Effect of metal oxides modification on CO₂ adsorption performance over mesoporous carbon

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Abstract:

Porous carbon materials have been modified by various metal oxides (CeO_2 , CuO , NiO and Mn_3O_4) with different weight loadings (10 – 30%). The obtained composite materials were characterized by scanning electron microscope (SEM), N_2 adsorption isotherms, X-ray diffraction (XRD) and thermogravimetric analysis (TGA), and investigated as sorbents for selective capture and removal of carbon dioxide. The overall CO_2 adsorption capacity of AMC decreases upon metal oxides modification due to the reduction in the total surface area of the composite. Interestingly, CO_2 adsorption capacity of AMC at relative low pressure range (below 0.4 bar) is increased with high metal oxides loading (30%), especially for NiO modified AMC. This is explained by the increased interaction strength between CO_2 and the metal oxides than with the carbon surface. The CO_2/N_2 selectivity values of the AMC modified with metal oxides are generally higher than the parent AMC, with the 30% NiO -modified AMC showing 72% increase in the selectivity. This enhancement in selectivity is attributed to an increased interaction between CO_2 and the introduced metal oxides, which is supported by the increased isosteric heats of adsorption of CO_2 after metal oxides modification. The results presented here demonstrate that the adsorption properties including capacity and selectivity of carbon materials are influenced by both their textural characteristics (such as surface area and pore volume) and the surface chemistry, which can be affected by the type and concentration of introduced metal oxides.

Keywords: Carbon, CO_2 capture, Metal oxides, Selectivity

1. Introduction

The prospect of a worsening climatic situation due to global warming is a subject of widespread public concern [1]. It has become commonly accepted that CO₂ is the most important greenhouse gas affecting climate change, and also represents an important future carbon feedstock [2-4]. The best mitigation of the greenhouse gas of CO₂ emission is to capture CO₂ before its release into atmosphere and then sequester it. In recent years, great efforts have been directed towards the development of new technologies for the efficient adsorption or storage of large quantities of carbon dioxide [5, 6]. The commercial carbon dioxide capture technologies used today have several disadvantages, such as high energy consumption, high costs, and the corrosion of the equipment and toxicity [7, 8].

One of the promising technologies for CO₂ removal is the chemical adsorption of CO₂ on solid sorbents. Various porous materials with high surface area, pore volume, fine structure and chemical properties have been widely investigated including zeolites [9-11], metal-organic frameworks (MOFs) [12-14], activated carbons [15-20], boron nitride [21, 22], modified silica materials [23-25], and metal oxides [26-30]. Of the sorbents mentioned so far, activated porous carbon have been extensively used in CO₂ capture and storage because of its low cost, high availability, large surface area, excellent thermal stability and chemical resistance, easy-to-design structure and surface functionalization, and relative low energy requirement of regeneration [31]. However, CO₂ capture with carbon materials is commonly based on physical adsorption, which makes the adsorbents sensitive to temperature and relatively poor in selectivity. For these reasons, recent research activities on carbon-based CO₂ adsorbents were mainly focused on improvements in CO₂ uptake and selectivity through the optimization of pore

structure, surface modification and synthesis of carbon-based hybrid composites [32, 33]. In comparison with pore size optimization, surface modification is more easily realized and controlled by synthetic methodology. Many studies have proven that the CO₂ capture capacity of activated carbons can be significantly increased by introducing nitrogen functional groups into their structures [34-36]. In addition, there are other treatments, such as oxidation and fluorination, are also investigated. Dai et al. reported that the amidoxime group which contains both nitrogen and oxygen functionality sonochemically grafted onto a porous carbon matrix can serve as an effective sorbent for the selective capture of CO₂ [37].

The ability to modify the carbon surface is especially important because it offers a means to incorporate surface functional group with enhanced affinity for CO₂ to increase the adsorption capacity. With high stability, abundant availability and inexpensive cost, metal oxides has attracted considerable attention for its potential applications in doping or loading on carbon materials to further improve the CO₂ capture capacity [38, 39]. However, the roles of metal oxides in the surface modification of carbon materials, and thereby affecting the selective adsorption of CO₂ on carbon materials still remain to be explored.

In this work, soft-templated mesoporous carbons (MCs) with pore diameter of ~ 10 nm were synthesized and used as parent carbons for metal oxides loading. The selected metal oxides (Ni, Ce, Mn and Cu) used in this work exhibit weak basic properties which is advantageous in terms of acidic CO₂ capture. CO₂ and N₂ adsorption were tested on these AMCs functionalized with various metal oxides. The presence of metal oxides, such as NiO and CeO₂, provided a significant improvement in the CO₂/N₂ selectivity due to increased CO₂ interaction while the overall capacity was reduced due to a decrease in the surface area. Enhanced CO₂ adsorption capacity is observed at low CO₂ pressure region for AMCs modified with 30% NiO. The results

here suggest that surface modification with dispersed metal oxides could be a promising approach to improve CO₂ selective adsorption performance, and may be instructive for the surface modification of other kinds of carbon materials reported in the literature.

2. Experimental

2.1. Materials

The following raw materials were used as provided: Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, Alfa Aesar); Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O Acros Organics); Manganese (II) nitrate tetrahydrate (Mn(NO₃)₂·4 H₂O, Sigma-Alorich); Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6 H₂O).

2.2. Samples preparation

Pristine mesoporous carbon (MC) was synthesized by carbonization of nanostructured polymeric composites as previously reported [40], which were obtained by self-assembly of block copolymer (Pluronic F127) and phenolic resin (phloroglucinol-formaldehyde) under acidic conditions via an established soft-templating route¹. In a typical synthesis, 26.2 g of phloroglucinol, 52.4 g of F127, 10.0 mL of aqueous HCl (37 wt.%) and 1300 mL of ethanol were loaded into a 2 L flask. The mixture was heated with stirring to reflux. 26.0 g of aqueous formaldehyde (37wt.%) was then added to this solution. F127-phenolic resin polymeric composites were formed as precipitates. The reaction mixture was stirred for 2 h and then filtered. The yellow polymer particles were dried in an oven at 393 K for 3 h. Carbonization was carried out under flowing N₂ by heating the polymer particles to 1123 K with a heating rate of 5°C/min and maintaining the final temperature for 2 h. To improve the porosity of MC, it was subjected to NaNH₂ activation according to the methodology developed in literature [41]. In brief, 1 g of MC

and 2 g of NaNH_2 were mixed in a nickel crucible, heated in a tubular furnace under flowing N_2 to 1123 K at $10^\circ\text{C}/\text{min}$, and then kept at the final temperature for 0.5 h. The resultant powder was washed with deionized water to neutral, followed by drying at 393 K for 12 h. The obtained activated MC was denoted as AMC. The yield for carbonization of PR-F127 composite to prepare MC is 34%. The yield for activation of MC to prepare AMC is 25%. The mesoporous supported metal oxides are prepared by wet impregnation method. The desired amount (10% and 30% weight loadings of metal oxides) of metal salts ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$) firstly dissolved in mixed solution of 30 ml distilled water and 10 ml ethanol. And then AMC was added to the solution and stirred for 6 hrs. Afterwards, the solvents were directly evaporated out, and the obtained samples were calcined at 673 K under N_2 flowing, and denoted as Me-AMCs (Me = NiO, Mn_3O_4 , CeO_2 , and CuO).

2.3. Characterizations

The scanning electron microscope (SEM) imaging was performed on the Zeiss Auriga microscope with an electron beam operation of 5keV, which is a dual beam FIB (Focused Ion Beam) with a field emission electron column for high resolution electron imaging and a Canion Ga+ column for precision ion beam milling.

Nitrogen adsorption isotherms were measured at 77K using a Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Prior to the adsorption measurements, the metal oxides modified AMC sample powders were degassed under flowing nitrogen for 2h at 473K to remove any residual water and surface species. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05 to 0.25. The total pore volume (V_t) was estimated from the N_2 adsorption isotherm at a relative pressure $P/P_0=0.97$. The micropore volume (V_m) was estimated from N_2 adsorption isotherm through t-plot method.

The pore size distributions (PSD) were calculated using the Barrett-Joyner-Halenda (BIH) algorithm for cylindrical pores according to the improved Kruk-Jaroniec-Sayari (KJS) method.

X-Ray diffraction (XRD) were collected on a PANalytical powder diffractometer using $\text{CuK}\alpha$ radiation. The working voltage was 40KV, and the current was 40mA. The intensity data were collected at room temperature in 2θ range of $20 - 90^\circ$.

The metal oxides loading of metal oxides modified AMC samples was measured on a thermogravimetric analysis (TGA) device (Model Seiko 6300 TG/DTA, RT Instruments, Inc.). An ~ 10 mg sample was placed in a ceramic crucible and transferred to the TGA chamber. The weight left after samples calcined at 1023 K in air was used to calculate the metal oxides loading based on their oxidation state as indicated by XRD results.

CO_2 and N_2 adsorption measurements were carried out at 303K and 273K using Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Prior to the CO_2 and adsorption measurements, all AMC and metal oxides doped AMC samples were treated under flowing nitrogen for 5 h at 453K.

3. Results and Discussion

3.1. Characterization of physical properties Figure 1 shows representative SEM images of AMC and metal oxides modified AMC for NiO-AMC (10% and 30%) and CeO_2 -AMC (10% and 30%) . Comparison of the microscopy images, it is clearly there is no obvious change in the primary structure of the AMC after metal oxides modification. Regardless of the type of metal oxides, the modified AMCs exhibit a similar morphology that is characterized by the worm-like, and disordered porous structure. The less surface roughness observed for the modified AMCs is possibly due to that the AMC surface is polished by impregnation and calcination process with

introduction of metal oxide species. The metal oxides with both low and high loading are not visually apparent, which suggests that the dispersion of metal oxides occurred mainly within the pores of AMC. The representative TEM images (the support information Figure S1) confirmed that metal oxides particle well distributed within the pores of AMC, and particle size are mainly in the range of 6 to 8 nm.

The porous structure of the AMC and metal oxides modified AMC materials were investigated using nitrogen adsorption at 77 K. **Figure 2** presents a comparison of the N₂ adsorption isotherms and corresponding pore size distribution for these AMC samples. The adsorption isotherms have a similar shape and the pore size distributions (PSDs) indicate that the porosity of pure and modified AMC materials is made up of mesopores with a size of around 10 nm. All isotherms can be identified as typical Type IV, also indicating the mesoporous nature of the samples. Table 1 presents a summary of the corresponding textural properties and actual metal oxides content (measured from TGA) of all the samples. The BET surface area and total pore volume of the parent AMC is 2475 and 2.1 cm³/g, respectively. As given in **Figure 2**, the modification of AMC with metal oxides results in a reduction of both surface area and pore volume compared to the unmodified AMC sample. The decrease was more severe with higher metal oxides loading to 30 % for all modified samples.

The XRD patterns of the AMC and modified AMC samples are shown in **Figure 3**. It can be seen that only the characteristic broad peak of the graphitic structure with 2θ at 43° is detected on the pure AMC sample. This diffraction peak weakens or disappears with the introduction of metal oxides. In addition, the distinct diffraction peaks due to CeO₂ (JCPDS card no: 34-0394), NiO (JCPDS card no: 44-1159), Mn₃O₄ (JCPDS card no: 24-0734) and CuO (JCPDS card no: 48-1548) are seen in the corresponding oxide modified AMC samples, respectively, regardless of

their loading. This indicates that all the metal oxides are well crystallized in/on AMC. The typical peaks of metal oxides become sharper when their loadings are increased to 30% due to increased crystallinity.

3.2. CO₂ adsorption The CO₂ and N₂ adsorption capacities of all AMC samples were investigated at two temperatures (273 and 303 K) and the results are shown in **Table 2 and Figure S2, respectively**. **Figure 4** compares the CO₂ adsorption isotherms measured at 303 K for the pure AMC and AMC modified by various metal oxides with two different metal oxides loadings, 10 % and 30 %. For the pure AMC, the CO₂ adsorption capacity at 303 K is 2.25 mmol/g at 1 bar, comparable to the values measured in other studies on activated carbon [37, 38] though the CO₂ uptake values for activated carbon can vary extensively depending on the treatment procedures [15]. For all metal oxides modified AMC samples, the CO₂ total capacity for both loadings were lower than the original AMC, attributed to the decrease in the surface area and pore volume for metal oxides modified AMC as shown in **Table 1**.

At low loading (10%) of metal oxide, it can be seen that the CO₂ capacities differ slightly for the modified AMC samples: ~2.00 mmol/g for Mn₃O₄-AMC-10, ~1.90 mmol/g for NiO-AMC-10 and CeO₂-AMC-10 and ~ 1.80 mmol/g for CuO-AMC, following the general trend of decreasing surface area of these samples. To clearly show the effect of metal oxides on the CO₂ adsorption behavior, the CO₂ capacities are normalized to the total surface area as presented in Table S1. It is worth mentioning that the CO₂ capacities for the modified samples are still lower than or close to that for the pure AMC with low loading of metal oxide (10%). This indicates that the adsorption capacity does not exclusively correlate with loaded metal oxides (surface chemistry) at this concentration. Instead, the relationship might be correlated to the texture parameters such as surface area and pore volume, which are mainly originated from pure AMC

itself. With increased metal oxides loading, as shown in **Figure 4B**, the CO₂ total capacities show further slight decrease for the AMC samples modified with CuO and Mn₃O₄ due to their largely decreased surface area (**Table 1**). The NiO and CeO₂ concentration has little effect on CO₂ total adsorption capacity regardless of the severely decreased surface area. It is remarkable that when the CO₂ total capacities are normalized to surface area (Table S1), the metal oxide modified AMCs actually show a higher capacity than the pure AMC with 30% loading at both temperature. This suggests that CO₂ adsorption capacities are relied on the loaded metal oxides (surface chemistry) at this high concentration. It is also noted that NiO and CeO₂ modified AMC samples showed a higher capacity than CuO and Mn₃O₄ modified samples at all loadings when the CO₂ capacities are normalized to surface area. Interestingly, CO₂ adsorption capacity for NiO-AMC-30 is enhanced dramatically at lower pressure (below 0.4 bar) when compared with the pure AMC and NiO-AMC-10 samples. For all other modified samples, a slight increasing of CO₂ adsorption at low pressure is also observed at 30% metal oxides loading in comparison with the pure AMC. This indicates that both type and concentration of metal oxides play an important role on low pressure CO₂ adsorption behavior.

It is difficult to make a direct comparison of the effect of different metal oxides on the adsorption capacity of CO₂ on AMC because metal oxides affect both the surface chemistry (acid-base property) and the available surface area of the AMC samples. A balance of the two consequences is at play for the low and high loading of metal oxides on AMCs. At low loading (10%), the texture parameter or more complicated factors of the AMC takes over the surface chemistry from the oxides so that the modified AMC samples exhibit lower CO₂ capture capacity than the pure AMC sample. In the case of metal oxides modification with high loading (30%), more percentage of the surface of the AMC is covered with metal oxides and thus the surface

chemistry is more important for CO₂ adsorption than purely the surface area (texture parameter) at low CO₂ coverage. This leads to the general increase in CO₂ adsorption at low pressure for all the modified AMC samples although the total CO₂ capacity of the Me-AMC-30 samples is lower than AMC samples because of the dramatically decreased surface. A well balanced surface chemistry and surface area may be the reason for the similar CO₂ capture capacity (**Table 2**) for NiO and CeO₂-modified AMCs regardless of the oxide loading even though the surface areas are quite different (**Table 1**).

3.3. CO₂/N₂ selectivity and interaction energy

For a low-cost capture of CO₂ the selected sorbent must satisfy both large CO₂ uptake and good selectivity against other molecules (i.e. N₂) competing for the adsorption sites. Ideal selectivity values were obtained by applying a linear fit to the adsorption isotherms (CO₂ and N₂ (Figure S2)) at low pressure (below 0.2 bar) and calculating the ratios of the slopes. This provides a suitable measure of the selectivity at pressures appropriate for flue gas applications where the CO₂ partial pressure will be much less than 1 bar [34-37]. The CO₂/N₂ selectivity for all samples is presented in Table 2. Notably, for all the modified AMC samples (Table 2), metal oxides modification leads to significant improvement in the ideal CO₂/N₂ selectivity.

Figure 5 gives the ideal CO₂/N₂ selectivity for the NiO and CeO₂-modified AMC samples. The calculated ideal CO₂/N₂ selectivity for NiO-AMC-30 is 72% higher than that of the parent AMC with the selectivity increasing from 10.4 to 17.9 (Table 2). The CO₂/N₂ selectivity for CeO₂-AMC-30 and CeO₂-AMC-10 is 50.5 % and 30.0 % higher than the parent AMC, respectively. This enhancement in selectivity is ascribed to the surface chemistry factor, i.e., the increased interaction between CO₂ and the metal oxides dispersed on the carbon surface which would be highly advantageous for practical applications.

To understand the strong interaction, the CO₂ adsorption isotherms of the metal oxides modified AMC and parent AMC samples measured at 303 K and 273 K were fitted to a dual-site Langmiur-Freundlich model for calculation of isosteric CO₂ adsorption heat by using the Clausius-Clapeyron equation [34-37]. The curves for the calculated heats of adsorption are shown in **Figure 6**. For AMC modified with metal oxides modified at low loading, the initial heat of adsorption is clearly higher than the original AMC regardless of the type of metal oxides, which indicates relatively stronger interaction between the CO₂ molecular and the metal oxides on the AMC. As the CO₂ surface coverage increases, a decreased heat of adsorption is observed for the AMC samples until reaching a stable value in the range of 20 - 22 kJ/mol which is similar to the heats of adsorption for original AMC. This suggests that the CO₂ is mainly adsorbed on carbon surface at higher CO₂ surface coverage. For the AMC samples modified with higher loading of metal oxides, the heat of adsorption of CO₂ initially increases with CO₂ sorption before reaching a stable heat of adsorption, especially for the NiO-AMC-30 and CeO₂-AMC-30. Overall, the addition of metal oxides to the AMC surface resulted in an increase in the heat of adsorption at low coverage indicative of enhanced CO₂ interactions with surface functional groups. Therefore, more and strongly bonded CO₂ is expected for metal oxides modified AMC with higher heat of adsorption energy than on parent AMC. The evident yet unexpected rise of the heat of adsorption for CO₂ on the NiO-AMC-30 sample at low surface coverage is an indication of strongest interaction between CO₂ and the NiO component, which could explain the highest CO₂ adsorption capacity at low pressure and highest ideal CO₂/N₂ selectivity.

4. Conclusions

CO₂ sorption has been studied over activated mesoporous carbon (AMC) and metal oxides (CeO₂, CuO, Mn₃O₄ and NiO) modified AMC. Stronger interaction with CO₂ is introduced upon the loading of metal oxides on the AMC due to the different surface chemistry of oxides than the carbon surface. The altered surface chemistry and surface area are the two main factors affecting the CO₂ adsorption capacity and ideal CO₂/N₂ selectivity. The surface area factor plays the main role in determining the total CO₂ adsorption capacity at 1 bar so that the pure AMC shows higher capacity than the modified samples. However, at low CO₂ coverage, the surface chemistry factor appears to dominate the adsorption of CO₂ for the AMC samples with high loading of metal oxides (30%) so that their CO₂ adsorption capacities are generally higher than the pure AMC. The introduced strong interaction between metal oxides and CO₂ is shown to be beneficial to the ideal CO₂/N₂ selectivity for all the modified samples over the pure AMC sample. The NiO-AMC-30 sample gives highest CO₂ /N₂ selective with 72% increase over the pure AMC. This enhancement in selectivity is highly advantageous for practical applications. Overall, the results here highlight the importance of both surface texture characteristics and surface chemistry for improving the selective adsorption of CO₂, which are affected by the type and concentration of the metal oxides on AMC. It also point to an interesting yet also challenging direction to improve the performance of carbon-based CO₂ sorbents: highly dispersed metal oxides on carbon surface with minimal decrease of surface area to facilitate improved CO₂/N₂ selectivity without the loss of CO₂ sorption capacity.

Acknowledgements

This work is supported by the Center for Understanding and Control of Acid gas-induced Evolution of Materials for Energy of EFRC, an Energy Frontier Research Center funded by U.S. Department of Energy, Office of Science, Basic Energy Science.

Appendix A. Supplementary data

Additional TEM images, N₂ adsorption isotherms and normalized CO₂ capacities are available in the supporting information.

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Figure captions

Figure 1 The representative SEM images of a) CeO₂-AMC-10, b) NiO-AMC-10, c) AMC, d) CeO₂-AMC-30 and e) NiO-AMC-30.

Figure 2 N₂ adsorption isotherms A, C) and corresponding pore size distribution B, D) for the pure AMC and metal oxides-AMC.

Figure 3 The XRD patterns of AMC and varied metal oxides modified AMC with different metal oxides concentration.

Figure 4 CO₂ adsorption isotherms for the AMC and AMC modified by various metal oxides up to a maximum pressure of 1 bar at 303 K.

Figure 5 The ideal CO₂/N₂ selectivity for representative metal oxides modified AMC samples at 303 K.

Figure 6 The curves for the calculated heats of adsorption for metal oxides modified AMC and parent AMC.

Table 1 The BET surface area, pore volume and actual metal oxides content (measured from TGA) of all samples.

Samples	Surface area (m ² /g)	V _t * (cm ³ /g)	V _m * (cm ³ /g)	MeOx (wt%)
AMC	2475	2.1	0.7	-
CeO ₂ -AMC-10	1906	1.8	0.4	11.2 %
CuO-AMC-10	2097	1.9	0.5	8.9 %
Mn ₃ O ₄ -AMC-10	2267	2.1	0.6	7.8 %
NiO-AMC-10	2006	1.8	0.5	11.6 %
CeO ₂ -AMC-30	1269	1.2	0.3	40.1%
CuO-AMC-30	1099	1.0	0.3	43.6 %
Mn ₃ O ₄ -AMC-30	1139	1.1	0.3	44.0 %
NiO-AMC-30	1145	1.1	0.3	37.3 %

*: V_t: total pore volume; V_m: Micropore volume.

Table 2 Adsorption properties of AMC and metal oxides modified AMC

Samples	CO ₂ adsorption at 273K (mmol/g)		CO ₂ adsorption at 303K (mmol/g)		CO ₂ /N ₂ selectivity	
	0.1bar	1 bar	0.1 bar	1bar	273K	303K
AMC	0.91	4.66	0.32	2.25	10.4	10.3
CeO ₂ -AMC-10	0.68	3.39	0.32	1.85	13.8	13.4
CuO-AMC-10	0.65	3.66	0.21	1.80	11.6	10.8
Mn ₃ O ₄ -AMC-10	0.71	3.84	0.28	2.00	11.1	10.9
NiO-AMC-10	0.72	3.67	0.29	1.90	11.6	11.0
CeO₂-AMC-30	0.76	3.13	0.44	1.77	15.5	15.5
CuO-AMC-30	0.62	2.40	0.37	1.42	11.7	12.3
Mn₃O₄-AMC-30	0.67	2.55	0.38	1.48	12.7	12.2
NiO-AMC-30	1.08	3.30	0.62	2.02	17.9	17.6

Figure 1. The representative SEM images of a) $\text{CeO}_2\text{-AMC-10}$, b) NiO-AMC-10 , c) AMC , d) $\text{CeO}_2\text{-AMC-30}$ and e) NiO-AMC-30 .

Figure 2. N_2 adsorption isotherms A, C) and corresponding pore size distribution B, D) for the pure AMC and metal oxides-AMC.

Figure 3. The XRD patterns of AMC and varied metal oxides modified AMC with different metal oxides concentration.

Figure 4. CO₂ adsorption isotherms for the AMC and AMC modified by various metal oxides up to a maximum pressure of 1 bar at 303 K.

Figure 5. The ideal CO_2/N_2 selectivity for representative metal oxides modified AMC samples at 303 K.

Figure 6. The curves for the calculated heats of adsorption for metal oxides modified AMC and parent AMC.

TOC:

Graphic Abstract