetic data – rate of the reaction (A) and Arrhenius plots for solid foam (B) and monolith (C).

Both, CuOx-MnOx@foam and CuOx-MnOx@monolith catalysts exhibit comparable rates of conversion of toluene within the temperature range 250-325^{0}C (Fig. 5A). At reaction temperature of 350^{0}C, the toluene conversion rate is about 20% over foam supported catalyst than over monolith supported one, indicating its better catalytic performance.

The apparent activation energies obtained from Arrhenius plots (Figs 5B, C) range from 58.4 kJ·mol^{-1} (ceramic foam catalyst) to 69.1 kJ·mol^{-1} (monolith) and are within domain reported in the literature: 37-150 kJ·mol^{-1} [21, 22]. In the latter case, higher activation energy is slightly compensated by a pre-exponential factor ln$A$=21.3 for monolith and ln$A$=19.1 for foam. The higher pre-exponential factor for monolith supported catalyst can be explained when we consider the geometrical area of both supports. Having comparable level of coverage with washcoat and the same type of active sites present in both catalyst samples, higher geometrical surface area of monolith (ca. 1300 m^2·m^{-3}) makes the collision of reagents with the catalyst active sites more frequent than for the foam case (1073 m^2·m^{-3}).
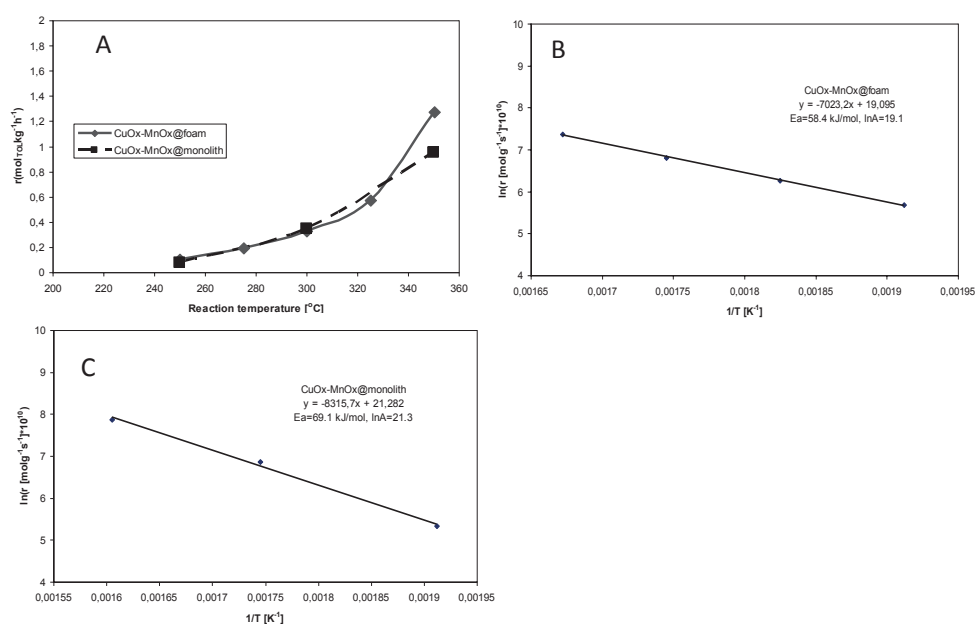
Fig. 5. Kinetics of toluene oxidation: A – reaction rate; B – Arrhenius plots (foam); C – Arrhenius plots (monolith)

Rys. 5. Kinetyka dopalania toluenu: A - szybkość reakcji; B - wykres Arrheniusa (piana); C - wykres Arrheniusa (monolit)

Regarding Arrhenius plot for monolith catalyst (Fig. 5C), the line tends to bend for higher temperatures. Consequently, the activation energy for higher temperatures is slightly smaller than for the lower ones. This can be the result of the mass transfer resistance between catalyst surface and flowing fluid. Such phenomenon doesn't appear for solid foam catalyst (cf. Fig. 5B) showing more intense mass transfer compared with the monolith. Indeed, monoliths display rather moderate transfer intensity, usually lower than the foams; this can reduce the overall process rate especially for fast catalytic reactions at elevated temperatures, as was also discussed in our former study [22].

3. CONCLUSIONS

Open cellularceramic foam with the Mn-Cu oxide reaction catalyst deposited was experimentally tested to evaluate its performance in the VOC combustion reaction. VOC was represented by toluene vapour in an excess of air. The Mn-Cu oxide catalyst was washcoated from slurry solution at the ceramic foam studied. For comparison, the same catalyst, using the same washcoating procedure, has been deposited at the classic 100 cpsi ceramic monolith.

As judged from the microtomography and SEM pictures (Fig. 2), almost all external surface of the foam is covered by the catalyst layer. However, the layer is not perfectly tight, both tomography and SEM show many small cracks. The cracked catalyst layer may significantly limit the foam catalyst activity.

Catalytic tests of toluene combustion proved satisfactory performance of the foam supported catalyst. At higher temperatures, the toluene conversion was elevated by about 20% for solid foam compared to monolith despite lower geometric surface area of the foam (by ca. 25%). The Arrhenius plots presented (Figs. 5B, C) suggest that better conversion for the foam catalyst may be attributed to higher mass transfer intensity of the foam-based reactor.

SYMBOLS - OZNACZENIA

A – pre-exponential term in Arrhenius equation, $m^3 \cdot kg^{-1} \cdot s^{-1}$
stała przedwykładnicza w równ. Arrheniusa

C – reactant concentration, $mol \cdot m^{-3}$
stężenie reagenta

d_p, d_s – dimension of foam's pore, strut respectively, m
średnica odpowiednio poru lub mostka piany

E_a – activation energy, $kJ \cdot mol^{-1}$
energia aktywacji

$F_{tol, in}$ – inlet toluene molar flow rate, $mol \cdot s^{-1}$
wlotowy molowy strumień toluenu

m,n – exponents in eq. (2)
wykładniki w równ. (2)

r – reaction rate, $mol \cdot kg^{-1} \cdot s^{-1}$
szybkość reakcji

T – temperature, K
temperatura

S_v – catalyst specific surface area, $m^2 \cdot m^{-3}$
powierzchnia właściwa katalizatora

W_{cat} – catalyst weight, kg
masa katalizatora

X – conversion
konwersja

ε – porosity
porowatość

SUBSCRIPTS AND SUPERSCRIPTS - INDEKSY DOLNE I GÓRNE

tol   – refers to toluene
dotyczy toluenu

in, out   – denotes reactor inlet or outlet, respectively
dotyczy odpowiednio wlotu lub wylotu reaktora

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DOPALANIE LOTNYCH ZWIĄZKÓW ORGANICZNYCH NA KATALIZATORZE NANIESIONYM NA PIANIE CERAMICZNEJ

Zasadniczymi typami heterogenicznych reaktorów katalitycznych są reaktor ze złożem usypanym [1] i reaktor monolityczny [2]. Pierwszy z nich wykazuje zadowalająco intensywny transport ciepła i masy, lecz znaczne opory przepływu mediów i ograniczoną efektywność katalizatora wskutek oporów dyfuzji wewnętrznej. Monolit posiada niewielkie opory przepływu i znaczną efektywność katalizatora, lecz współczynniki transportu ciepła i masy są niewielkie, niewystarczające dla szybkich reakcji. W poszukiwaniu optymalnych wypełnień katalitycznych rozważane są m.in. piany stałe [3] oferujące znaczną powierzchnię właściwą, dużą porowatość (stąd niewielkie opory przepływu) oraz zadowalającą intensywność procesów transportowych. Celem pracy jest ocena funkcjonowania piany ceramicznej z naniesionym katalizatorem w reakcji dopalania lotnych związków organicznych (LZO), reprezentowanych tu przez toluen, i porównanie katalizatora naniesionego na pianę z takim samym katalizatorem naniesionym na standardowy monolit ceramiczny.

Badaną pianą był Vukopor S 20 PPI (PPI – liczba porów na cal); parametry geometryczne podano w tabeli 1. Materiał piany zawiera głównie SiC oraz Al_2O_3. Dla naniesienia na nią katalizatora γ-Al_2O_3 (Puralox) impregnowano wodnym roztworem $Mn(NO_3)_2 \cdot 4H_2O$ i $Cu(NO_3)_2 \cdot 2H_2O$. Stosunek Mn/Cu wynosił 1:1. Sporządzono zawiesinę Puraloxu (CuOx-MnOx@Puralox) z dodatkiem bohemitu. Zawiesinę naniesiono na pianę Vukopor S 20PPI oraz dla porównania na monolit ceramiczny 100 cpsi (kanałów na cal kwadratowy) przez dwukrotne zanurzenie, suszenie i końcową kalcynację. Przeprowadzono badania dyfraktometryczne (XRD) katalizatora oraz analizę ziarnową zawiesiny, określono też jej lepkość plastyczną. Przygotowane katalizatory, naniesione na monolit i pianę, poddano badaniom w reakcji dopalania toluenu w strumieniu powietrza w reaktorze rurowym.

Podczas prowadzonych badań mikrotomograficznych morfologii badanych pian stwierdzono rozbieżność pomiędzy wartością PPI podaną przez producenta a wynikającą z własnych pomiarów. Jest to zapewne wynik odmiennych definicji liczby PPI, problem często spotykany dla pian stałych.
Analizę ziarnową zawiesiny katalizatora przedstawiono na rys. 1; dominujące średnice ziaren to ok. 0,1mm i 1mm. Lepkość zawiesiny określono na 35 mPas. Pokrycie piany oceniono metodą wagową na 9% - 10% masowych w stosunku do piany stałej. Obrazy piany z naniesionym katalizatorem – wykonane skaningową mikroskopią elektronową (SEM) i mikrotomografią komputerową przedstawiono na rys. 2.

Na rys. 3 przedstawiono widmo XRD katalizatora na pianie Vukopor. Stwierdzono obecność faz katalitycznych Mn_2O_3 i CuO, jednak refleksy są mało intensywne, co może być wynikiem dobrej dyspersji Mn i Cu. Stwierdzono sygnał pochodzący od Al_2O_3 nośnika (piany).

Wyniki konwersji toluenu, obliczonej wzorem (1), dla katalizatora pianowego i monolitu przedstawiono na rys. 4. W tabeli 2 podano wartości temperatur T50 i T90 (temperatur odpowiadających konwersji odpowiednio 50% i 90%). Powyżej temperatury 300°C widoczna jest większa konwersja na pianie, zapewne wynikająca z intensywniejszego transportu masy dla pian, istotnego w zakresie szybszego przebiegu reakcji. Szybkość reakcji odnoszono do masy katalizatora, obliczano ją wzorem (3) i korelowano równaniem (2) z założeniem pierwszego rzędu względem toluenu i zerowego względem tlenu (znaczny nadmiar). Szybkość reakcji w funkcji temperatury oraz wykresy Arrheniusa dla piany i monolitu zestawiono na rys. 5. Energia aktywacji dla piany wyniosła 58,4 $kJ \cdot mol^{-1}$ a dla monolitu 69,1 $kJ \cdot mol^{-1}$. Powierzchnia właściwa piany wynosiła 1073 $m^2 \cdot m^{-3}$ a monolitu 1300 $m^2 \cdot m^{-3}$.

Na podstawie obrazów SEM i tomografii stwierdzono, że naniesiona warstwa katalityczna pokryła prawie całą powierzchnię piany (rys. 2), lecz wykazywała wiele pęknięć. Potwierdza to analiza XRD: piki od tlenków Mn i Cu są stosunkowo słabe, za to wyraźnie widoczny jest tlenek glinu z materiału piany. Badania reakcyjne wykazały zadowalające funkcjonowanie katalizatora naniesionego na pianę: powyżej 300°C zapewniał on konwersję lepszą, niż monolit, prawdopodobnie wobec intensywniejszego transportu masy reagentów do powierzchni katalizatora.