Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://jca.edu.vn

Preparation of Ni-ZrO_2 catalyst via the Pechini sol-gel method for CO_2 methanation

Ba Long Do[1,2,3], Tri Nguyen[1,*], Thi Thuy Van Nguyen[1],
Phung Anh Nguyen[1], Anh Cam Ha[2,3], Cam Loc Luu[1,2,3,*]

[1] *Institute of Advanced Technology, Vietnam Academy of Science and Technology, No.1B, TL29 Str., An Phu Dong ward, Ho Chi Minh City, 701000, Viet Nam*
[2] *Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Str., Ho Chi Minh City, 701000, Viet Nam*
[3] *Vietnam National University Ho Chi Minh City, Ho Chi Minh City, 701000, Viet Nam*
** Email: ntri@iat.vast.vn; camloc.luu@gmail.com*

ARTICLE INFO

Received: 14/06/2026
Accepted: 30/06/2026
Published: 30/06/2026

Keywords:
CO_2 methanation;
Nickel; zirconia;
sol-gel; Pechini

ABSTRACT

This investigation utilized a Pechini (sol-gel) method to prepare a Ni-ZrO_2 catalyst for the CO_2 methanation reaction, which is a crucial reaction that can promote the transition of renewable energy by producing storable methane fuel. By using this reaction to evaluate the catalytic activity of the prepared catalysts, a suitable citric acid molar ratio and calcination temperature in the preparation were chosen. Several techniques, including XRD, SEM, H_2-TPR, CO_2-TPD, and N_2 physisorption, were employed to characterize the sample with the best performance. The catalyst prepared with a citric acid/metallic precursors molar ratio of 1/1, and a calcination temperature of 650 °C was found to induce the best catalytic performance among tested samples with a 50% CO_2 conversion temperature of 323 °C. This performance is attributed to a synergy of the catalyst's physicochemical properties, including a small nickel crystallite size of 28.9 nm, an average surface area of 44.6 m^2/g, a reduction degree of 52.7%, and a basicity of 0.42 mmol/g.

Introduction

Designing efficient catalysts for the low-temperature CO_2 methanation reaction is an intriguing area of research that has garnered the attention of researchers worldwide. Since the reaction is exothermic and favorable at low temperatures, reducing the operating temperature with suitable catalysts can decrease the formation of C or CO side-products produced at higher temperatures. Furthermore, reducing the reaction temperature can also decrease the energy consumption in the thermal catalytic methanation process. Given the expectation that methanation will play an important role in the future energy transition, great emphasis has been placed on investigating catalysts for this reaction at low temperatures.

The use of noble metal-based catalysts can help achieve good catalytic performance at low temperatures in the methanation reaction [1,2]. Nevertheless, the high cost limits the availability of these noble-metal-based catalysts in practical applications. Hence, nickel-based catalysts have become more attractive due to nickel's reasonable cost and availability. On the other hand, this catalyst has lower activity at 300 °C compared to noble-metal-based catalysts, and nickel is prone to sintering [2]. Hence, it is necessary to investigate different

https://doi.org/10.62239/jca.2026.037

methods to enhance the performance of nickel-based catalysts. Engineering catalysts by altering the support materials has been an effective strategy to enhance the catalyst's activity for low-temperature CO_2 methanation. In this regard, ZrO_2 has shown potential in producing effective Ni/ZrO_2 catalysts for the methanation reaction [3,4]. This is attributed to the suitable redox properties and surface reactive sites of ZrO_2 [5]. In addition, it has been found that abundant Ni-ZrO_2 interfaces can effectively promote the catalytic performance in the CO_2 methanation reaction [4]. In this aspect, preparing catalysts as well-mixed oxides via simple routes, such as co-precipitation or the sol-gel method, etc., is a strategy worth considering.

Sol-gel is a powerful method for preparing mixed oxides with desirable properties for various applications. Compared to other methods, sol-gel is convenient to prepare nanomaterials at larger scale [6]. In the sol-gel approaches, Pechini has been noted as a versatile technique for controlling and engineering nanomaterials. The technique uses carboxylic acids, e.g., citric acid, as gelling agents to create metallic complexes. Subsequently, polyols, e.g., ethylene glycol, are used to create scaffolds to maintain the uniform dispersion of metallic precursors at the atomic scale [7]. As the process closely relates to gel formation, the amount of gelling agents was observed to significantly influence the properties of the resulting materials. For example, the citric acid/nickel nitrate molar ratio in a sol-gel method was found to be able to induce different residual carbon content, and thus influence the Ni^0/Ni^{2+} ratio in the Ni/NiO materials [8]. Another factor to consider in the sol-gel method is the calcination temperature. It was stated that the sol-gel or the Pechini method can be processed at low temperatures, since a temperature of below 400 °C is sufficient to oxidize the organic components [7]. However, it was also mentioned that the process parameters in the sol-gel preparation can be changed to be suitable for the production of effective materials in different applications [9]. While lower calcination temperature could induce small nanoparticles, in studies preparing catalysts via sol-gel or Pechini method, the catalysts were calcined at a high temperature range, usually above 400 °C [10,11]. In CO_2 methanation, it was found that a higher calcination temperature in the Pechini method was also required to prepare an active $LaNiO_3$ catalyst [12]. Hence, calcination temperature in the sol-gel method should be investigated to develop an active catalyst in the CO_2 methanation reaction.

The catalysts' properties can be engineered via changing the catalysts' preparation method. In the investigation of the catalytic CO_2 methanation, Ni/ZrO_2 catalysts have been prepared by various methods, including impregnation [13], combustion [3], plasma-assisted impregnation [4], or co-precipitation [14]. However, as far as our knowledge goes, the utilization of sol-gel method to prepared Ni/ZrO_2 catalyst in form of mixed Ni-Zr oxide still has valuable research gaps. Hence, it can be concluded that if a Ni-ZrO_2 catalyst is prepared by the Pechini method for the methanation reaction, the amount of citric acid and the calcination temperature are important factors warranting investigation. On this basis, this work employed the Pechini method to produce a Ni-ZrO_2 catalyst derived from a NiO-ZrO_2 mixed oxide with fine dispersion of Ni and ZrO_2 within the structure. The catalytic activity measured in the CO_2 methanation reaction would be used to rationalize the amount of citric acid and calcination temperature used in preparing the catalyst material. Subsequently, various techniques would be used to study the characteristics of the best-performing catalyst within the scope of this study.

Experimental

Chemical

Citric acid monohydrate (Xilong, >99.5%), $ZrOCl_2{\cdot}8H_2O$ (Thermo Scientific, >98%), $Ni(NO_3)_2{\cdot}6H_2O$ (Thermo Scientific, >99%), ethylene glycol (Xilong, >99%).

Methods

Catalyst preparation

A mixture containing 5 mmol of $ZrOCl_2$, 5 mmol of nickel nitrate hexahydrate $Ni(NO_3)_2$, and citric acid (CA) was dissolved in 30 mL of deionized water. The amount of CA was prepared to achieve molar ratios of CA/(Ni+Zr) = x, where x = 1, 2, and 3. The solution was magnetically stirred, then 1.70 mL of ethylene glycol was added. The resulting mixture was stirred for 30 min, then heated to 80 °C to gradually evaporate the water. After the mixture had formed a gel-like state, the beaker was placed in an oven and dried overnight at 60 °C. The obtained precursor was subsequently calcined through sequential heating stages at 150 °C for 15 min, 350 °C for 15 min, and finally at *y* °C for 1 h (y = 450, 550, 650, and 750). The sample would be denoted as NiZr(x)(C-y), where x is the CA/(Ni+Zr) molar ratio, and y is the calcination temperature used to prepare the sample. For characterization, the as-reduced sample would be denoted as NiZr(x)(C-y)(R).

Catalytic activity measurement

The prepared catalysts were studied in the methanation reaction under atmospheric pressure with a volumetric

https://doi.org/10.62239/jca.2026.037

WHSV of 30,000 mL/(g.h). In a typical catalytic activity measurement, 0.150 g of calcined catalyst was prepared in a fixed-bed quartz reactor with an inner diameter of 9 mm. The catalyst was activated at 500 °C for 2 h with a H_2 flow of 3 L/h, prior to the activity measurement. After the reduction step, a 4.5 L/h flow rate of an inlet gas containing a $CO_2/H_2/N_2$ molar ratio of 6/24/70 was introduced into the reactor. The catalytic activity was measured in a temperature range of 200–400 °C, with an interval of 50 °C. The CO_2 conversion and CH_4 selectivity were measured at each temperature by monitoring the flow rates of CO_2, CH_4, and CO in the outlet, and CO_2 in the feed gas. Besides, the T50 temperature, at which 50% CO_2 conversion was obtained, was also used to compare the catalytic activity among samples

Characterization

The physicochemical properties of the catalyst were investigated using several techniques, including XRD (Bruker D2 PHASER X-ray Diffractometer), SEM (JEOL 7401 FE-SEM), N_2 physisorption (Nova 2200e instrument), temperature programmed CO_2 desorption (CO_2-TPD), and temperature programmed H_2 reduction (H_2-TPR). The as-reduced catalyst was prepared by a reduction process at 500 °C for 2 h under a H_2 atmosphere. After the reduction, the catalyst would be slowly cooled down to room temperature under a N_2 atmosphere and then transferred to a capped bottle for storage. This reduced catalyst would be used for the characterization of the as-reduced sample.

Results and discussion

The catalytic activity of the samples prepared with different amounts of CA and calcination temperatures is presented in Fig. 1. Some studies have suggested that a higher CA/metallic precursor molar ratio can induce a more porous texture, thereby improving catalytic performance [15]. However, the result in this work exhibits a contrasting trend. At a calcination temperature of 450 °C, a lower amount of CA used in the preparation procedure induced higher catalytic activity of Ni-ZrO_2 catalysts in the CO_2 methanation reaction. Based on the results in Fig. 1a, a CA/(Ni+Zr) molar ratio of 1/1 was used to prepare Ni-ZrO_2 catalysts by the Pechini method to further investigate the influence of calcination temperature. The result in Fig. 1b exhibits that the catalytic activity of Ni-ZrO_2 catalysts gradually increased when the calcination temperature rose from 450 °C to 650 °C. Higher calcination temperature of 750 °C deteriorated the performance of the catalyst in the reaction. Among test samples, NiZr(1)(C-650) outperformed other catalysts with the lowest T50 value of 323 °C. It should be noted that this T50 value is also significantly higher than that of a Ni/ZrO_2 prepared by a two-step precipitation method in our previous study [14]. This shows an advantage of preparing the catalyst in the form of mixed oxides via the Pechini method. With the recorded catalytic performance, NiZr(1)(C-650) was chosen to be the sample with suitable surveyed factors for exploration of physicochemical properties.

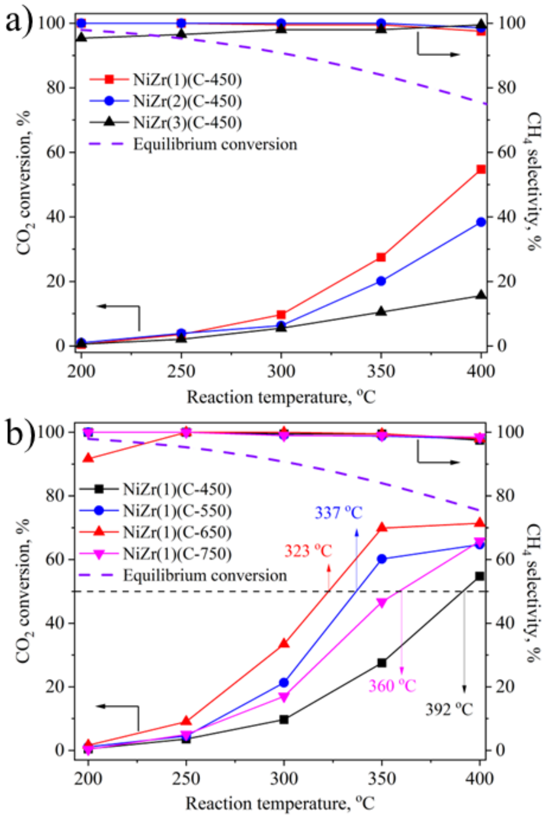

Fig. 1: Influence of CA/metallic precursor molar ratio (a) and calcination temperature (b) on the catalytic activity of NiZr(x)(C-y) catalysts in CO_2 methanation

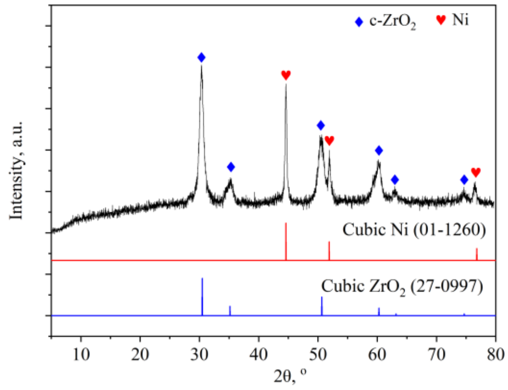

Fig. 2: XRD pattern of the as-reduced NiZr(1)(C-650)(R) sample

https://doi.org/10.62239/jca.2026.037

Fig. 2 illustrates the XRD pattern of the as-reduced NiZr(1)(C-650)(R) sample. Diffraction peaks corresponding to the cubic ZrO_2 (JCPDS No. 27-0997) and cubic Ni (JCPDS 01-1260) are observed in Fig. 2. The formation of the cubic ZrO_2 phase was induced by the partial incorporation of Ni^{2+} into the ZrO_2 crystal structure [14]. The monoclinic ZrO_2 crystallite phase would be more stable compared to the tetragonal phase or cubic phase [16]. Tetragonal or cubic ZrO_2 phase was stated to be metastable, whose formation would require high annealing temperatures above 1000 °C [16]. However, through preparation methods mixing well both Ni and Zr precursors, e.g., co-precipitation, NiO and ZrO_2 can be finely dispersed in the structure, promoting the incorporation of Ni^{2+} into the ZrO_2 crystal structure and leading to the stable existence of cubic ZrO_2 [14,17]. This is similar to studies using of another element, such as yttrium, to stabilize the cubic or tetragonal ZrO_2 phase [18]. On the other hand, this phenomenon was not observed on Ni/ZrO_2 catalysts prepared via the conventional impregnation method, which is suggested not to induce good interaction of Ni and ZrO_2 as compared to co-precipitation or sol-gel methods [13]. Hence, this behavior can be considered an indicator of fine dispersion of Ni and ZrO_2 in the catalyst structure. The crystallite sizes of Ni and ZrO_2 calculated by the Debye Scherrer equation are 28.9 nm and 11.3 nm, respectively. A smaller ZrO_2 crystallite size could induce a higher density of Ni-ZrO_2 interface, improving the partial reduction of ZrO_2 and increasing the basicity [4].

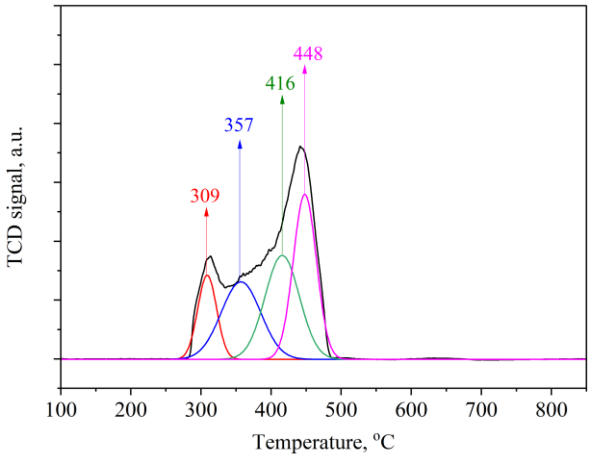

Fig. 3: H_2-TPR profile of the as-calcined NiZr(1)(C-650) sample

The reducibility of the calcined NiZr(1)(C-650) sample is investigated with the H_2-TPR profile illustrated in Fig. 3. The TPR profile can be deconvoluted into smaller reduction peaks, with temperatures of 309 °C, 357 °C, 416 °C, and 448 °C. These reduction peaks would correspond to the exposed NiO on the surface and NiO species with different metal-support interactions with ZrO_2 [19]. It was worth noting that the reduction peak at 357 °C might indicate the presence of NiO species with good dispersion in the NiO-ZrO_2 structure [20]. On the other hand, the reduction peaks at temperatures higher than 400 °C could indicate the presence of bulk NiO. This might relate to the large Ni crystallite size of 28.9 nm, determined through the XRD pattern. Nevertheless, it should also be noted that the reduction temperature range of the NiZr(1)(C-650) is lower than that of several Ni/ZrO_2-based catalysts [3,4]. This phenomenon might relate to the small sizes of NiO and ZrO_2, induced by the Pechini method with a suitable CA amount and calcination temperature. The H_2 consumption amount corresponding to the TPR profile in Fig. 3 is 2.66 mmol/g, corresponding to a reduction degree of 52.7% respectively. The surface morphology of the as-reduced NiZr(1)(C-650)(R) sample is presented in Fig. 4, showing clumps of small particles.

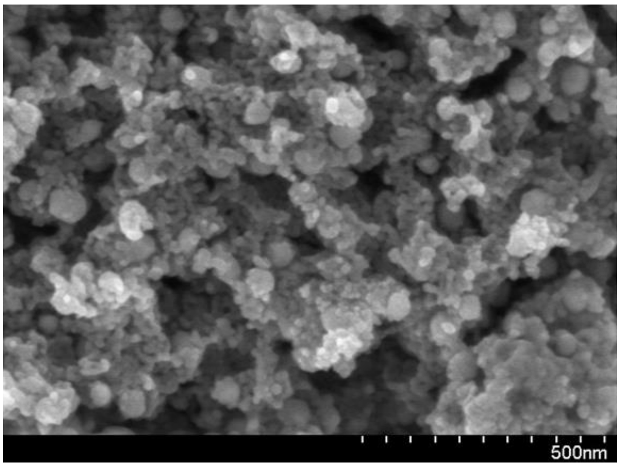

Fig. 4: SEM image of the as-reduced NiZr(1)(C-650)(R) sample

The agglomeration of the particles as observed in the SEM image (Fig. 4) produced the porous structure of the catalyst. The textural properties of the as-reduced NiZr(1)(C-650)(R) sample is studied by the N_2 physisorption with the results shown in Fig. 5. The shape of the N_2 isotherm (Fig. 5a) indicates that there are various porous structures in the catalyst structure. This behavior is in line with the BJH pore diameter distribution exhibited in Fig. 5b. The N_2 physisorption revealed that the NiZr(1)(C-650)(R) sample possesses a S_{BET} value of 44.6 m^2/g, a pore diameter of 9.21 nm, and a pore volume of 0.124 cm^3/g.

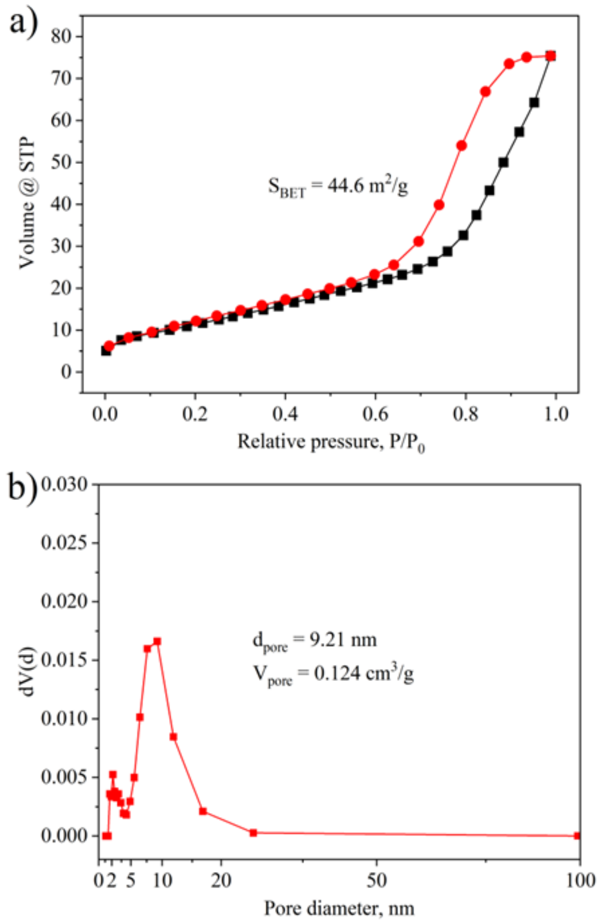

Fig. 5: N_2 physisorption analysis results on the as-reduced NiZr(1)(C-650)(R) sample

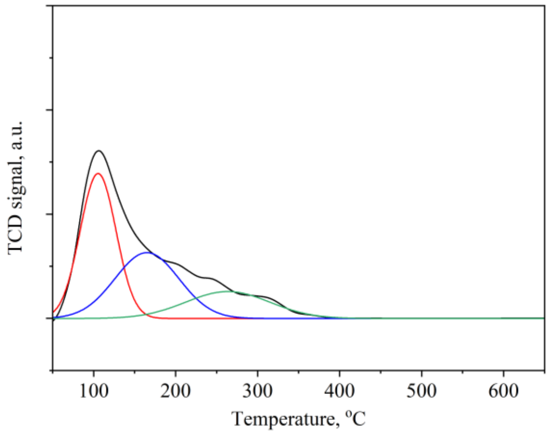

Fig. 6: CO_2-TPD profile of the as-reduced NiZr(1)(C-650)(R) sample

The interaction of the catalyst's surface with CO_2 or the basicity can be assessed through the CO_2-TPD technique. The CO_2-TPD profile of the as-reduced NiZr(1)(C-650)(R) sample (Fig. 6) shows that the catalyst's surface is composed of weak and medium basic sites, corresponding to the CO_2 desorption peak temperature below 200 °C and in the range of 200–400 °C, respectively. Especially, the presence of weak and medium basic sites could provide suitable interaction with the CO_2 molecules in the reaction environment, promoting the CO_2 adsorption and activation [21]. Consequently, this feature would lead to the enhancement of catalytic activity in the CO_2 methanation reaction. The total CO_2 desorption amount determined from the TPD profile is 0.42 mmol/g, corresponding to the density of both weak and medium basic sites.

Conclusion

This study has found a suitable CA amount and calcination temperature used for the preparation of the Ni-ZrO_2 catalyst via a Pechini method for the CO_2 methanation reaction. The sample prepared with suitable factors exhibited suitable characteristics for enhanced performance, including small ZrO_2 crystallite size, weak and medium basic sites, and reducibility of small NiO species. The synergy of these characteristics produced a Ni-ZrO_2 catalyst with good performance in the CO_2 methanation reaction, corresponding to a T50 value of 323 °C. This investigation might act as a foundation for future engineering works, such as the incorporation of promoters or other materials with high surface area, so that the performance of the Ni-ZrO_2 catalyst prepared by the Pechini method could be enhanced in the methanation reaction.

Acknowledgments

This research is funded by the National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2025.159.

References

1. J. Xu, X. Su, H. Duan, B. Hou, Q. Lin, X. Liu, X. Pan, G. Pei, H. Geng, Y. Huang, J. Catal., 333(1) (2016) 227-236. https://doi.org/10.1016/j.jcat.2015.10.025
2. C. Wang, H. Sun, X. Liu, X. Jin, Y. Feng, H. Shi, D. Wang, Y. Zhang, Y. Wang, Z. Yan, Fuel, 345(115) (2023) 128238. https://doi.org/10.1016/j.fuel.2023.128238
3. K. Zhao, W. Wang, Z. Li, J. CO2 Util., 16(3) (2016) 236-244. https://doi.org/10.1016/j.jcou.2016.07.010
4. X. Jia, X. Zhang, N. Rui, X. Hu, C.-J. Liu, Appl. Catal. B Environ., 244(1) (2019) 159-169. https://doi.org/10.1016/j.apcatb.2018.11.024

5. L. Li, J. Yang, X. Wu, P. Da Costa, C. Hu, Appl. Catal. A Gen., 690(1) (2025) 120643. https://doi.org/10.1016/j.apcata.2025.120643
6. D. Bokov, A.T. Jalil, S. Chupradit, W. Suksatan, M.J. Ansari, I.H. Shewael, G.H. Valiev, E. Kianfar, Adv. Mater. Sci. Eng., 2021(1) (2021) 5102014. https://doi.org/10.1155/2021/5102014
7. Z. Yao, U. Sasaki, X. Zhang, L. Liu, K. Takada, Chem. Mater., 27(24) (2015) 8475-8480. https://doi.org/10.1021/acs.chem-mater.5c01685
8. K. Mahendraprabhu, P. Elumalai, J. Sol-Gel Sci. Technol., 73(2) (2015) 428-438. https://doi.org/10.1007/s10971-014-3554-7
9. M.A. Vargas-Urbano, L. Marín, W.M. Castillo, L.A. Rodríguez, C. Magén, M. Manotas-Albor, J.E. Diosa, K. Gross, Materials, 15(15) (2022) 5266. https://doi.org/10.3390/ma15155266
10. E. Demiröz, S.F. Kurtoğlu-Öztulum, K.E. Ercan, B. Erdivan, B. Güleryüz, Y. Kocak, U.Ü. Ünal, E. Ozensoy, A. Uzun, Ind. Eng. Chem. Res., 54(44) (2015) 16053-16061. https://doi.org/10.1021/acs.iecr.5c01750
11. K. Rida, M.A. Peña, E. Sastre, A. Martinez-Arias, J. Rare Earths, 30(3) (2012) 210-215. https://doi.org/10.1016/S1002-0721(12)60025-8
12. M. Barreau, D. Salusso, J. Zhang, M. Haevecker, D. Teschner, A. Efimenko, F. Bournel, J.-J. Gallet, E. Borfecchia, K. Sobczak, J. Mater. Chem. A, 12(13) (2024) 7605-7615. https://doi.org/10.1039/D3TA07391B
13. H.P. Phan, T. Nguyen, B.L. Do, N.K. Duc, C.A. Ha, C.L. Luu, Arab. J. Sci. Eng., 49(6) (2024) 8291-8302. https://doi.org/10.1007/s13369-024-08772-6
14. B.L. Do, C.L. Luu, T. Nguyen, Mater. Sci. Eng. B, 329(1) (2026) 119427. https://doi.org/10.1016/j.mseb.2026.119427
15. C. Wu, P.T. Williams, Appl. Catal. B Environ., 102(1-2) (2011) 251-259. https://doi.org/10.1016/j.apcatb.2010.12.005
16. M. Mosavari, A. Khajehhaghverdi, R.M. Aghdam, Inorg. Chem. Commun., 157(1) (2023) 111293. https://doi.org/10.1016/j.inoche.2023.111293
17. M. Yamasaki, H. Habazaki, T. Yoshida, E. Akiyama, A. Kawashima, K. Asami, K. Hashimoto, M. Komori, K. Shimamura, Appl. Catal. A Gen., 163(1-2) (1997) 187-197. https://doi.org/10.1016/S0926-860X(97)00142-7
18. Z. Huang, W. Han, Z. Feng, J. Qi, D. Wu, N. Wei, Z. Tang, Y. Zhang, J. Duan, T. Lu, J. Sol-Gel Sci. Technol., 90(2) (2019) 359-371. https://doi.org/10.1007/s10971-019-04930-y
19. M. Zhang, X. Zhou, J. Yang, T. Yang, Z. Liu, Y. Han, Fuel, 349(115) (2023) 128705. https://doi.org/10.1016/j.fuel.2023.128238
20. H. Lu, X. Yang, G. Gao, J. Wang, C. Han, X. Liang, C. Li, Y. Li, W. Zhang, X. Chen, Fuel, 183(1) (2016) 335-343. https://doi.org/10.1016/j.fuel.2016.06.084
21. C. Lv, L. Xu, M. Chen, Y. Cui, X. Wen, C.-E. Wu, B. Yang, F. Wang, Z. Miao, X. Hu, Fuel, 278(118) (2020) 118333. https://doi.org/10.1016/j.fuel.2020.118333