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COMPARATIVE STUDY OF CONTINUOUS-FLOW MICROREACTORS BASED ON SILICA MONOLITHS MODIFIED WITH LEWIS ACID CENTRES

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Silica multichannel monoliths modified with zirconia, titania and alumina have been used as reactive cores of microreactors and studied in chemoselective reduction (MPV) of cyclohexanon/benzaldehyde with 2-butanol as a hydrogen donor. The attachment of metal oxides to the silica surface was confirmed by FT–IR spectroscopy, and dispersion of metal oxides was studied by UV–Vis spectroscopy. the catalytic activity of the lewis acid centres in both chemical processes decreased in the order zirconia > alumina > titania. This activity is in good agreement with dispersion and coordination of metal species. good stability of zirconia-grafted reactors was confirmed. high porosity of the monoliths and the presence of large meandering flow-through channels with a diameter of ca. 30 μm facilitate fluid transport and very effective mixing in the microreactors. The whole synthesis process is perfectly in line with trends of modern flow chemistry.

Keywords: flow chemistry, silica monolith, Lewis acid centres, MPV reduction

1. INTRODUCTION

Chemoselective reduction of carbonyl compounds, known as Meerwein-Ponndorf-Verley (MPV) reaction is traditionally carried out in batch reactors. The MPV reaction is a highly selective reduction reaction involving hydrogen transfer mechanism between aldehydes and ketones and secondary alcohols (Zhang et al., 2012). In contrast to a reaction carried out in the presence of hydrogen or strong reducing agents – metal hydrides, the selective reduction of the carbonyl group, allows to obtain α, β – unsaturated alcohols, preserving all other functional groups in the molecule (Corma et al., 2003). This feature is of particular relevance for the pharmaceutical and chemical industries. The MPV reaction with Lewis-type acid centres coordinates only the carbonyl group while multiple bonds remain intact. The reduction is performed under mild process conditions and usually in the presence of metal alkoxides (Campbell et al., 2001). However, these highly selective homogeneous catalysts should be used in stoichiometric amounts relative to the substrates and difficulties in separation are a major limitation of their use. Replacement of the homogeneous catalysts with the heterogeneous ones eliminates some of the drawbacks. The main problem is, however, the sensitivity of immobilized metal alkoxides to moisture, causing a decrease in their activity or deactivation (Quignard et al., 1999).

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Recently, we have proposed a continuous-flow monolithic silica microreactor activated with anchored isolated zirconium species for the MPV reduction to overcome these drawbacks (Koreniuk et al., 2015). This approach fits modern flow chemistry carried out using microreactor technology, which is critical for both significant process intensification and miniaturization. It simplifies chemical processes, facilitates automation and better control, catalyst regeneration and storage, and allows to separate the catalyst from contact with adverse external factors. The microreactors provide a much larger surface area, compared to the conventional reactors, and a very high surface-to-volume ratio enhances heat exchange and mixing (Reschetilowski, 2013). In recent years process miniaturization has opened new paths towards creating a new generation of catalysts.

In this work we compare the performance of continuous-flow microreactors, with Lewis acid centres originated from zirconia, alumina and titania incorporated into silica multichannel monolith, in the MPV reduction of cyclohexanon/benzaldehyde with 2-butanol as a hydrogen donor. Structural, physicochemical properties and catalytic activity of the reactors were studied.

2. EXPERIMENTAL

Silica monolithic supports were synthesized according to a procedure described previously by Koreniuk (Koreniuk et al., 2015). Briefly, a mixture of PEG35000, nitric acid, water, CTAB and TEOS, after complete dissolution, was placed in polypropylene tubes at 40°C, and allowed to gel. The solid rods were treated in 1 M ammonia solution at 90°C, for 9 hours, washed with water and dried. Subsequently, organic template was removed by calcination in air at 550°C.

The monoliths were dried at 200°C prior to functionalization. Modification was carried out using the grafting method. Metal precursors: zirconium isopropoxide, aluminium di-s-butoxide ethylacetoacetate, titanium diisopropoxide bis (acetyloacetonate) were dissolved in ethanol. Monolithic carriers were soaked with the precursor solution to obtain metal/Si mass ratio equal to 0.05, treated one day at 70°C, washed with excess of anhydrous ethanol, evaporated and finally calcined at 500°C.

The structural properties of monoliths were determined using various instrumental techniques. The parameters of mesostructure were calculated from low-temperature nitrogen adsorption isotherms (Micromeritics, ASAP2010). Scanning electron microscopy (Hitachi HD-2300A) and mercury porosimetry (Quantachrome, PoreMaster 60) was applied to determine the size of the flow-through channels created by the system of connected macropores. Studies involving spectroscopic methods FT-IR (Nicolet6700, DRIFT collector) and UV-Vis (Varian, Carry 100, Labsphere DRA-CA-3300) provided information about the physicochemical properties of metal attached to the silica carrier.

Catalytic activity was investigated in Meerwein-Ponndorf-Verley reaction. 2-butanol was used as a hydrogen donor in the reduction of cyclohexanone and benzaldehyde. Experiments were conducted in 4 cm-long microreactors, at 95°C, with the flow rate of 0.03 ml/min. Carbonyl compound/alcohol molar ratio was fixed at 1 : 52. Process efficiency was monitored by gas chromatography (HP-5 column, FID detector). Pressure drop for a reagent mixture was measured using differential pressure controller (UNIC5000, Ex-Calibra).

3. RESULTS AND DISCUSSION

Silica monolithic materials with a trimodal pore structure were prepared using sol-gel process coupled with phase separation and pore templating. Polyethylene glycol undergoes phase separation, induced by polymerization of TEOS and gives rise to a continuous structure of larger flow-through channels, whereas cationic surfactant used as the template promotes formation of mesopores.

SEM image depicted in Fig. 1 clearly demonstrates a bi-continuous structure consisting of connected macropores and silica skeleton. The highly open and tortuous structure facilitated fluid transport and effective mixing. The average macropore diameter, determined by the mercury porosimetry, was found to be 30 μm and the total pore volume in the monoliths was about 4.2 cm^3/g (Fig. 2).

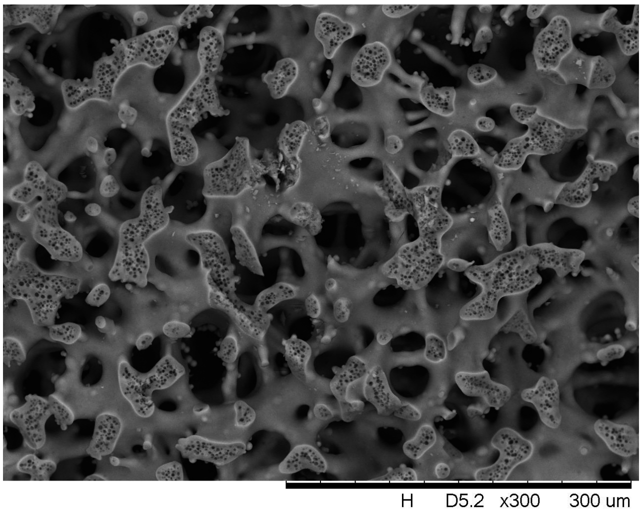

Fig. 1. SEM image of silica monolith

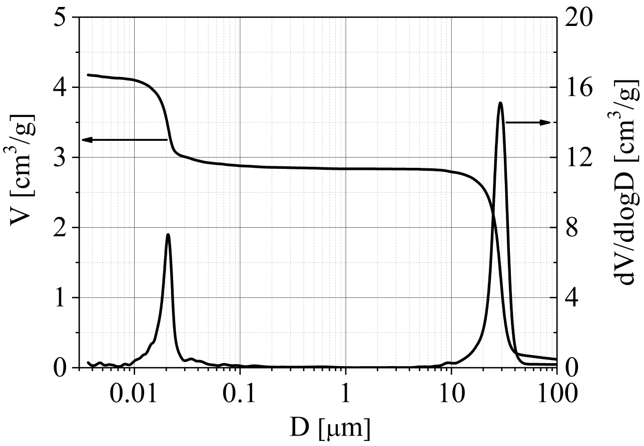

Fig. 2. Pore volume vs. pore diameter for silica monolith obtained by mercury porosimetry; cumulative and differential curves

Texture parameters of the samples were estimated from low temperature adsorption/desorption data. The isotherm, depicted in Fig. 3 is typical for mesoporous materials. Cylindrical pores of average diameters of about 2.5 and 23 nm, generated in silica skeleton, allowed to obtain a large surface area above 300 m^2/g and mesopore volume about 1 cm^3/g, that is still larger than in the most typical mesoporous materials.

FT-IR DRIFT spectra of all the modified samples in the wavelength range of 3700–3800 and 850–1400 cm^{-1} are shown in Fig. 4. The spectrum of untreated silica was used as a reference. A decrease in intensity or complete disappearance of the band at a wavelength of 960 cm^{-1}, assigned to stretching vibration of Si–OH bond, confirm the metal incorporation into the support surface. It is also corroborated by reduced band intensity at 3750 cm^{-1}, which corresponds to isolated hydroxyls on the silica. The broad band in the range of 1000–1250 cm^{-1}, characteristic for the Si–O–Si asymmetric stretching is clearly

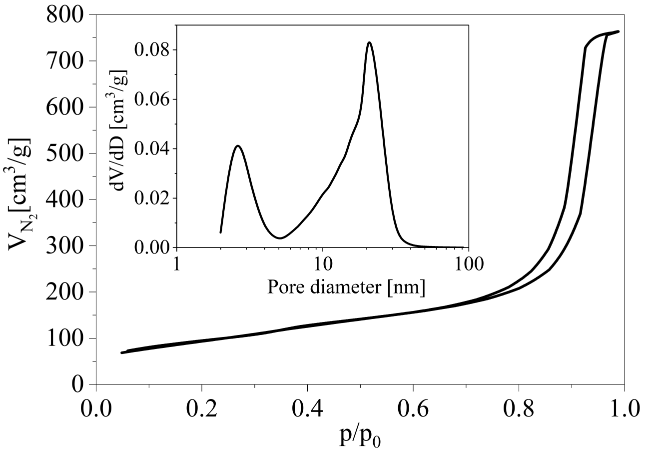

Fig. 3. Adsorption/desorption isotherm and mesopore size distribution of silica monolith

weakened. All these changes are due to Si–O–metal bond formation (Telalovic et al., 2011). Differences between spectra of Al, Zr and Ti functionalized samples can be attributed to a better dispersion of Al and Zr on silica surface. Titanium species tend to agglomerate owing to highly reactive nature of the metal precursor. This finding correlates well with the results obtained from UV–Vis analysis.

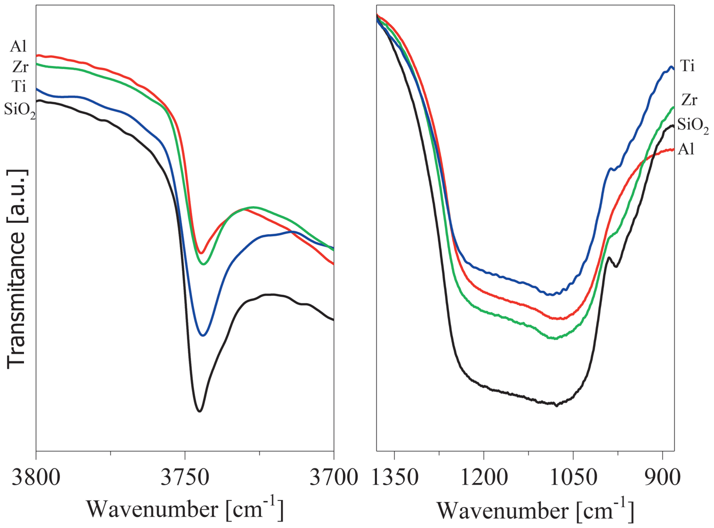

Fig. 4. DRIFT FT-IR spectra of Al-, Ti-, Zr-modified samples

Figure 5 shows UV–Vis spectra for the metal-modified samples. In zirconia-grafted monolith maximum absorption occurred at 209 nm, and it is attributed to ligand-to-metal charge transfer from oxygen ions to isolated zirconium cations in a tetrahedral coordination. The broad absorption band in the range of 200 to 350 nm recorded for titania-modified monolith confirmed the presence of oligomeric titanium-oxygen species in this material. Aluminium deposited onto silica surface was in tetrahedral coordination, confirmed by absorption band with maximum at 265 nm, which corroborates the good distribution of this metal onto silica surface (Beck et al., 2001; Morey et al., 1999).

The results of catalytic studies of the microreactors activated with Al, Zr, Ti oxides are summarized in Fig. 6. As can be seen the highest conversion in the MPV reduction of both cyclohexanone and benzaldehyde was achieved in ZrO_2 functionalized microreactors, and it was almost three times higher than that obtained in the alumina functionalized reactor. It can be related to a slightly better distribution of zirconium species onto the silica surface, and also propensity of the alumina to generate Brønsted acid sides, which do not catalyse the MPV reaction (Shylesh et al., 2009).

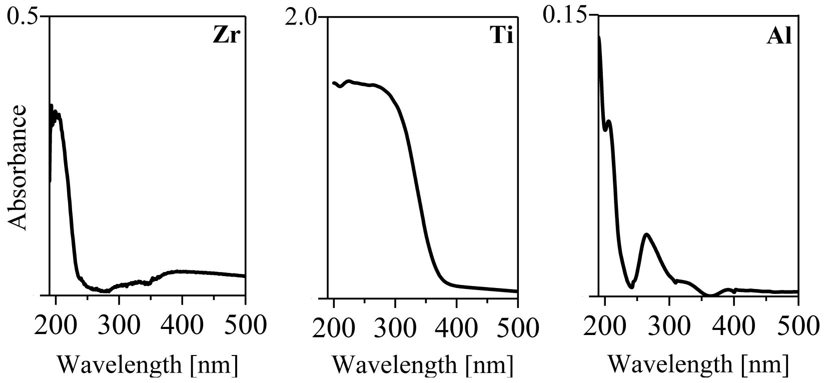

Fig. 5. UV-Vis spectra of Zr-, Ti-, Al-modified samples

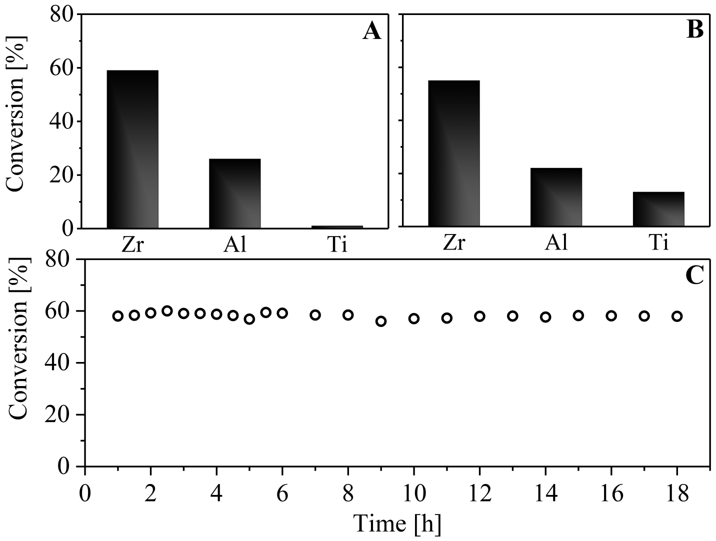

Fig. 6. Average conversion of cyclohexanone (A) and benzaldehyde (B) in zirconia-, alumina- and titania-doped microreactors under the same reaction conditions. Stability of Zr-modified microreactor (C)

Titanium-doped monolith was inactive in cyclohexanone reduction or showed poor activity in case of aldehyde. The formation of large TiO_2 agglomerates, which was confirmed by FT-IR and UV-Vis analysis, has detrimental impact on catalytic properties of the proposed microreactor. Moreover, according to Quignard (Quignard et al., 1999), Ti complexes appeared to be difficult for use in the processes involving alcohols, since they tend to leach into a protic solvent.

The zirconia-modified microreactor was tested in a 18 h-long experiment. It demonstrated good catalytic stability, and only small fluctuations of conversion, ca. 2%, were observed. Pressure drop was monitored during the process, and it was equal to 0.066 kPa/cm for the applied flow rate.

4. CONCLUSIONS

The performed studies clearly show that:

- silica multichannel monoliths can be easily functionalized with Lewis acid centres and used as a core of catalytic microreactors in the Meerwein–Ponndorf–Verley chemoselective reduction of ketones and aldehydes,

- the activity of acid centres in MPV reaction strongly depended on the nature of incorporated metals and their coordination and dispersion,
- the microreactors modified with zirconia, showed better activity in chemoselective reduction of cyclohexanone/benzaldehyde with 2-butanol as a hydrogen donor than those functionalized with alumina and titania,
- good stability of the zirconia-grafted reactors was confirmed.

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REFERENCES

Beck C., Mallat T., Burgi T., Baiker A., 2001. Nature of active sites in sol-gel TiO_2–SiO_2 epoxidation catalysts. *J. Catal.*, 204, 428–439. DOI: 10.1006/jcat.2001.3407.

Campbell E.J., Zhou H.Y., Nguyen S.T., 2001. Catalytic Meerwein-Pondorf-Verley reduction by simple aluminum complexes. *Org. Lett.*, 3, 2391–2393. DOI: 10.1021/ol0162116.

Corma A., Domine M.E., Valencia S., 2003. Water-resistant solid lewis acid catalysts: Meerwein-Ponndorf-Verley and Oppenauer reactions catalyzed by tin-beta zeolite. *J. Catal.*, 215, 294–304. DOI: 10.1016/S0021-9517(03)00014-9.

Koreniuk A., Maresz K., Mrowiec-Białoń J., 2015. Supported zirconium-based continuous-flow microreactor for effective Meerwein-Ponndorf-Verley reduction of cyclohexanone. *Catal. Commun.*, 64, 48–51. DOI: 10.1016/j.catcom.2015.01.021.

Koreniuk A., Maresz K., Odrozek K., Jarzębski A. B., Mrowiec-Białoń J., 2015. Highly effective continuous-flow monolithic silica microreactors for acid catalyzed processes. *Appl. Catal. A*, 489, 203–208. DOI: 10.1016/j.apcata.2014.10.047.

Morey M.S., Stucky G.D., Schwarz S., Froba M., 1999. Isomorphic substitution and postsynthesis incorporation of zirconium into MCM-48 mesoporous silica. *J. Phys. Chem. B*, 103, 2037–2041. DOI: 10.1021/jp980844t.

Quignard F., Graziani O., Choplin A., 1999. Group 4 alkyl complexes as precursors of silica anchored molecular catalysts for the reduction of ketones by hydrogen transfer. *Appl. Catal. A.*, 182, 29–40. DOI: 10.1016/S0926-860X(98)00421-9.

Reschetilowski W., 2013. *Principles of microprocess technology. Microreactors in preparative chemistry: Practical aspects in bioprocessing, nanotechnology, catalysis and more*. Wiley-VCH Verlag GmbH & Co. KGaA. 1–12.

Shylesh S., Kapoor M.P., Juneja L.R., Samuel P.P., Srilakshmi Ch., Singh A. P., 2009. Catalytic Meerwein-Ponndorf-Verley reductions over mesoporous silica supports: Rational design of hydrophobic mesoporous silica for enhanced stability of aluminum doped mesoporous catalysts. *J. Mol. Catal. A: Chem.*, 301, 118–126. DOI: 10.1016/j.molcata.2008.11.020.

Telalovic S., Ramanathan A., Ng J. F., Maheswari R., Kwakernaak C., Soulimani F., Hanefeld U., 2011. On the synergistic catalytic properties of bimetallic mesoporous materials containing aluminum and zirconium: The prins cyclisation of citronellal. *Chem. Eur. J.*, 17, 2077–2088. DOI: 10.1002/chem.201002909.

Zhang, Bo, Tang, Minhui, Yuan, Jian, Wu, Lei., 2012. Support effect in Meerwein-Ponndorf-Verley reduction of benzaldehyde over supported zirconia catalysts. *Chin. J. Catal.*, 33, 914–922. DOI: 10.1016/S1872-2067(11)60370-7.

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