Electrospun TiO_2/WO_3 Nanofibers as a catalyst for combustion gases

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Introduction

Electrospinning is modern preparation method of fibers with very small diameter (lower than 500 nm). The technology is based upon creation of Taylor cones and subsequent flow of material from free liquid surface under high applied voltage. The electrospinning from thin film of a polymer solution has the advantage of larger production compare to needle-type electrospinning and could be used in industrial scale.

The electrospinning is known quite well for polymer fine fibers production but attention is also focused on inorganic fibers preparation as for example metal oxides (TiO_2, ZrO_2, Al_2O_3) [1]. Attractive application of inorganic fibers in nanoscale could be combustion catalysis where titanium, vanadium and tungsten oxides are well known for high temperature catalysis [2, 3, 4]. The initial results of TiO_2/WO_3 fiber preparation and their catalytic activity are shown in this paper.

Experimental

Fiber preparation was done it two steps: electrospinning and calcination. Fresh fiber material was prepared using electrospinning method on equipment NS LAB 500 (Elmarco s.r.o.) from polymer solution containing Ti and W precursor. The electrospinning was done under 60 – 70 kV form cylinder rotating electrode. Amount of W precursor was chosen as 3, 5, 10 and 20 % w/w of WO_3 in final fiber material (TiO_2/WO_3). Pure TiO_2 and WO_3 fibers were prepared for comparison with fibers of mixed oxides. Fresh fibers were calcinated at 400, 600 and 800 ℃. Final material was characterized using SEM (diameter, length), EDX, XRD and surface area measurement (BET).

Basic catalytic activity of fiber material was measured on defined pollutant (chlorbenzene). 1 μg of pollutant was added on catalytic fiber material (30 mg) and heated for 10 minutes at temperature of combustion gas production 220℃. Catalytic activity was evaluated in terms of elimination of pollutant by GC/MS at 220 ℃.

Results and Discussion

Shape of final fiber material is dependent mainly on calcination temperature and tungsten oxide amount. Examples of fiber material are shown on figure 1 to figure 6 where the lowest (3 w/w %) and the highest (20 w/w %) used amount of WO_3 in TiO_2 fibers calcinated at 400, 600 and 800 ℃ are seen. The main difference has been found on material of TiO_2 + 3 % w/w WO_3 calcinated at 800 ℃ (fig. 3) with fiber diameter 120 nm and material of TiO_2 + 20 % w/w WO_3 calcinated at 400 ℃ (fig. 4) with fiber diameter 430 nm. Generally the thicker fibers were prepared the higher amount of WO_3 or lower calcination temperature was used. Length of all prepared fibers has been measured in the range of tents to hundreds of micrometers.

Amount of tungsten oxide in fiber material was confirmed by EDX analysis. The accuracy of WO_3 amount in TiO_2 fibers was in 0.5 % range. Similar results were measured by XRD analysis. The analysis also showed phase composition of all samples. Fibers calcinated at 400 and 600 ℃ are monophasic (TiO_2 in anatase phase) but the phase change from anatase to rutile of TiO_2 has been observed in samples calcinated at 800 ℃. The amount of rutile phase depends on tungsten oxide quantity (rutile phase amount decreases from 60 to 6 % for 3 to 20 w/w % WO_3 respectively).

Surface area turned out to be one of the key factors for a good catalytic activity. The surface area as a dependence on temperature is shown on figure 7. Lower calcination temperature provided a higher surface area of final fiber material (up to 100 m^2/g). Higher

temperature used for calcination probably led to close surface pores on the nanofibers and support crystal growth of metal oxides with a result of surface area decreasing to a few tens of m^2/g. The similar surface area is observed only for pure TiO_2 material calcinated at 400 and 600 ℃ in anatase phase. Higher calcination temperature of TiO_2 caused change of phase composition to rutile and also lower surface area of fiber material.

Figure 8 shows catalytic activity of prepared fiber material evaluated as pollutant elimination at temperature 220 ℃. The calcination temperature influenced catalytic activity in the same way as surface area measurement but no clear dependence of catalytic activity and surface area has been observed. All samples calcinated at 400 ℃ provide higher catalytic activity than the rest of tested material with the best catalytic activity of 20 w/w % WO_3 in TiO_2 fiber sample.

Conclusion

Catalytic activity of fiber material containing TiO_2 and WO_3 is dependent on the calcination temperature and related surface area of fiber material (the lower calcination temperature the higher surface area and catalytic activity). The best catalytic activity is achieved for TiO_2/WO_3 nanofibers with highest amount of WO_3 calcinated at the lowest temperature (TiO_2 with 20 % w/w WO_3 calcinated at 400 ℃).

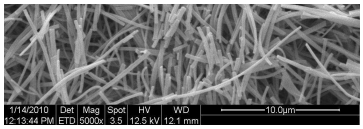

Fig. 1. TiO_2 with 3 % w/w WO_3 calcinated at 400 ℃.

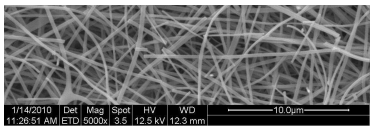

Fig. 2. TiO_2 with 3 % w/w WO_3 calcinated at 600 ℃.

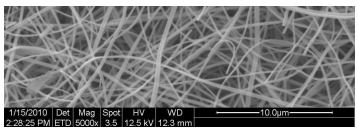

Fig. 3. TiO_2 with 3 % w/w WO_3 calcinated at 800 ℃.

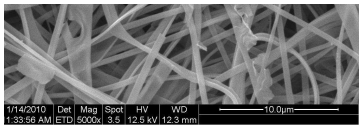

Fig. 4. TiO_2 with 20 % w/w WO_3 calcinated at 400 ℃.

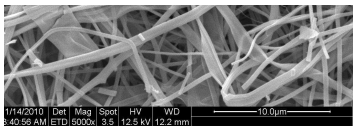

Fig. 5. TiO_2 with 20 % w/w WO_3 calcinated at 600 ℃.

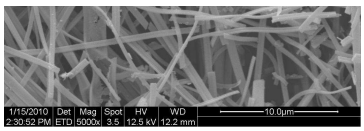

Fig. 6. TiO_2 with 20 % w/w WO_3 calcinated at 800 ℃.

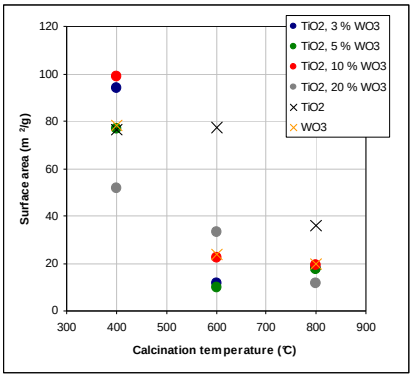

Fig. 7. Surface area of TiO_2 with 3, 5, 10 and 20 % w/w WO_3 and 100 % TiO_2 and WO_3.

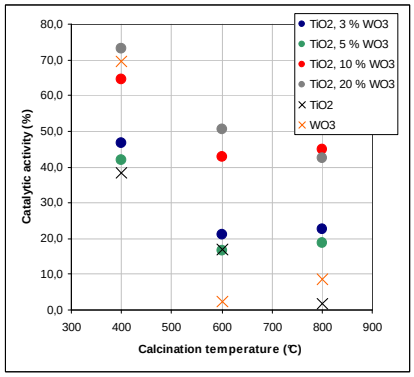

Fig. 8. Catalytic activity of TiO_2 with 3, 5, 10 and 20 % w/w WO_3 and 100 % TiO_2 and WO_3.

References

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[2] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, Effect of vanadia and tungsten loadings on the physical and chemical characteristics of V2O5-WO3/TiO2 catalysts, J. Mol. Cat. A: Chemical 208 (2004) 257–265.

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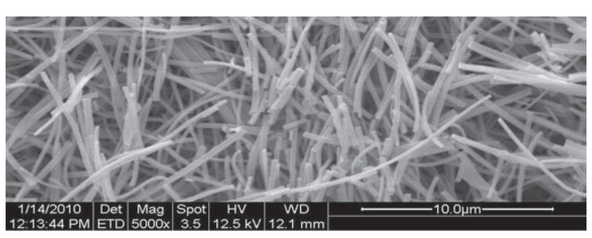
Electrospinning is modern preparation method of fibers with small diameter (hundreds of nanometers) collected in non-woven material. It gives also possibility to prepare inorganic fibers where electrospun material is calcinated at high temperature (usually more than 500 °C) to achieve desired crystallinity. The electrospinning was used for preparation of TiO_2 fibers containing WO_3. Both oxides are well known as important catalyst which could be used for high temperature catalysis.

EXPERIMENTAL

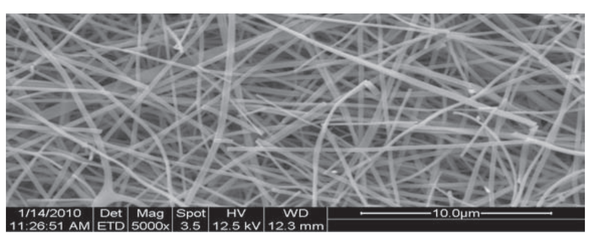
- polymeric solution containing Ti and W precursor used for electrospun material preparation (electrospinning on Nanospider LAB 500)
- calcination of electrospun material at 400, 600, 800 °C
- catalytic activity evaluated as elimination of model pollutant (chlorbenzene) by GC/MS analysis at 220 °C

RESULTS

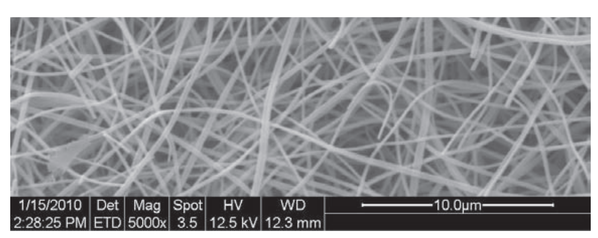
- **fibers:** diameter minimum: 120 nm of TiO_2 with 3 % w/w WO_3 calcinated at 800 °C
  diameter maximum: 430 nm of TiO_2 with 20 % w/w WO_3 calcinated at 400 °C
  length: tens to hundreds micrometers
- final amount of WO_3 confirmed by EDX and XRD analysis



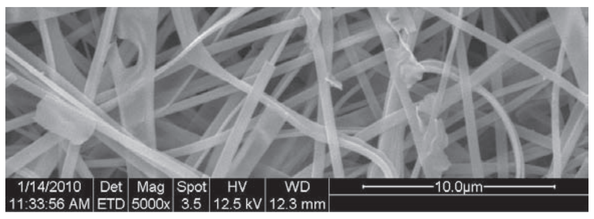
TiO_2 with 3 % w/w WO_3 calcinated at 400 °C



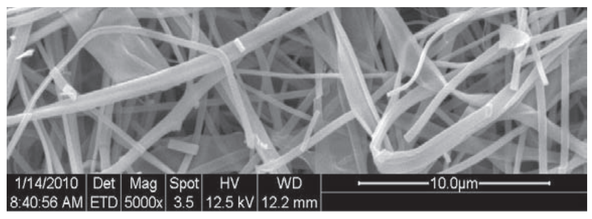
TiO_2 with 3 % w/w WO_3 calcinated at 600 °C



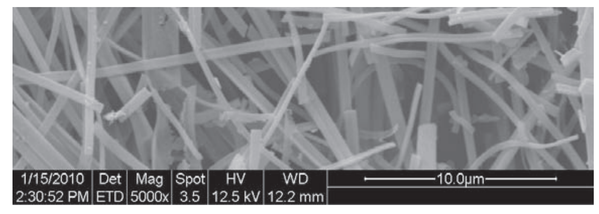
TiO_2 with 3 % w/w WO_3 calcinated at 800 °C



TiO_2 with 20 % w/w WO_3 calcinated at 400 °C

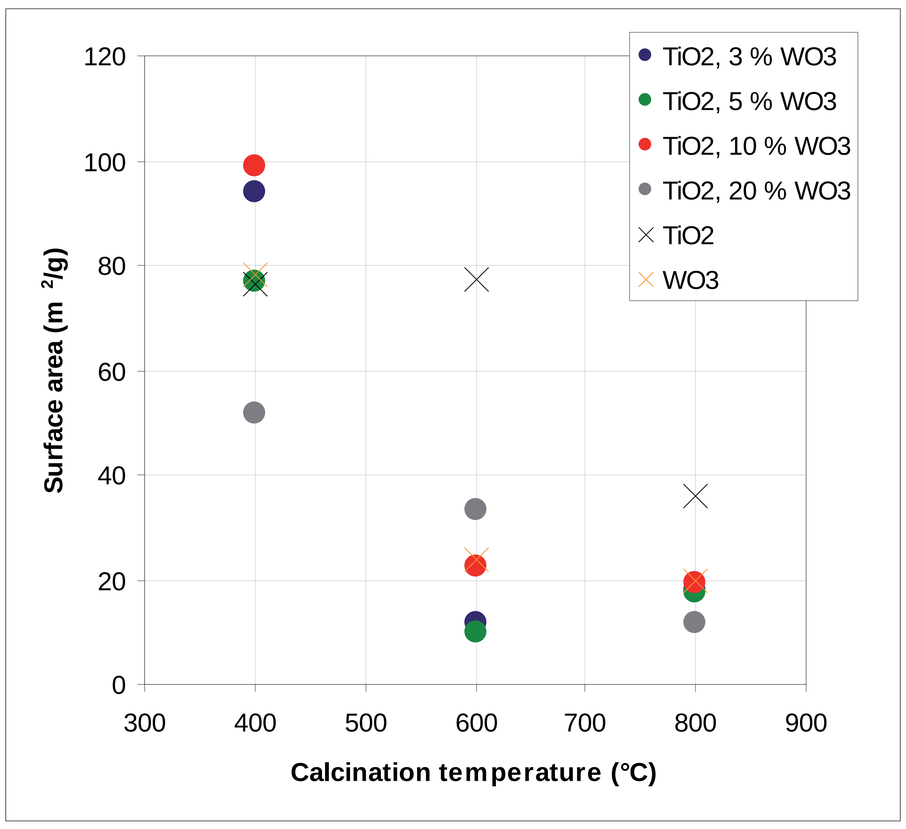


TiO_2 with 20 % w/w WO_3 calcinated at 600 °C



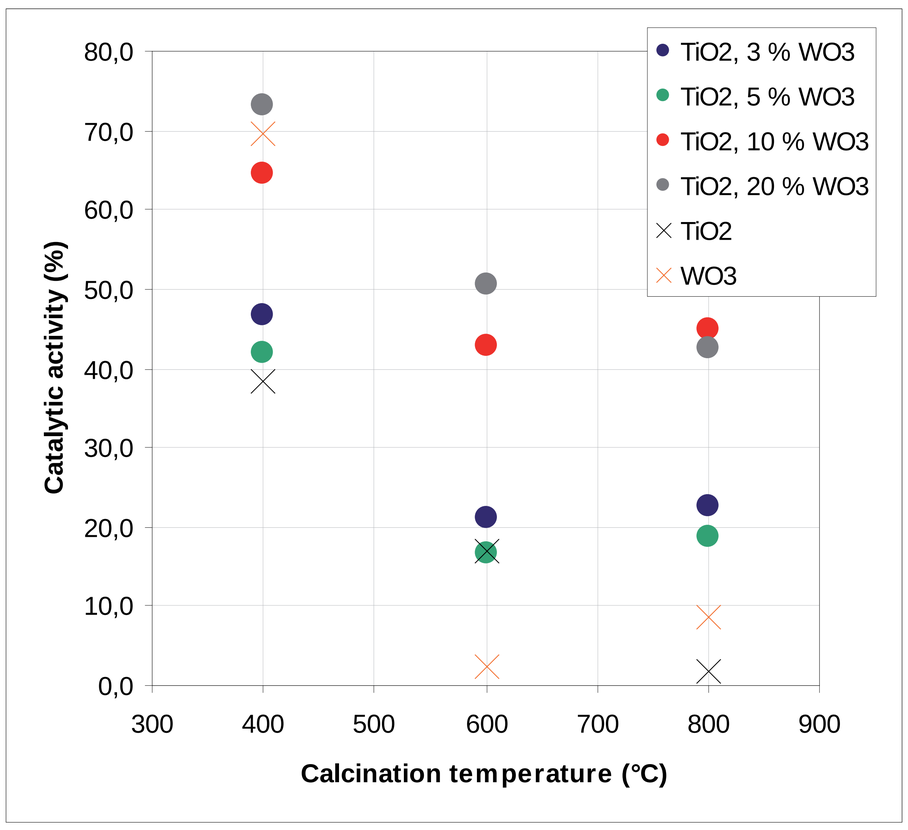
TiO_2 with 20 % w/w WO_3 calcinated at 800 °C

Surface area: measured by nitrogen adsorption analysis (BET):



Surface area of TiO_2 with 3, 5, 10 and 20 % w/w WO_3 and 100 % TiO_2 and WO_3

Catalytic activity:



Catalytic activity of TiO_2 with 3, 5, 10 and 20 % w/w WO_3 and 100 % TiO_2 and WO_3

CONCLUSION

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