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L-V | Carbon2Polymers: CO Conversion to Polycarbonates

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The aim of subproject L-V is to investigate the reaction of CO gas from a steel mill with Cl_2 for producing polycarbonates via phosgene as a key intermediate (Fig. 1). We investigate the interaction of Cl_2 with commercial activated carbons at different temperature via tracking formed gaseous products to draw structure-activity relationships. In close cooperation, the solvent-free phosgenation of phenol and life cycle assessment test is carried out at Covestro and RWTH Aachen, respectively.

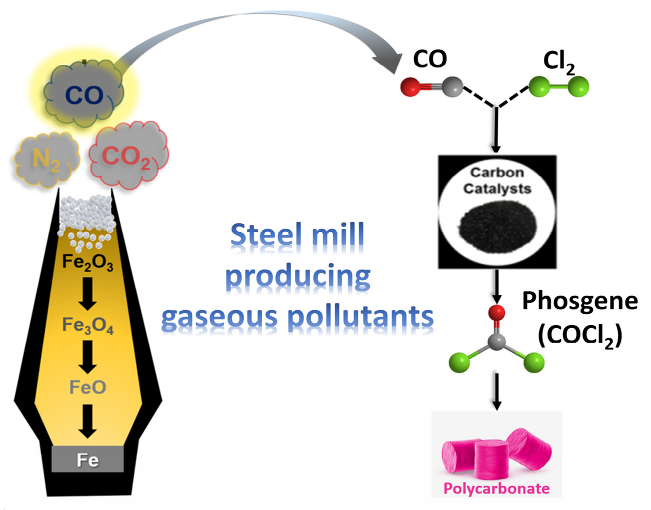

Figure 1: Steel mill exhaust CO gas conversion to polycarbonate.

Experimental approach

Cl_2 activation is a crucial step for phosgene generation. The interaction must not be too strong, otherwise, Cl_2 will deactivate the carbon (Fig. 2a).[1] By measuring the amount of Cl_2 ads./des. on carbon at a temperature in a temperature programmed desorption, the reversibility and the nature of Cl_2 interaction with carbon are examined. Fig. 2b shows the set-up to evaluate the activated carbon's Cl_2 adsorption capacity since those parameters give important hints for catalytic performance.[2]

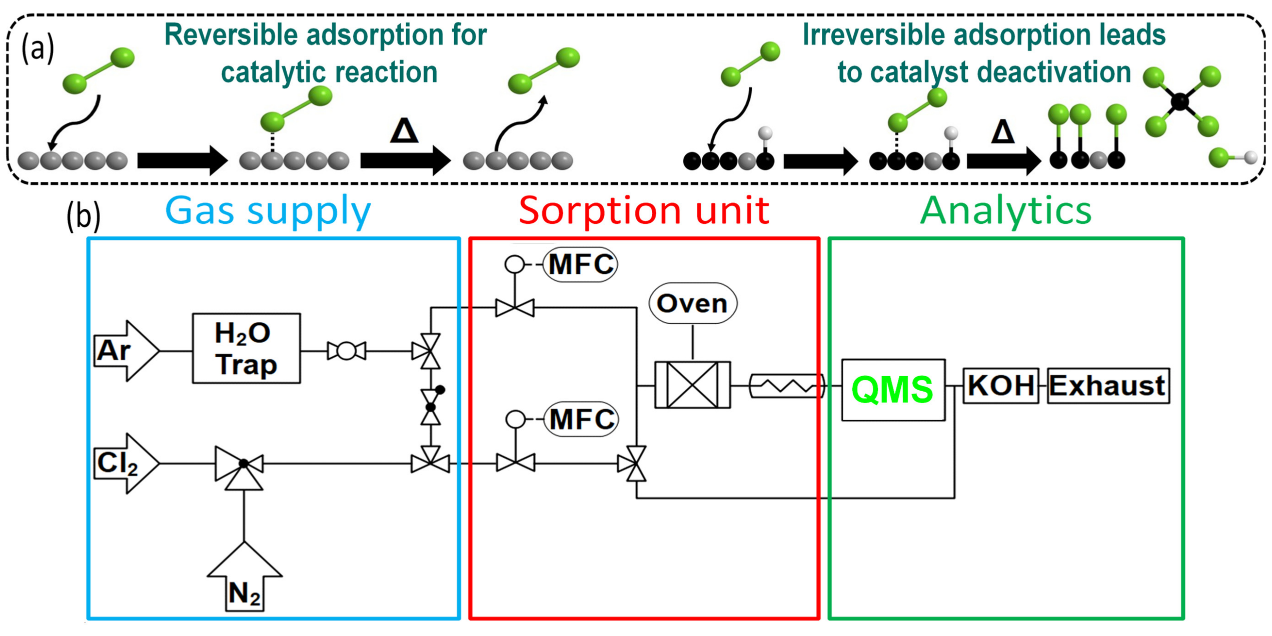

Figure 2: (a) Scheme for reversible and irreversible Cl_2 adsorption on graphitic (left) and non-graphitic (right) carbon. (b) Set-up for Cl_2 interaction analysis.[3]

Activity/stability testing of activated carbon

The Cl_2 adsorption/desorption experiment is carried out in tubular bed reactors over activated carbon.[3] Fig. 3a,b shows various gaseous side products including Cl_2 evolved during Cl_2 ads./des. experiment RT and T_3 (high temp.) on commercial activated carbon. At higher temperature CCl_4 (carbon tetrachloride) and $COCl_2$ (phosgene) side-products formed: Deactivating carbon. At higher temperature, the adsorbed Cl_2 decreases over cycle test, and desorbed Cl_2 is negligible (Fig. 3c,d). The lack of balance between the adsorbed and desorbed Cl_2 suggests the loss of Cl_2 gas in the side reactions, hence, deactivating the catalysts.

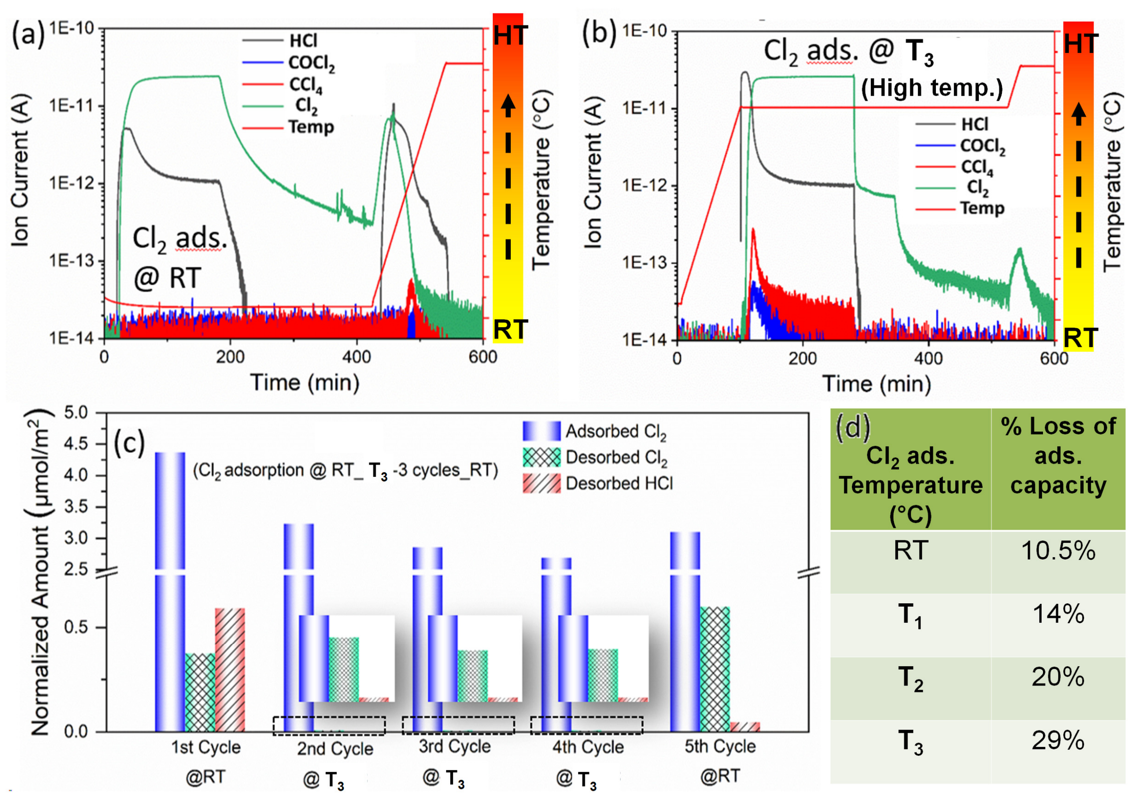

Figure 3: Gases evolved during Cl_2 ads. at RT (a), and T_3 (b) on commercial C. Amount of Cl_2 ads./des. and HCl des. over 5 cycles at RT-T_3 (3 cycles)-RT (c) on activated C. (d) % loss of Cl_2 ads. capacity at different temperature.

In-situ structural analysis

A higher amount of Cl remains irreversibly adsorbed on carbon (damaging sp^2 graphitic sites). *In situ* measurement confirms a substantial loss of carbon graphitization upon exposure to Cl_2 exposure (Fig. 4), consistent with the outcomes of activity/stability test.

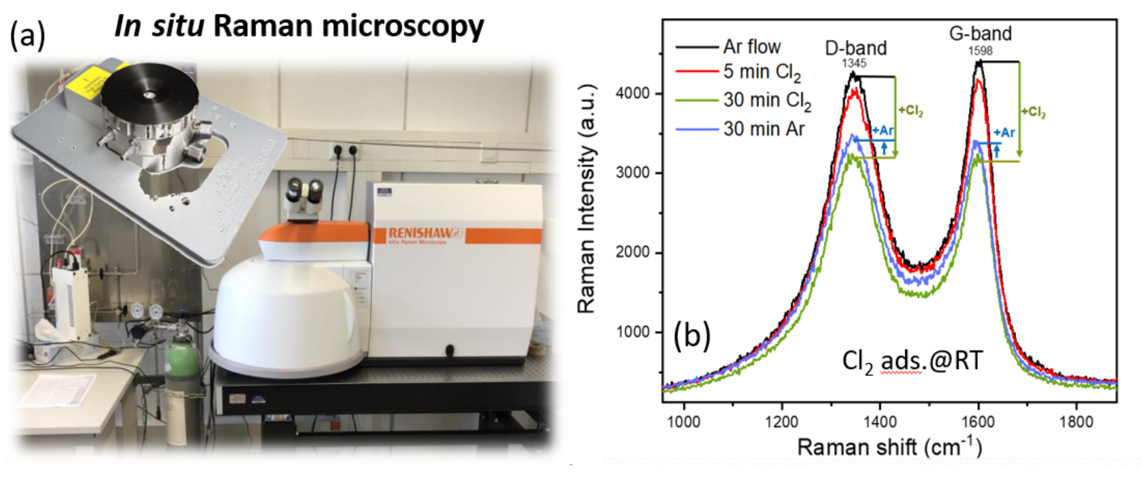

Figure 4: (a) *In-situ* Raman cell and microscope. (b) Raman spectra of activated carbon during Cl_2 ads. for different time at RT.

Work progress and outlook for phase II

- Cl_2 adsorption experiments of graphitic carbon nitride
- Exploring N doping in carbon material for stable Cl_2 adsorption
- *In situ* Raman analysis at higher temperatures
- *In situ* Raman analysis of N-doped carbon materials

[1] G. Centi, K. Barbera, S. Perathoner, N. K. Gupta, E. E. Ember, J. A. Lercher, ChemCatChem **2015**, 7, 3036–3046.
[2] A. Bähr, G.-h. Moon, J. Diedenhoven, J. Kiecherer, E. Barth, H. Tüysüz, Chem. Ing. Tech. **2018**, 90, 1513–1519.
[3] A. Bahr. Design of Nanostructured Carbon-Based Materials for Thermo- and Electrocatalytic Applications, **2021**, Ph.D. thesis.

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A KEY BUILDING BLOCK FOR THE CLIMATE PROTECTION

CO_2 reduction by cooperation of process industrial sectors