RECYCLING OF SPENT SOLID CO2 ADSORBENTS VIA CATALYTIC PYROLYSIS FOR THE RECOVERY OF MESOPOROUS SILICA AND VALUABLE HETEROAROMATIC CHEMICALS

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Solid adsorbent looping technology (SALT) is a promising CO_2 capture technology. SALT utilises strongly basic solid adsorbents, such as polyethyleneimine (PEI) supported on mesoporous silica (Si-PEI). One of the key drivers for the success of the technology is the reduction of the adsorbent replacement costs below 10€ per tonne of CO_2 captured. A way through which this can be achieved is by the reduction of the virgin raw materials needed for the production of the Si-PEI adsorbent. In this work, we have investigated the recovery of mesoporous silica from spent Si-PEI adsorbents using pyrolysis for the removal of the impregnated PEI. In addition, we investigated the recovery of the pyrolysis vapours and the composition of the produced pyrolysis oils. Furthermore, we screened various catalysts for the upgrading of the PEI vapours to maximise the concentration of commercially interesting chemical monomers in the pyrolysis oils.

Oxidised (spent) Si-PEI, obtained from a previous work [1], was pyrolysed in a bench-scale fixed bed reactor, initially without catalyst, at temperatures of 400, 500, 600 and 650 °C to determine the temperature effect on the properties of the recovered silica and on the yield of pyrolysis oil. Subsequently, the Si-PEI was pyrolyzed at 600 °C, and the produced vapours were upgraded using ZSM-5-based, USY-based, MgO, ZrO_2 or ZrO_2/TiO_2 catalysts. After pyrolysis at >500 °C, followed by oxidation at the same temperature, the residual C and N on the recovered silica were reduced to ca. 0.1-0.2 wt.%. Correspondingly, the pore volume increased from 0.4 cm^3/g to 1.1-1.3 cm^3/g. These values were only marginally affected at higher pyrolysis temperatures. The yield of the produced pyrolysis oils was 41%, and they were composed of a dark phase (19-20% yield) containing 12% H_2O and a light phase (20-22% yield) containing 24-28% H_2O. The most abundant compounds in both phases were pyrazines, followed by a few pyridines, pyrroles and imidazoles. However, most of the compounds (ca. 80% peak area) could not be identified by GC-MS, attributed to the presence of high-MW oligomers in the oils. The catalysts increased the C content of the organic compounds in the dark phase and reduced their H and O content, attributed to cracking, dehydrogenation and deoxygenation reactions. The effect increased with increasing catalyst-to-feed (C/F) ratio. Correspondingly, the catalysts reduced the organics in the light phase due to the migration of deoxygenated compounds to the dark phase. The catalysts greatly increased the concentration of pyrazines in both phases, as well as the concentration of pyridines, pyrroles and imidazoles, while the unidentified compounds decreased to as low as 13% (dark phase) and 0% (light phase). This was attributed to the cracking of the high-MW oligomers and the production of low-MW compounds that could be resolved by the GC-MS. All catalysts were effective for the upgrading of the PEI vapours, while the ZrO_2/TiO_2 and ZrO_2 catalysts exhibited the highest activity.

Our work showed that PEI can be effectively stripped off from spent Si-PEI adsorbents via pyrolysis at >500 °C, and mesoporous silica can be recovered for re-impregnation with fresh PEI. Meanwhile, catalytic upgrading of the PEI vapours can crack high-MW oligomers and yield pyrolysis oils with commercially interesting heteroaromatic chemicals, such as pyrazines.

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References
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