Understanding of Ammonia Absorption of Magnesium Chloride Supported with Porous Materials

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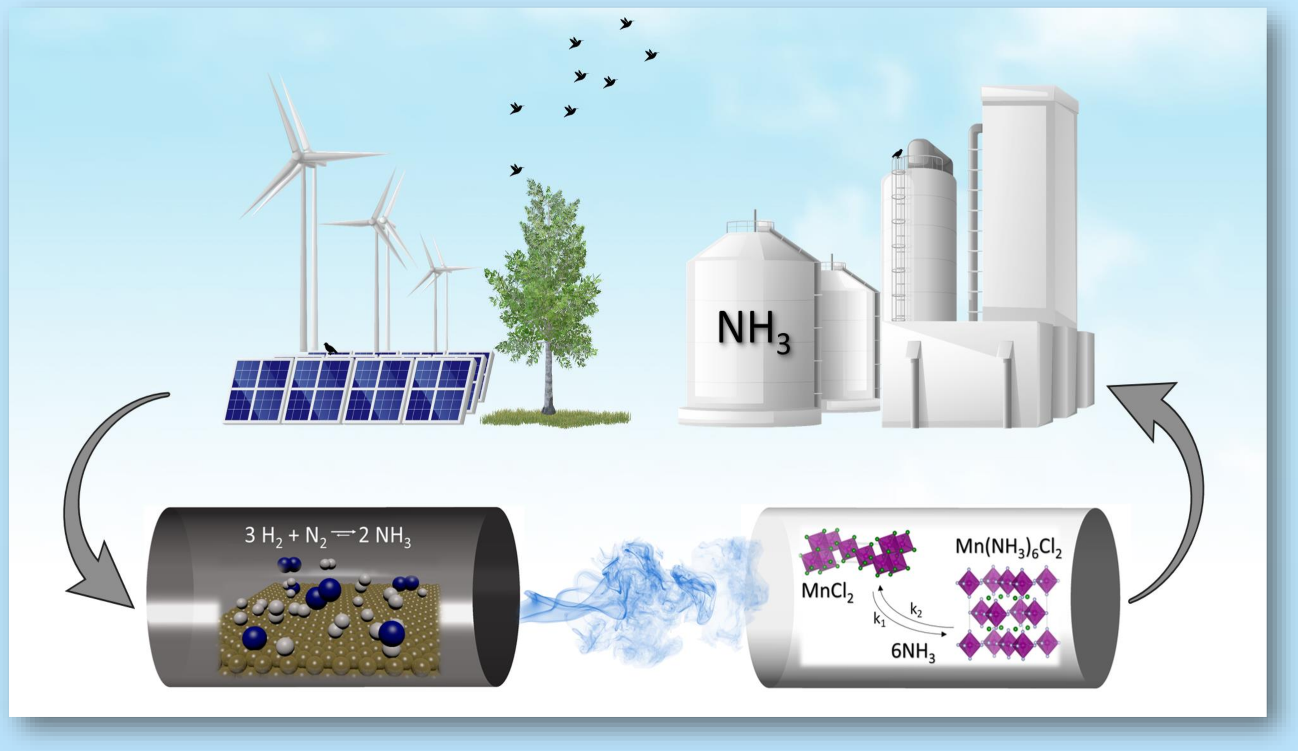
Introduction

Ammonia is a promising green energy vector of the future, due to its high energy density and carbon neutrality. The challenge remains a more efficient production of ammonia from abundant, but intermittent renewables.[1] In the conventional synthesis, ammonia is separated by an energy-intensive condensation.[2] Ammonia synthesis can be improved by efficiently separating ammonia by solid absorbents prior to the recycle. Metal halides are a viable option, by coordinatively absorbing ammonia.[3] In this study, $MgCl_2$ supported on porous materials (SiO_2, MCM-41, H-ZSM-5) was investigated in terms of ammonia capacity.



Results

N_2 Physisorption and $MgCl_2$ Distribution

SiO_2 and H-ZSM-5 were obtained commercially, while MCM-41 was synthesized according to the literature. MCM-41 displays a type 4 isotherm, which indicates that the material is mesoporous. N_2 physisorption analyses of the supports (SiO_2, MCM-41, H-ZSM-5) and 50 wt% $MgCl_2$ impregnated supports reveal a significant decrease in BET surface areas and pore volumes upon impregnation with $MgCl_2$ (**Fig. 1**, **Table 1**). This reduction indicates that $MgCl_2$ is well dispersed in the pores of the supports a conclusion further corroborated by EDS elemental mapping.

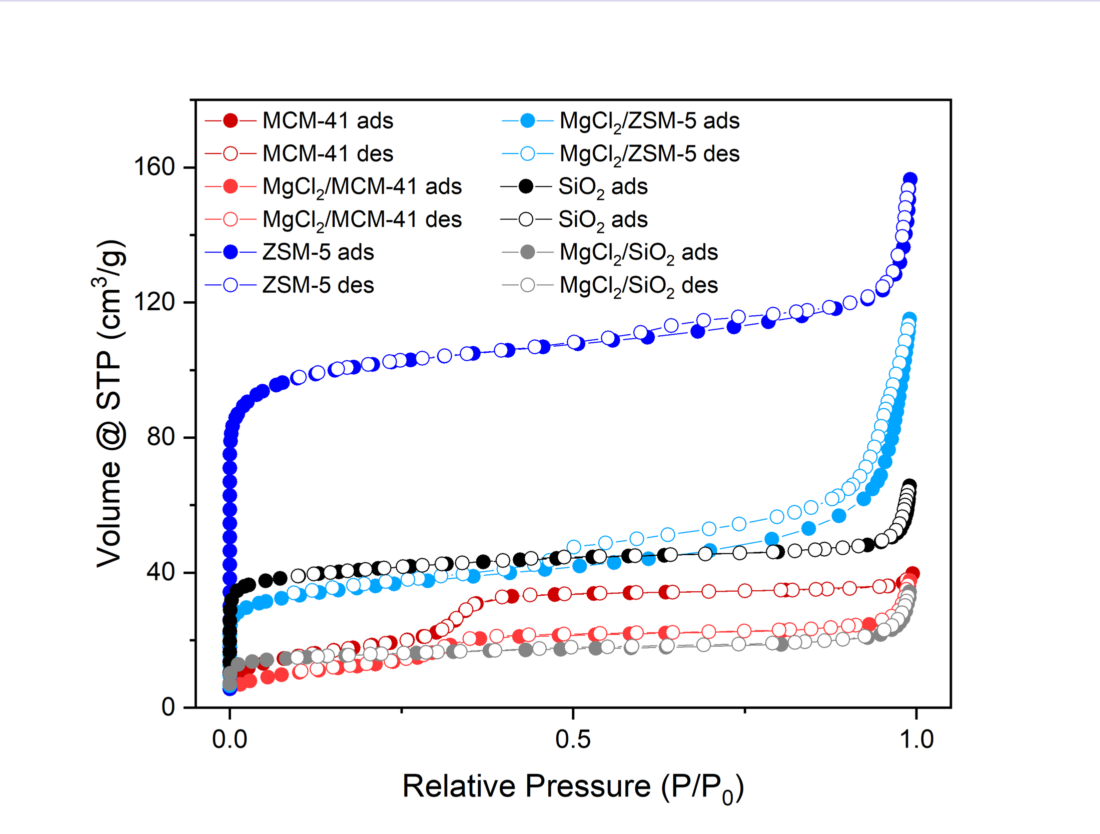


Fig. 1: N_2 physisorption isotherms of MCM-41, SiO_2, ZSM-5, $MgCl_2$/MCM-41, $MgCl_2/SiO_2$, and $MgCl_2$/ ZSM-5.

Table 1: Ammonia sorption capacity, BET surface area, average pore volume and average pore size of supports and impregnated materials.

Material	NH_3 Capacity [mg/g]	S_{BET} [m²/g]	Pore volume [cm³/g]	Average pore size [nm]
MCM-41	6.1	1032	0.9	3.5
H-ZSM-5	19.0	392	0.2	2.0
SiO_2	14.6	556	0.3	2.2
$MgCl_2$/MCM-41	86.0	157	0.1	3.3
$MgCl_2$/H-ZSM-5	275.7	131	0.1	4.0
$MgCl_2/SiO_2$	111.8	204	0.1	2.0

NH_3 Absorption/Desorption

Ammonia reacts with metal halides to form a metal coordination complex, which is accompanied by a change in crystal structure, as shown in **Fig. 3**. Sorption measurements were conducted at 25 °C and 1 bar. The ammonia sorption capacity increased significantly upon impregnation of the supports with $MgCl_2$.

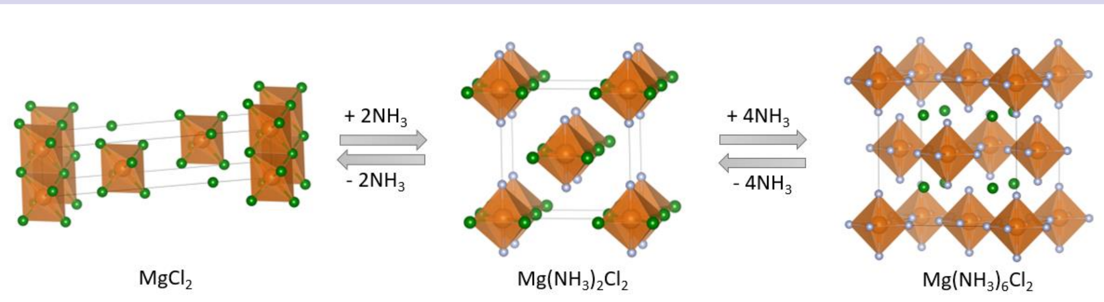


Fig. 3: Crystal structures of a) $MgCl_2$, b) $Mg(NH_3)_2Cl_2$, c) $Mg(NH_3)_6Cl_2$ with space groups R-3m, Cmmm, and Fm-3m, respectively. Colour scheme: Mg-orange, N-gray, Cl-green, H is omitted for clarity.

Methods

Synthesis of supported materials:
- Wet impregnation (WI)
- Ar atmosphere

Structural Characterization:
- EDS, BET analysis
- Temperature-programmed desorption (TPD)

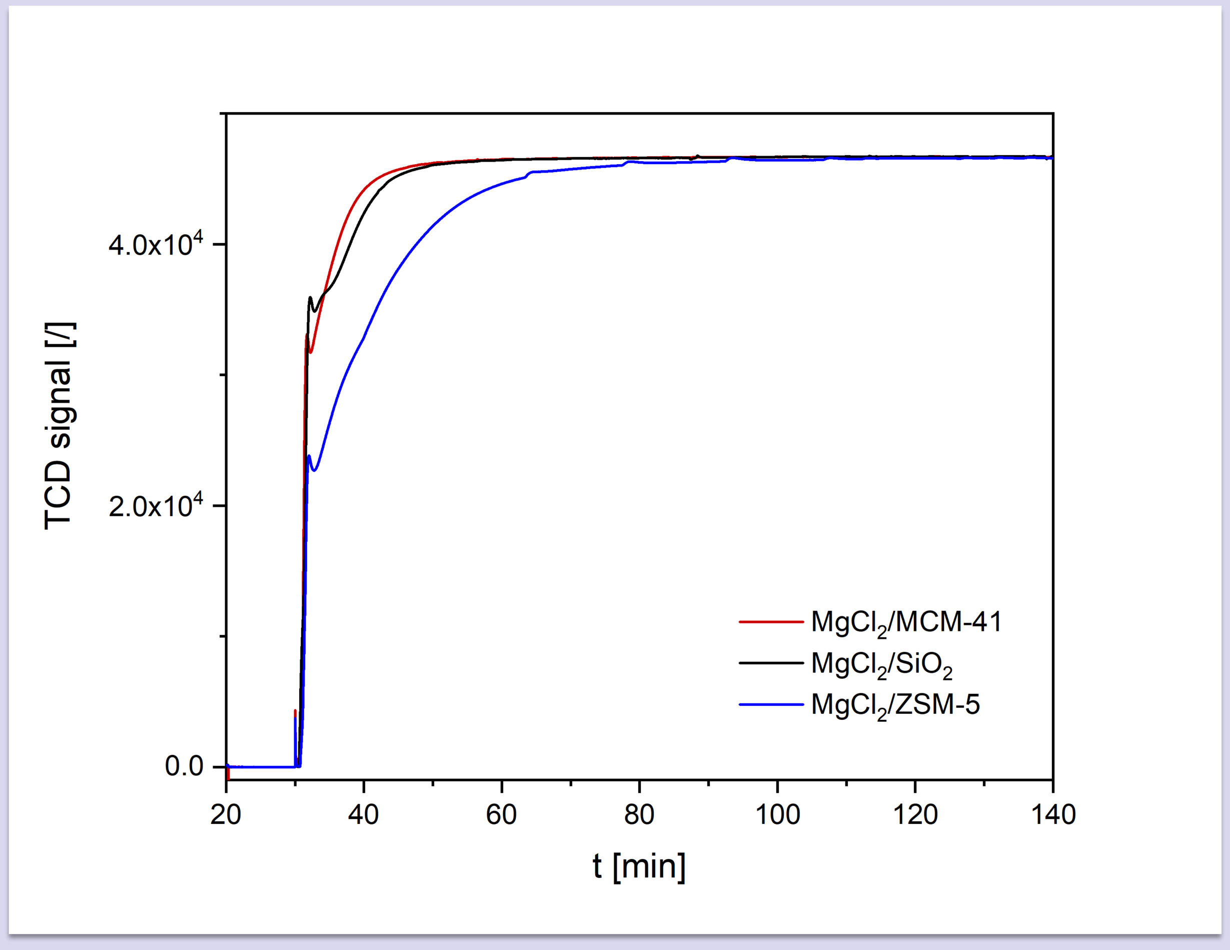


Fig. 2: Breakthrough analysis of impregnated materials.

Among the supported materials H-ZSM-5 supported $MgCl_2$ exhibited the highest uptake (**Fig. 2**, **Table 1**), even though its BET surface area is the lowest among supports, potentially due to the acidic nature of the support.

Conclusions

Magnesium chloride on different supports (H-ZSM-5, SiO_2 and MCM-41) was successfully prepared *via* a wet impregnation method, and was characterized by different characterization techniques (EDS, BET, TPD). According to the obtained ammonia capacity of different materials, the support has a significant impact on the ammonia capacity. The findings indicate that the acidity of the support plays an important role in ammonia absorption capacity at low temperatures with H-ZSM-5 supported $MgCl_2$ exhibiting the highest NH_3 capacity. The results indicate the applicability of the synthesized sorbent in ammonia separation process, for instance in integrated ammonia synthesis – separation process.

References

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