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Mechanochemical Scholl Reaction as Synthethic Approach to Porous Polymers

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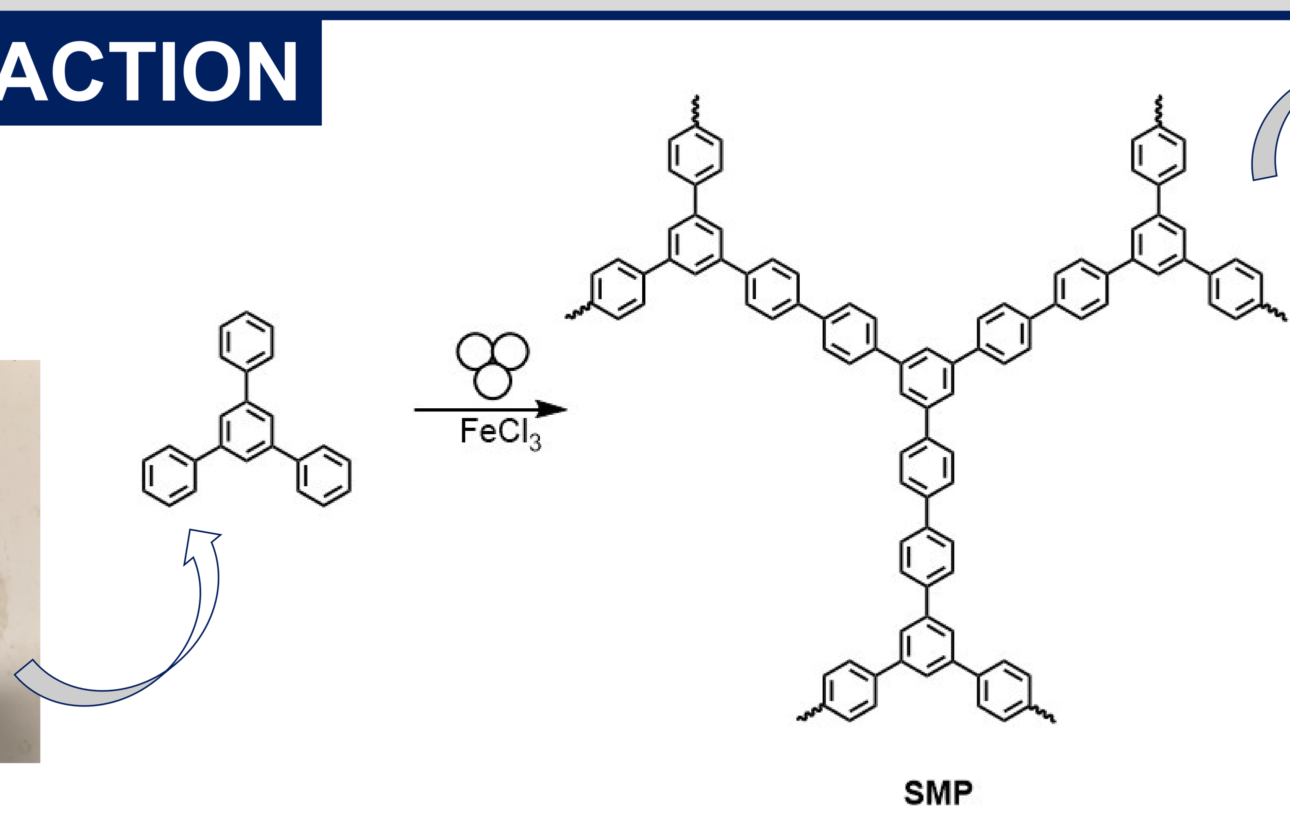
INTRODUCTION

The synthesis of porous materials with a high surface area is of high importance as these are the key components for example catalysis or gas storage.[1-4] In recent years, several different porous materials including metal organic frameworks (MOFs) and microporous organic polymers (MOPs) were investigated.[2,3,5] Another class are porous organic polymers (POPs), which combine porous materials with polymers. The synthesis most likely proceeds via Friedel-Crafts-alkylation leading to highly crosslinked polymers.[1,2,3] A different synthetic approach to generate MOPs is the so-called Scholl reaction. Two aryl compounds are coupled by elimination of hydrogen, which results in the formation of the new aryl-aryl bonds, under the addition of a lewis acid like $AlCl_3$ or $FeCl_3$.[2] This type of reaction is not dependent on functional groups for the coupling and does not require harsh reaction conditions and expensive transition metal or noble metal catalysts. The Scholl reaction can be carried out without any solvent under mechanical conditions. In earlier studies, it was shown that the addition of a low boiling solvent leads to higher surface areas.[3] Herein, we report the influence of dichlormethane (DCM) on different milling parameters of the mechanochemical Scholl reaction of 1,3,5-Triphenylbenzene.

MECHANOCHEMICAL SCHOLL REACTION

Standard reaction:

- 1 eq. 1,3,5-Triphenylbenzene
- 12 eq. of $FeCl_3$
- 22 ZrO_2 balls (Ø 10 mm)
- 30 min @ 30 Hz
- Mixer mill (*Retsch* MM500)



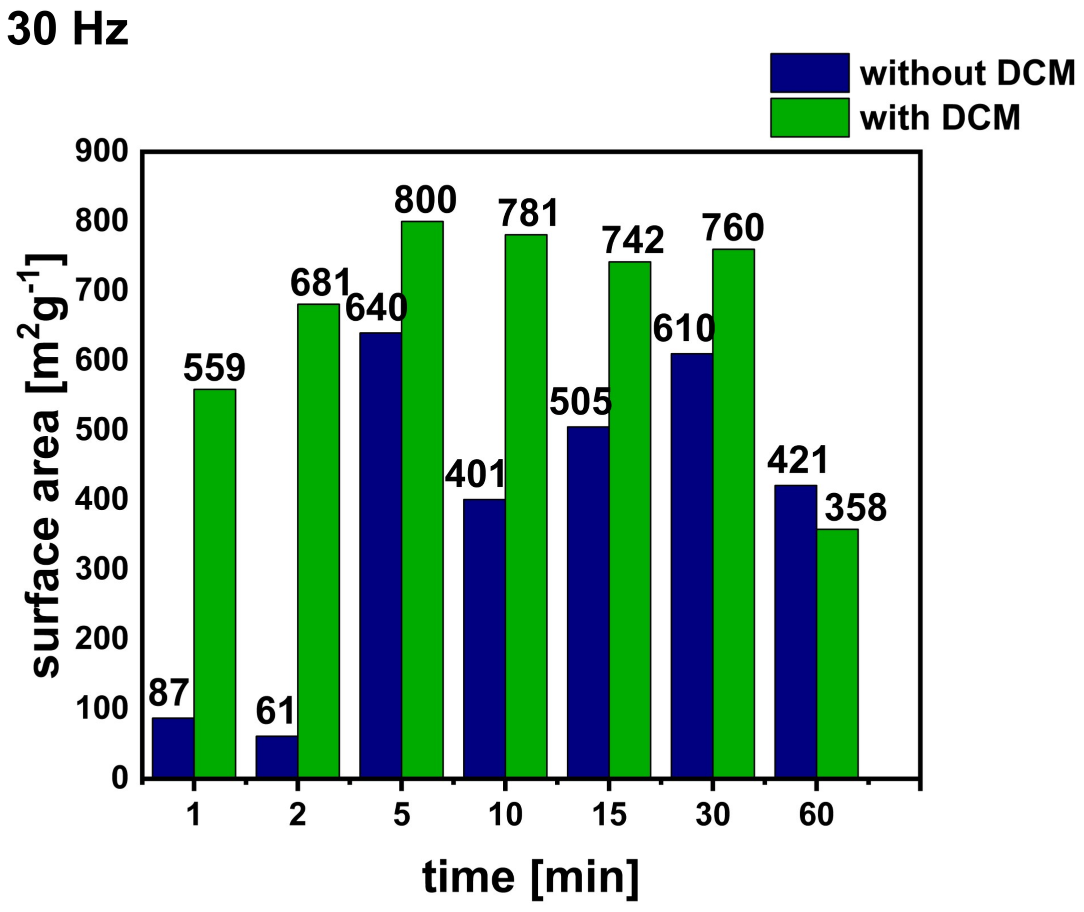
Result:

- Black porous SMP
- BET Surface area: 610 m^2g^{-1}
- Yield: 100%

INFLUENCE OF DIFFERENT MILLING PARAMETERS AND THE ADDITION OF DCM ON THE SURFACE AREA

TIME

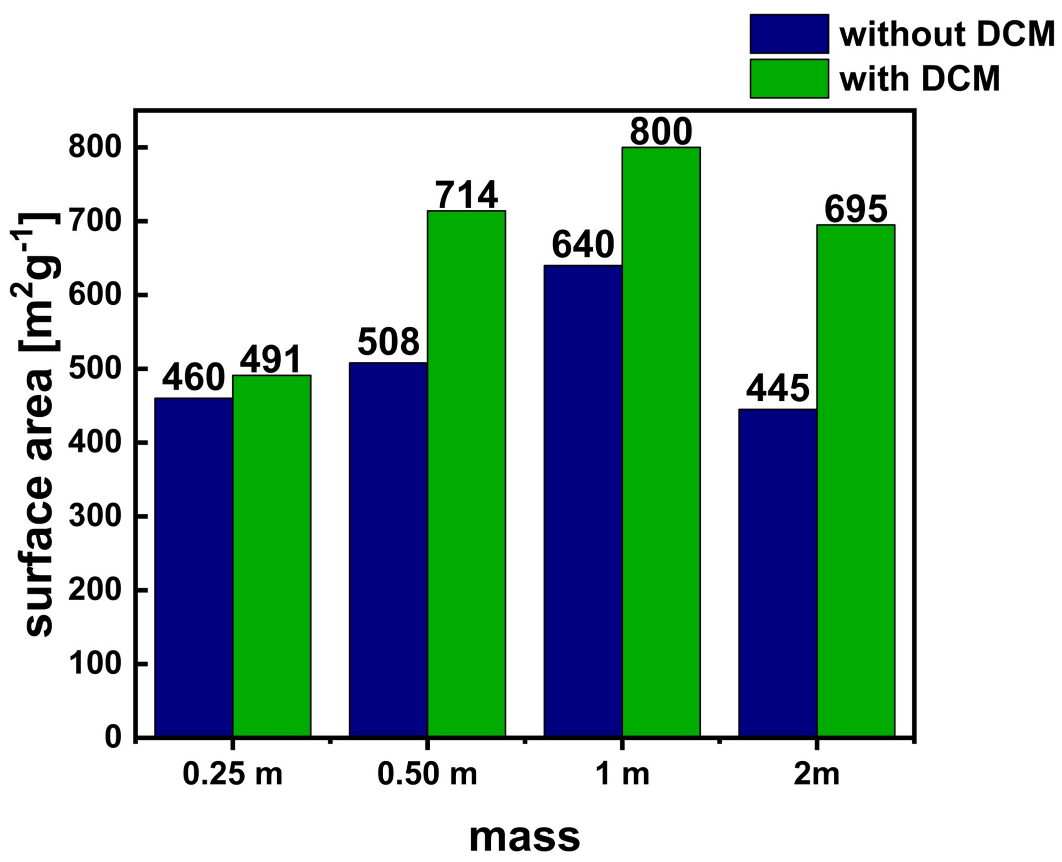
at 30 Hz



Reaction time of 5 min is sufficient
No correlation between reaction time and surface area of the SMP

POWDER TO BALL RATIO

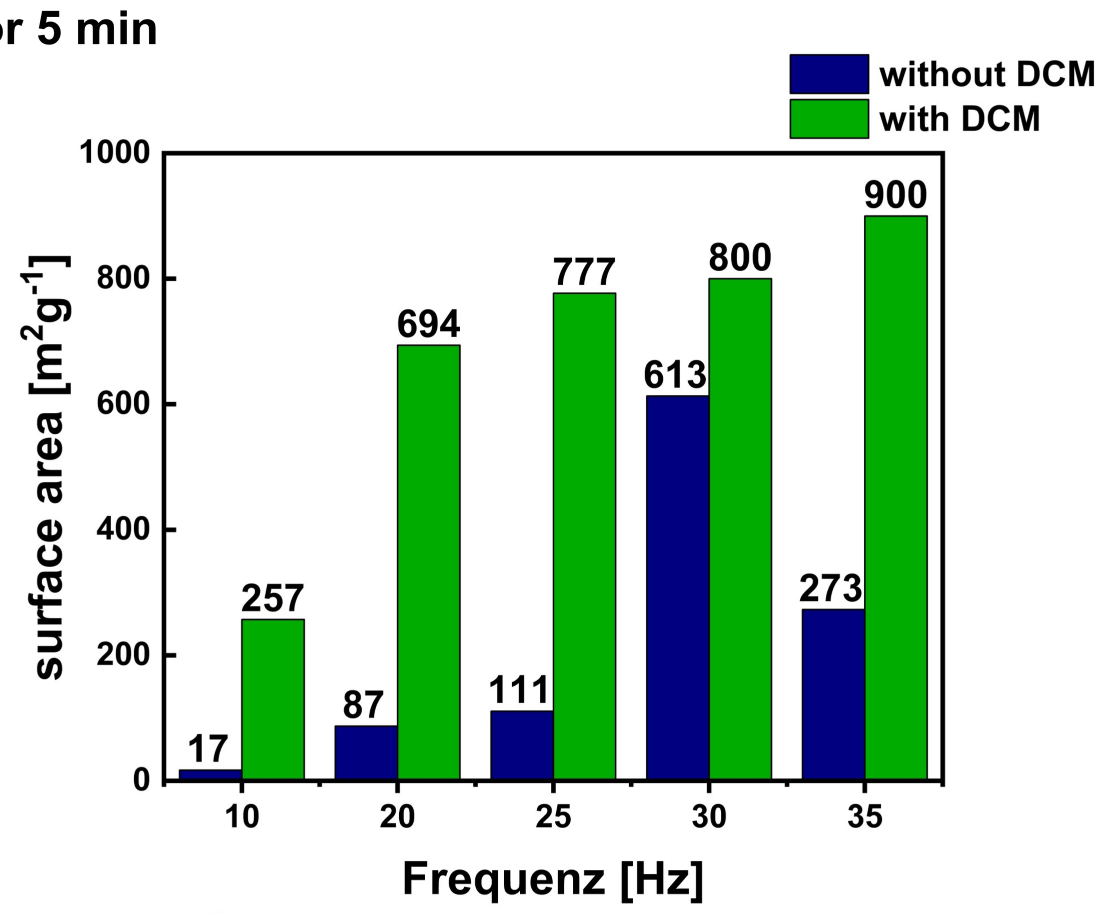
at 30 Hz for 5 min



Variation of ball to powder ratio does not lead to higher surface areas

FREQUENCY

for 5 min



Higher frequencies lead to higher surface area

ROLE OF ADDITIVES

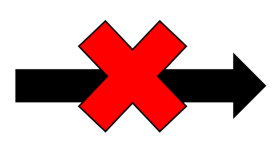
Surface area and reactivity can be controlled by addition of solvent and lewis acid

EFFECT OF SOLVENT

EtOH DCM + EtOH DCM

EFFECT OF LEWIS ACID

$FeCl_3$ $SbCl_5$ Mo_2Cl_{10}



$H_8CeN_8O_{18}$
$CuCl_2$
$AlCl_3$

CONCLUSION

In summary, the different experimental series showed that the mechanochemical Scholl reaction of 1,3,5-Triphenylbenzene results in a porous SMP with a surface area of 640 m^2g^{-1}.already after 5 min The addition of 1 mL DCM increases the resulting surface area of the synthesized SMP in the case of the tested milling parameters (time, frequency and powder to ball ratio). The choice of solvent is an important parameter for the synthesis of porous polymers as the addition of 1 mL of ethanol resulted in significant smaller surface areas. The used lewis acid is also important as other lewis acid than $FeCl_3$ showed significantly lower reactivity in this reaction leading to either no isolated product or lower yields. However, it is not clear how porosity develops during reactions especially in mechanochemistry as the mechanism is not understood yet.

Reference [1] D. Leistenschneider, N. Jäckel, F. Hippauf, V. Presser and L. Borchardt, *Beilstein J. Org. Chem.*, 2017, **13**, 1332–1341, DOI: 10.1039/C7SC00538E; [2] B. Li, Z. Guan, X. Yang, W. D. Wang, W. Wang, I. Hussain, K. Song, B. Tan and T. Li, *J. Mater. Chem. A*, 2014, **2**, 11930, DOI: 10.1039/C4TA01081G; [3] S. Grätz, S. Zink, H. Kraffczyk, M. Rose and L. Borchardt, *Beilstein J. Org. Chem.*, 2019, **15**, 1154–1161, DOI: 10.3762/bjoc.15.112; [4] C. Schneidermann, N. Jäckel, S. Oswald, L. Giebeler, V. Presser and L. Borchardt, *ChemSusChem*, 2017, **10**, 2416–2424, DOI: 10.1002/cssc.201700459; [5] S. Grätz, M. Oltermann, E. Troschke, S. Paasch, S. Krause, E. Brunner and L. Borchardt, *J. Mater. Chem. A*, 2018, **6**, 21901–21905, DOI: 10.1039/C8TA03684E