

Підготовка, категоризація та каталітична дія мезопористих оксидів галію та алюмінію

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Мезопористі оксиди галію та алюмінію (з атомним відношенням Ga/Al = 4/1 і 1/4) були синтезовані шляхом розщеплення з використанням вуглеводного матеріалу CMK-3, який є негативною копією SBA-15 у якості зразка та Ga(NO₃)₃/Al(NO₃)₃ у якості прототипів оксидної фази. Підготовлені матеріали пройшли категоризацію з допомогою рентгенодифракції (XRD) та N₂-фізичної сорбції. Було відкрито, що з використанням простого просочування за вологоємністю можна отримати мезопористі оксиди високого порядку Ga- та Ga-Al з гексагональною структурою SBA-15. Матеріали, окислені при 823 K показали 192-322 м²·г⁻¹ питомої поверхні за методом BET і середній розмір пор 6.4 -6.7 нм. Дана питома поверхня та загальний розмір пор зменшилися, при чому середній діаметр пор дещо збільшився при більшому атомному відношенні Ga/Al. Було вивчено каталітичну дію всіх підготованих матеріалів у процесі дегідронізації пропану до пропіну при наявності CO₂. Найвищий еквівалент пропану було отримано з блоку Ga₂O₃, хоча дуже швидко цей оксид втратив активність, і після 2 годин робочого часу він став майже неактивним. Мезопористі оксиди Ga- та Ga-Al (Ga/Al=4/1) мали дещо нижчу початкову активність, але в процесі деактивувалися значно повільніше. Селективність пропіну, отриманого з мезопористих оксидів була також вищою, ніж за наявності Ga₂O₃ отриманого через термальне розщеплення нітрату галію.

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Preparation, characterization and catalytic performance of mesoporous Ga and Ga-Al oxides

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Mesoporous Ga- and Ga-Al oxides were prepared by nanoreplication technique using CMK-3 matrix as a rigid template. The catalytic performance of mesoporous Ga₂O₃ and mixed Ga₂O₃-Al₂O₃ materials were investigated in the dehydrogenation of propane to propene with CO₂ at 823 K.

Keywords – nanoreplication, gallium-alumina oxides, dehydrogenation, propene, carbon dioxide.

I. Introduction

Nano-replication is recently explored as a new method for the synthesis of mesoporous metal oxides. Various mesoporous oxides, e.g. MgO, ZnO or TiO₂, were successfully prepared using siliceous or carbon mesoporous sieves as hard templates [1-3].

In this work, mesoporous Ga- and mixed Ga-Al oxides with different atomic ratio of Ga/Al were prepared by nano-replication. We used CMK-3 carbon sieve, that is a negative replica of SBA-15, as a rigid template. The obtained materials were characterized with various physicochemical methods and tested in the dehydrogenation of propane to propene in the presence of CO₂.

II. Experimental

SBA-15 was synthesized under acidic conditions using Pluronic P123 triblock copolymer and tetraethyl orthosilicate (TEOS) as a silica source according to the procedure described elsewhere [4]. CMK-3 carbon was prepared according to the literature procedure [3].

Pure Ga₂O₃ and Al-Ga mixed mesoporous oxides with the atomic ratios of Ga/Al equal to 1/4 and 4/1 were obtained by the modified nano-replication method reported in the literature [1].

The catalytic properties of mesoporous oxides were studied in the dehydrogenation of propane in the presence of CO₂. This process was carried out in a flow-type quartz reactor packed with 200 mg of catalyst (grain size 0.2-0.3 mm) at 823 K and under atmospheric pressure. The gas reaction mixture, flowing at a constant rate of 30 cm³·min⁻¹, consisted of C₃H₈:CO₂:He=1:5:9 (vol.%).

III. Results and discussion

Fig.1 displays the XRD patterns of pure SBA-15, CMK-3 as well as Ga and Ga-Al oxides obtaining by nano-replication. In the 2θ=1-6° range the pattern of SBA-15 shows three diffraction lines indexed to the

(100), (110) and (200) reflections characteristic for 2D hexagonal phase (space group $p6mm$). The negative replica of SBA-15 (CMK-3) exhibits one intensive (100) reflection slightly shifted towards a higher 2 theta value. Similarly, all the materials prepared by nanoreplication have one intensive reflection indexed to (100) and in some cases additional two weak (110) and (200) reflections. The appearance of these lines clearly indicates that mesoporous structure of SBA-15 materials can be replicated by using CMK-3 as a templating agent. By using the simple incipient wetness impregnation highly ordered mesoporous Ga- and Ga-Al oxides with a hexagonal structure of SBA-15 can be obtained.

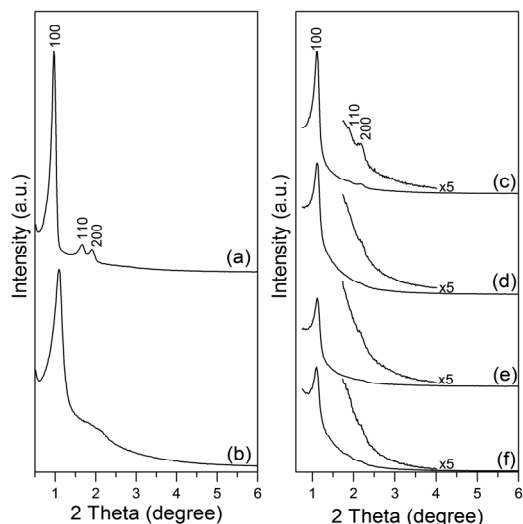


Fig. 1. XRD patterns of SBA-15 (a), CMK-3 (b), Ga-Al-O (Ga/Al = 1/4) (c), Ga-Al-O (Ga/Al = 4/1) (d), as well as used (e) and fresh (f) mesoporous Ga_2O_3 -m

The catalytic performance of the mesoporous oxides was studied in the dehydrogenation of propane to propene in the presence of CO_2 at 823 K. The variation of propane conversion and propene selectivity over all the tested materials is reported in Fig.2. For comparison the results collected for the reference Ga_2O_3 -t sample, obtained by the thermal decomposition of gallium nitrate, are shown as well.

The highest conversion of propane was achieved over Ga_2O_3 -t, however this sample rapidly lost activity and after 2 h of reaction it was almost inactive. As we reported in our previous paper such fast deactivation of Ga_2O_3 -t is due to coke deposition [5]. The mesoporous Ga_2O_3 -m and Ga-Al-O(Ga/Al=4/1) materials exhibit slightly lower initial activity than Ga_2O_3 -t, but both materials are deactivated much slower during the dehydrogenation process. This is probably due to the mesoporous structure that is less sensitive on pore blocking with coke.

Over all the investigated mesoporous materials obtained by nano-replication the primary product, propene, was produced at very high selectivity ($> 93\%$). It is also clear that the selectivity to propene drops slightly with the decrease in the Ga/Al atomic ratio of the mesoporous material. Moreover, propene was produced over Ga_2O_3 -t with much lower selectivity (85-92%) than in the presence of mesoporous Ga_2O_3 -m (95-97%). Such

difference in propene selectivity is probably caused by various phase compositions of both Ga_2O_3 materials. Zheng et al. [6] found that in the dehydrogenation of propane with CO_2 α - and β - Ga_2O_3 are more selective phases than δ - and γ - Ga_2O_3 . Moreover, the presence of large size mesopores can promote the dehydrogenation reaction due to the rapid diffusion of the products from pores preventing successive reactions decreasing the process selectivity.

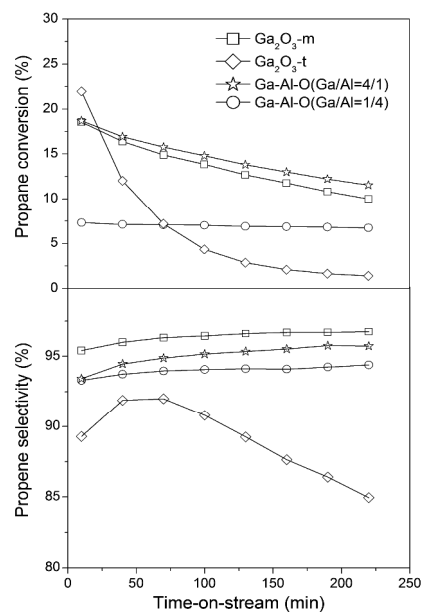


Fig. 2. Catalytic performance of mesoporous oxides in the dehydrogenation of propane to propene in the presence of CO_2 at 823 K

Conclusion

The nano-replication technique was successfully applied for the synthesis of mesoporous Ga and Ga-Al mixed oxide materials. All the materials showed high specific surface areas (192 - $322\text{ m}^2\cdot\text{g}^{-1}$) and pore architecture similar to that of SBA-15 (hexagonal structure). Pure mesoporous Ga_2O_3 -m and mixed Ga-Al-O(Al/Ga=1:4) exhibited a high activity and selectivity to propene. These materials appeared to be much higher stable in comparison with Ga_2O_3 obtained by thermal decomposition of gallium nitrate.

References

- [1] J. Roggenbuck, T. Waitz, M. Tiemann, 113 (2008) 575.
- [2] M. Kang, D. Kim, S. Yi, J. Han, J. Yie, J. Kim, Catal. Today, 93-95 (2004) 695-699.
- [3] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 122 (2000) 10712.
- [4] K. Zeńczak, P. Michorczyk, R. Rachwalik, J. Ogonowski, Czasopismo Techniczne, 1Ch (2010) 353.
- [5] P. Michorczyk, J. Ogonowski, Appl. Catal. A: General 251 (2003) 425.
- [6] B. Zheng, W. Hua, Y. Yue, Z. Gao, J. Catal. 232 (2005) 143.