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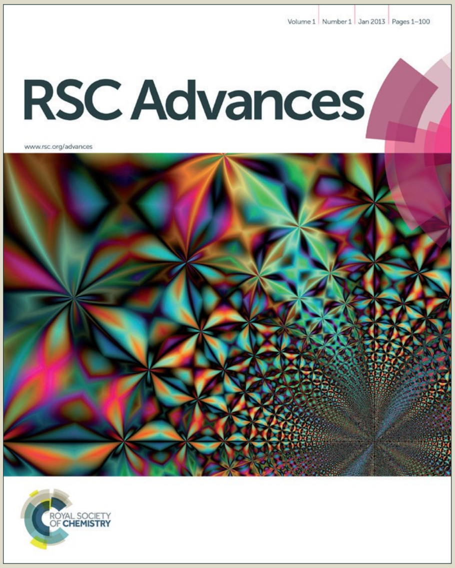

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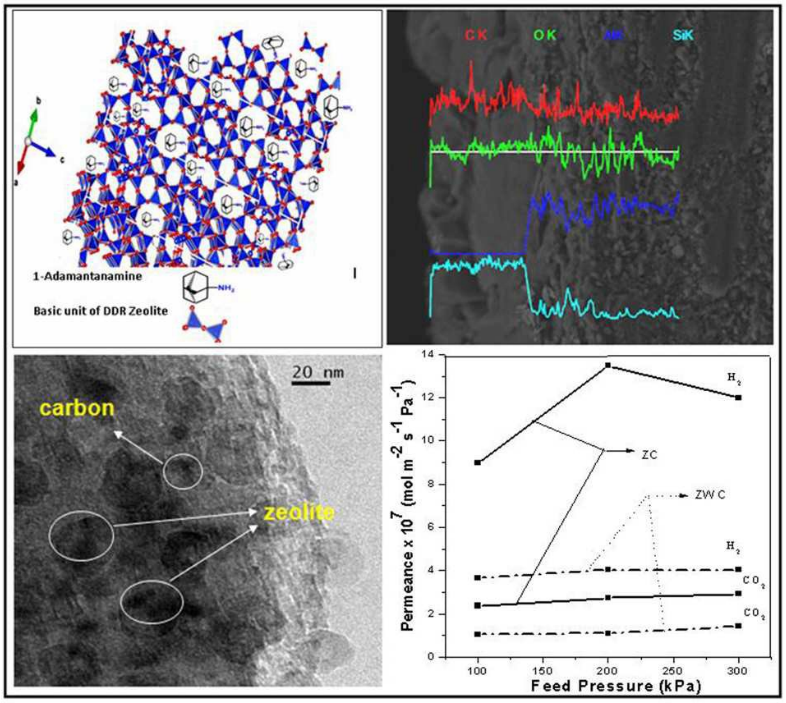

Carbon loading from decomposition of 1-adamantanamine in the DDR zeolite membrane pores makes H_2-CO_2 permeance and separation efficiency higher.

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Pore Modification Of Deca-Dodecasil-Rhombohedral Zeolite Membrane by Carbon Loading from In-situ Decomposition of 1-Adamantanamine for Improved Gas Separation

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Abstract

A simple method of pore modification coupled with the removal of surface defects of Deca-Dodecasil-Rhombohedral (DDR) zeolite membrane was developed by Carbon (C) deposition. The carbon deposition was achieved by the controlled decomposition of the structure directing agent (SDA), 1-Adamantanamine (1-ADA), into the membrane pore surface. The membranes synthesized with and without pore modification were characterized by Thermal analysis, X-ray diffraction analysis, Infra Red spectroscopy, Transmission electron microscopy, Raman spectroscopy etc. Finally, performances of the membranes were evaluated by permeance studies. The non wetting characteristics of C had imparted the hydrophobicity of the membrane pores leading to enhanced permeability of the gas mixture. The modified membranes had shown to offer relatively high hydrogen permeance of 13.47×10^{-7} $mol.m^{-2}.s^{-1}.Pa^{-1}$. The selectivity of H_2 / CO_2 was 4.9 based on single gas permeation and the separation factor was increased up to 8.5 for gas mixture (H_2-CO_2) at room temperature. In the light of these findings, the current technique is proposed to be useful for making a defect free C loaded membrane in a single step with a high separation selectivity and permeability in tandem. This is the novelty achieved.

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1. Introduction

Hydrogen (H_2), often referred to as “clean energy” [1] is required to be separated at a level of high purity, from a mixture of H_2 and CO_2 as products of Water Gas shift reaction [2]. The current methods of purification of H_2 are pressure swing adsorption (PSA) [3,4] fractional /cryogenic distillation [5, 6], membrane based separation process etc [7, 8]. These methods have their own merits and demerits. However, membrane based separation of H_2 assumes significant importance due to its energy saving potential. Inorganic membranes amongst others have the potential for H_2 separation at high temperature owing to their high thermal and chemical stabilities. Zeolites, a special class of inorganic membranes, are being routinely used in heterogeneous catalytic reaction, ion exchange, sensors, corrosion protection coatings, microelectronics device and are also being utilized for gas separation application due to their additional advantages such as well-defined pore structure with sub nanometer size, and good adsorption properties [9, 10]. Furthermore, zeolite membranes with small pore size have the potential to separate light gases based on molecular sieving effects. Decadodesil 3R framework, an efficient member of zeolite family, having pore diameter 0.36x 0.43 nm, has studied for various applications and most notably, has shown excellent performance in H_2 gas separations from other light gases like CO_2, N_2, CH_4 etc [11-13]. In gas separation applications, DDR membranes have however, encountered problems of inadequate permeance and H_2 selectivity over gases like CO_2 (0.33 nm), N_2 (0.34 nm) due to

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almost similar sizes of the kinetic diameters of permeating gases and DDR pore diameter (0.36 nm). For addressing these problems, efforts have so far been made towards eliminating defects present in polycrystalline zeolite membranes by post-synthetic treatments like hydrocarbon impregnation and coking [14, 15] surface coating [16, 17], chemical vapor deposition (CVD) using tetraethyl orthosilicate, methyl diethoxy silane [18, 19], and chemical liquid deposition (CLD) etc. [20]. Beside some advantages, these methods have distinct limitations such as significant reduction of flux due to the pore blockage of zeolite, pore modification requiring additional steps, and cost intensive methods due to incorporation of silane. On the other hand, the SDA needs to be removed after forming the pore structure of the zeolite from its pores by calcinations. The utilisation of the template is therefore, becoming a challenging task for making the zeolite synthesis process cost effective.

In order to avoid these shortcomings, the current research investigation has been undertaken to develop a method for synthesizing the zeolite membrane in an energy efficient manner realistically. In this method, the DDR zeolite membrane was synthesized on low cost clay-alumina support tubes by hydrothermal process followed by controlled heat treatment to deposit the C particles by decomposition of SDA (1-ADA) as a C source, on the zeolite pore surfaces at a temperatures 600 ^{0}C. The objective of deposition of the C is to modify the zeolite pores by reducing the size of the zeolitic and non-zeolitic pores that can effectively separate CO_2 from H_2. Additionally, the non wetting properties of C would impart the hydrophobicity of the membrane that would also increase the permeability of the gas mixture. Thus the combined effect of pore size contraction and non wetability of the membrane pores would enhance the overall membrane performance. On the other hand, as the cost of 1-ADA is quite high, if it can be used as precursor for C for pore modification of zeolite membrane, the process might be economically suitable. In fact, incorporating the modifying agents into the constricted pores makes the modification process difficult. To avoid this difficulty, carbonization by controlled heat treatment

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of the SDA, already present inside the pore could be a successful approach. The concept of the present development is schematically shown in Fig. 1.

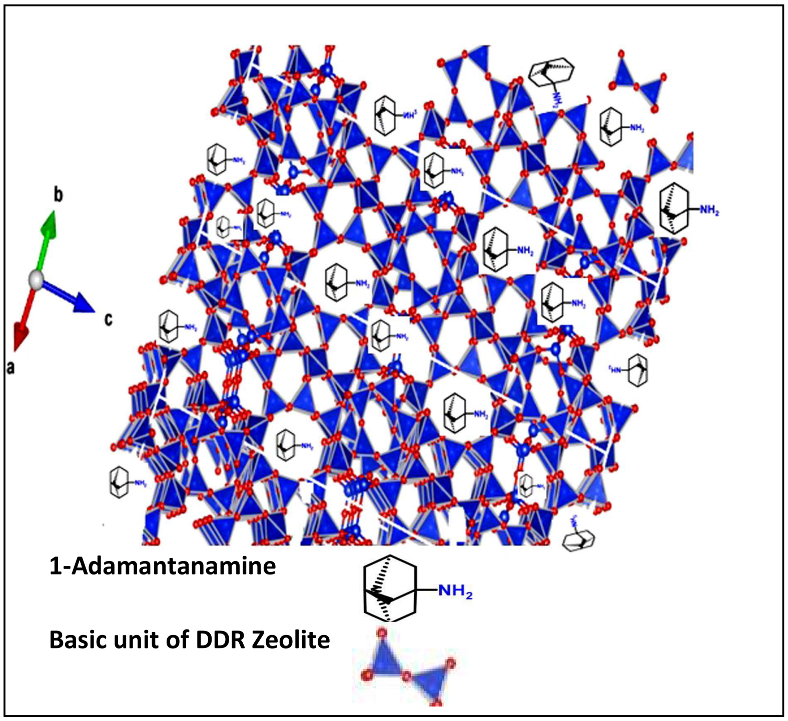

Fig. 1 Schematic representation of 1- adamantanamine loaded DDR zeolite structure in 8 - membered zeolitic pores.

The zeolite membranes synthesized were then characterized by various analytical techniques and finally performance was measured by separating H_2 from H_2/CO_2 gas mixtures. In order to isolate the impact on performance of C loading on DDR zeolite membrane for separating gas mixture, experiments were also carried out using DDR membrane without C loading and compared with those obtainable in case of DDR membrane with C loading. The novelty of the current development is the better performance of the membrane synthesized for higher H_2 permeance and separation efficiency compared to those reported in the literature. In this article, C loaded DDR membrane and DDR membrane without C loading are described as **ZC** and **ZWC** respectively.

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2. Experimental

2.1 *Materials*

The chemical reagents used for synthesis of DDR zeolite seeds are colloidal silica (Ludox HS-30 Sigma Aldrich), 1-ADA (Aldrich, India) and ethylene diamine (Merck, India). The molecular formula of 1-ADA is C_{10} H_{17} N and molecular weight is 153.1. Water was purified using a Millipore Milli-Q system (18.2 MΩ·cm). Hydrogen (99.99 %), carbon dioxide (99.99 %), were obtained from BOC India Ltd. An indigenous clay–alumina tube of specified dimension (diameter 10 mm, thickness 3mm and length 100 mm) was used as support for synthesis of the membrane.

2.2 *DDR seed synthesis*

A mixture of measured amount of colloidal silica and deionised water (DI water) was prepared in a glass beaker (mixture-1). The solution was stirred with a magnetic stirrer (SCHOTT Instruments GmbH, Germany) at 200 rpm for 30 minutes. In another mixture (mixture-2), 1-ADA was mixed with ethylene diamine and the calculated amount of DI water was added to the reaction mixture. After stirring the mixture-2 for 1 h, it was mixed slowly with mixture-1 under vigorous stirring constantly. All these procedures were carried out at room temperature. The resulting mixture was sonicated for 3 h. The energy input for sonication was 250 W. The molar composition of the sol used for the synthesis was 1 silica: 0.5 1-ADA : 4 ethylene diamine : 100 water. The powdered products were recovered through centrifugation, washed with DI water until pH < 8.

2.3 *Seeding of the support surface*

Seeding of the substrate was done by dispersing DDR seed crystals in DI water under ultrasonication for 2 h. Before seeding, the substrates were cleaned with acetone in ultrasonic cleaner (vibracell, USA) for 10–15 minutes just to remove the dust particles and oily matter. The outer surface of the support tubes was wrapped with Teflon tape so that the zeolite layer was formed inside the tube. The support substrate was dipped in a 3 wt% DDR zeolite seed suspension

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DI water 5 times for duration of 15 s. The seeded supports were dried after the dipping at 100^0 C for 24 h.

2.4 *Synthesis of DDR membrane on support surface*

DDR membrane (ZWC) was prepared by placing the seeded substrates vertically in an autoclave. The autoclave was filled with the sol having composition elaborated in Sec. 2.2 earlier. The autoclave was heated at temperature of 160 ^{0} C for 5 days. The zeolite coated membrane, synthesized in the process was washed thoroughly with DI water until the pH of the washing liquid became neutral. The membrane synthesized, was calcined in air at 600 ^{0}C for 5 h to remove the organic compounds. Carbon (C) loaded membranes (ZC) were synthesized following the same procedure as in case of ZWC. However, the only difference in this case was that the membrane was calcined after washing, in controlled atmosphere at 600^0 C for 24h whereby carbon got deposited onto it.

2.5 *Characterisation*

The crystalline structure and phase purity of the powder synthesized as seed and the membrane were determined by X-ray diffraction pattern (XRD) analysis. The XRD carried out on a Philips 1710 diffractometer using CuKa radiation (α =1.541 Å). The characteristics vibration bands for DDR seed crystal were investigated by Fourier Transformed Infrared spectra (FTIR) (Nicolet 5 PC, Nicolet analytical instrument, Madison, WI). Microstructure and pore size distribution of the support tube was studied by Field Emission Scanning Electron Microscopy (FESEM: model Leo, S430i, UK) and Mercury Porosimetry (Quantachrome Instruments, model Poremaster PM-60-13) respectively. Microstructure and morphology of the seed and membrane layer, elemental mapping with energy dispersive X-ray (EDAX), and cross sectional line scanning were examined using field emission scanning electron microscopy (FESEM) . The presence of the C in the membrane surface was observed through Transmission electron microscope (TEM). TEM and High resolution transmission electron microscopy (HRTEM) was performed using a Tecnai G2 30ST (FEI company, USA) operating at 300 kV. TEM samples were prepared by drop

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casting of dilute membrane powder solution followed by scratching off the coatings of the ZC and ZWC membrane layers onto the carbon-coated Cu grids. To identify the presence of C, Raman analysis was carried out by Raman microscope (RENISHAW inVia, K). X-ray photoelectron spectroscopy (XPS) measurements of the ZC membrane was carried out on an XPS system (PHI 5000 VersaProbe II, ULVAC-PHI, INC., USA) using a monochromatic Al Kα X-ray source (1486.6 eV). The pore size distribution of synthesized zeolite membranes (ZC and ZWC) has been measured by N_2 adsorption isotherm (Quantachrome Instruments Autosorb I Model No. ASIMP-LP2, USA)

Gas permeation was measured by a specially designed permeation cell developed in the laboratory indigenously. For permeation experiments, the membrane was mounted in a stainless steel permeation cell, sealed between two silicon O-rings. Simultaneously, the leak test was carried out before permeation experiment of each individual gas in order to obtain the correct data. The complete description of gas permeation measurement is given in the supporting information (Fig. S1).

3. Results and discussions

In our preceding work, the detailed study on the gradual formation of DDR zeolite within short period was described [21.] In that study, the mechanism of the pore formation between silica network and structure directing agent during the structure development of DDR zeolite membrane was proposed. Actually, SDAs play a key role for developing membrane pore morphology for DDR zeolite formation (Fig.S2 and Fig. S3). The C loaded DDR zeolite membrane was prepared from DDR zeolite and 1-ADA with heat treatment under controlled operating conditions as described earlier. The results obtained by various characterisations are discussed first followed by the performance analysis of the C loaded DDR zeolite membrane

The temperature and atmosphere of the calcination during preparation of ZC was determined by thermal analysis of the pure 1-ADA and also 1-ADA loaded membrane. The

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results of thermal analysis of the membranes before and after calcination of the membrane are shown in Fig. 2a-b.

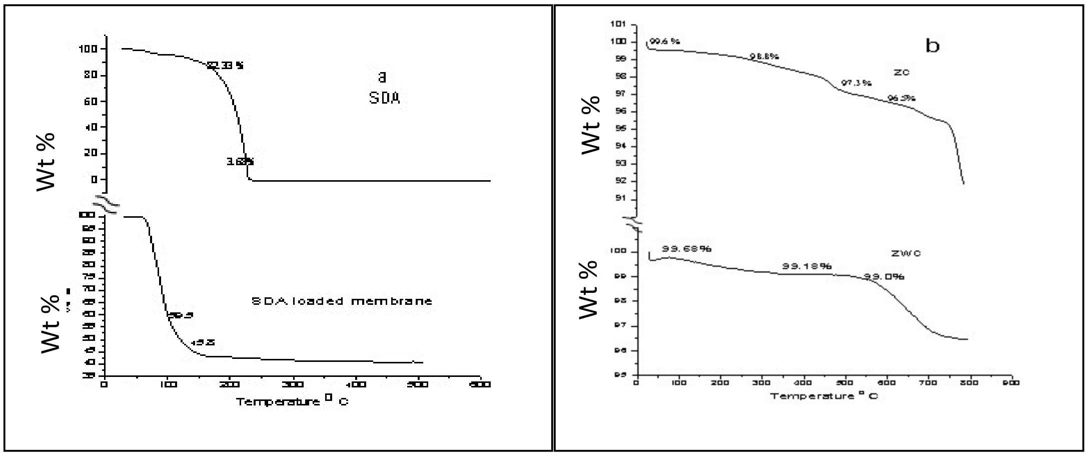

Fig. 2 TGA pattern of (a) only SDA (1-adamantanamine) and SDA loaded membrane (b) DDR membrane with C loading (ZC) and without C loading (ZWC).

Fig. 2a shows the TGA analysis of 1- ADA and 1-ADA loaded DDR membrane. It can be seen from the figure that in case of pure 1-ADA weight (wt.) loss upto 150 ^{0}C was ~ 7%. It might be due to the presence of moisture and other organic solvents. On further heating the wt loss reached up to 99.4%, might be perhaps due to complete decomposition and removal of 1- ADA (Fig. 2a). However, the decomposition behaviour is completely different in case of the membrane. The TGA analysis of the membrane was carried out simulating the conditions adopted during the membrane synthesis, i.e. the analysis was performed in N_2 atmosphere, up to 600^0 C with a heating rate of 10 ^{0}C per minute for partial oxidation of SDA. The wt. loss was recorded in the thermographs. The thermograph suggests a stepwise decomposition of the organic template, 1-ADA and others. The wt loss upto 41 % might be due to the decomposition of different organic components and also due to partial oxidation of 1-ADA. On further heating upto 600 ^{0} C the weight loss became constant at 54.32 %. Comparing this data with pure 1-ADA, it suggests that adsorbed species of 45% remained in the membrane even after it was kept at 600 ^{0}C. Based on this study, membranes were calcined at a temperature of 600 ^{0}C for 4h. Fig. 2b describes the

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thermal analyses of the ZC and ZWC membranes developed. In case of ZC membrane, the observed wt. loss of 3.4 % at 600^0 C might be due to the removal of moisture and other minute organic compounds present after removal of organics in ZC membrane. After calcinations, the crystalline structure of ZC membranes and powders identified were compared with those of uncalcined membrane by X-ray diffraction (XRD) analysis. Fig. 3a describes the XRD pattern of membranes before calcinations, while Fig. 3b and Fig. 3c show the XRD pattern of ZC membrane and corresponding powders respectively. All the diffraction peaks are almost similar and the d-values, i.e. (101), (004), (210), (008), (301), and (131) are in agreement with those reported in the literature besides the appearance of clay-Al_2O_3 signals from the support [22]**.**

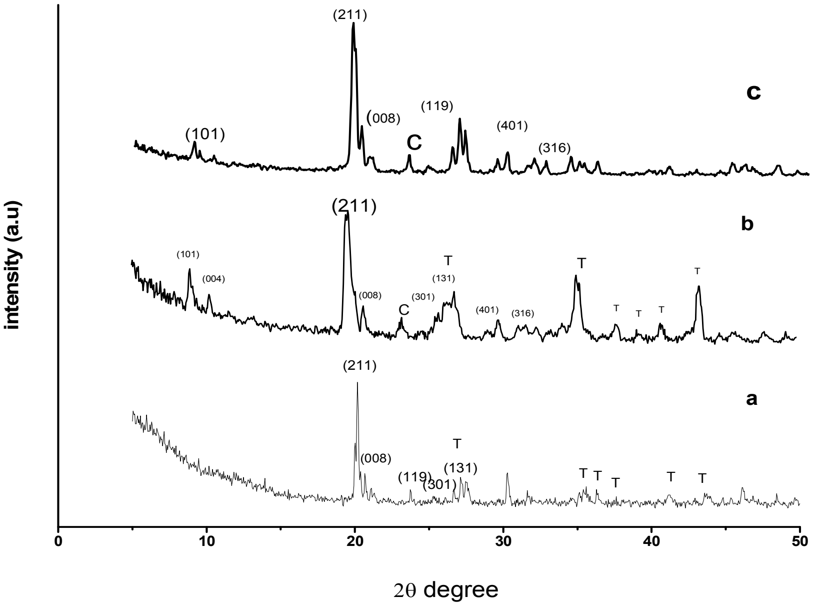

Fig. 3. XRD pattern of zeolite membrane (a) before calcination, (b) after calcination and C loading, (c) zeolite powder from ZC membrane where 'C'; denotes the peak for amorphous carbon and 'T' denotes the support.

The XRD pattern of the ZC membrane was almost identical that of uncalcined membrane with the appearance of only peak at 25.1 (2θ) confirming the formation of carbon (C) phases as shown in Fig. 3 a-b. The peak intensity was very small compared to other peaks. From this result, it is confirmed that there was no structural change of zeolite after incorporation of C. The lower

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intensity of the C peak in zeolite powder might be due to higher exposure of the powder compared to that of the membrane during calcinations and as a result, C loss observed was more.

The same observation was confirmed by IR analysis in Fig. 4. The samples showed strong vibration at 1385, 787, 767, 647, and 437 cm^{-1} etc. The characteristics band at 437 and 767 cm^{-1} are assigned to O-T-O (T=Si) bending and Si-O tetrahedral vibration respectively. The appearances of the peaks at 647 and 1640 cm^{-1} are attributed due to the double ring external linkage, vibration of water molecule. The peak at about 747 cm^{-1} is assigned to the symmetric stretching vibration of internal tetrahedron. The FTIR spectra further shows the additional peak at 1500 – 1550 cm $^{-1}$ that could be attributed due to C = C and C-NH bonds confirming the presence of C in sp^2 hybridization state and the source of C contributed from the decomposition of 1-adamantanamine [23, 24].

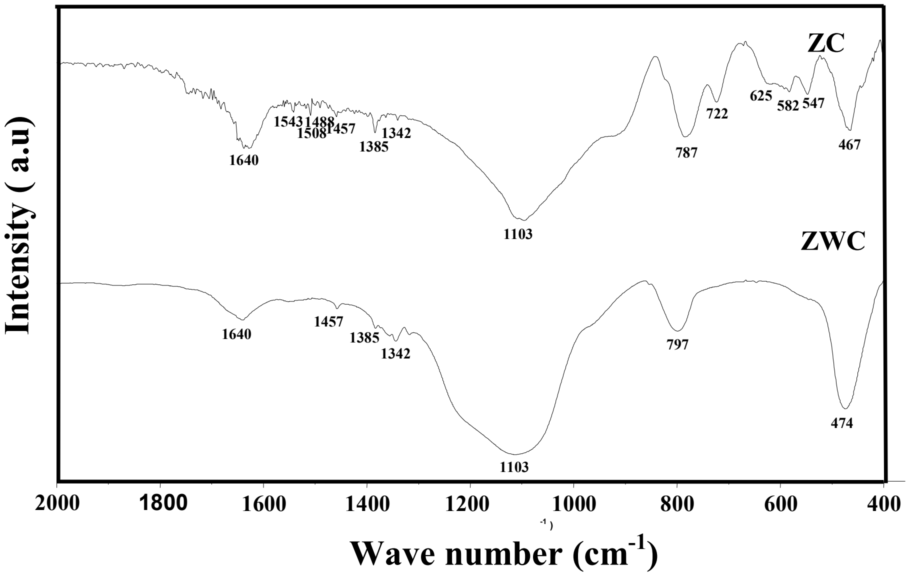

Fig 4 FTIR spectra for ZWC and ZC membranes.

After confirmation of the phase formation, the physical appearance of the membrane and the detail microscopic information of the membrane layer along with support tube were investigated as shown in Fig.5 and 6. Fig. 5 a-b show the morphology and pore size distribution of the support

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tube respectively. Both the figures depict that the support surface has an average pore size (d_{50}) ~1 micron with a narrow pore size distribution and the pores are homogenously distributed. Highly porous support with narrow size distribution makes it suitable for using as support for membrane growth.

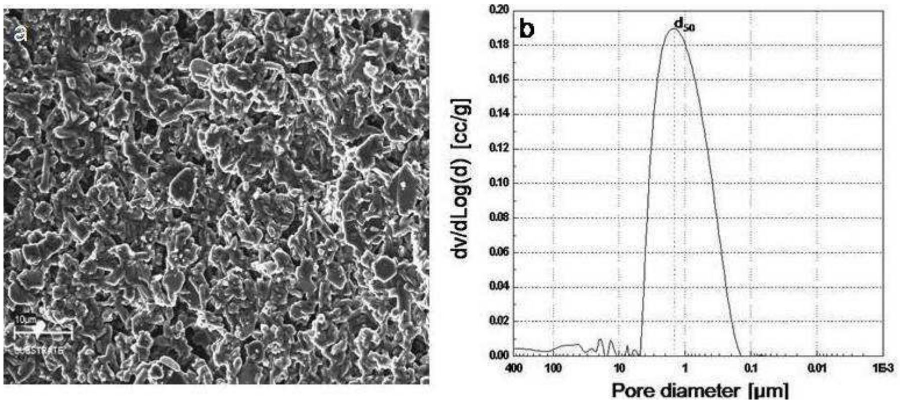

Fig. 5 (a) FESEM image of clay-alumina tubular support (b) Pore size distribution of clay-alumina support using mercury porosimetry.

Fig. 6a shows the photographs of the membranes, on which the black appearance over the membrane surface confirms the uniform distribution of the Carbon layer. To get the morphology, thickness and line scanning elemental analysis, the ZC membrane layer was monitored by FESEM. Fig. 6b describes the surface morphology of the membrane layer. It can be seen from the figure that the membrane layer was totally covered by uniform and compact cubic-shaped crystals without showing any visible cracks, pinholes or other macroscopic defects.

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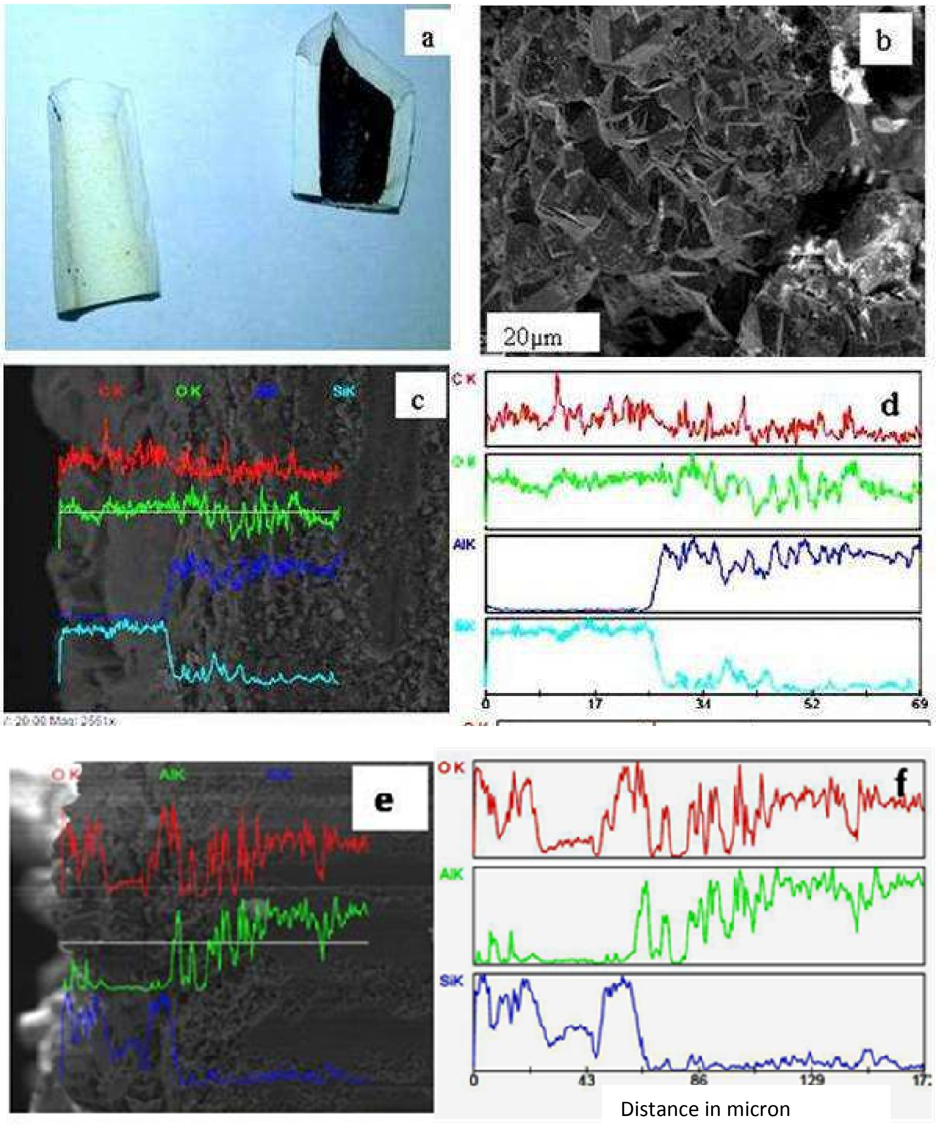

Fig. 6 (a) Photograph of ZWC and ZC membrane, FESEM micrograph of (b) ZC membrane layer; (c) cross-sectional view of ZC membrane; (d) the corresponding spectra of O, Si, Al and C during the elemental scan (distance in micron), (e) cross-sectional view of the of ZWC membrane, and (f) the corresponding spectra of O, Si, Al and C during the elemental scan (distance in micron)

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Fig. 6c shows the cross-sectional FESEM image of the well intergrown membrane having, a smooth interface without defects or non-zeolitic pores with a thickness of about 30 µm. Fig. 6 d shows the elemental analysis of the ZC membrane along the thickness developed on the support surface and there are no inter-crystalline gaps or defects in the layer. The line scanning shows that there was no signal of Al up to ~30µm, but intensity of the C peak increased sharply. It indicates that pure Si containing DDR zeolite phase was present upto ~30µm. Interestingly, though the presence of carbon was detected throughout the total membrane, but the increased intensity was detected only at the interface of the substrate and membrane layer. The deposition of the C layer at the interface might increase the hydrophobic as well as non wettable character of the membrane layer indicating positive effect on the overall performance of the membrane. Fig. 6 e-f show the cross section and line scanning of ZWC membrane. Comparing with ZC membrane, FESEM micrograph of ZWC membrane shows no carbon peak which denotes the absence of carbon in the structure. .

To obtain more detailed structural insight, ZC and ZWC samples were investigated by TEM analysis. Fig. 7 shows the TEM images of the membranes. Fig. 7a describes that carbon micro spheres were dispersed in zeolite matrix. Minute observation shows that core shell structured C spheres were also formed after heat treatment of the template loaded membrane. Fig. 7b describes the core and shell structure of the C spheres formed after heat treatment of DDR zeolite membrane. Fig. 7c shows the C spheres along with zeolitic materials. For carbon phase, both amorphous and nano crystalline phases were observed dispersed in zeolite matrix. Fig. 7d shows the HRTEM images of the C particle. The value of lattice spacing of 0.36nm confirms the presence of C**.** Fig. 7e shows the selected area electron diffraction (SAED) pattern of ZC membrane. The SAED pattern of the powders (scratched out from the membrane surface) confirms the presence of DDR zeolite and Carbon. For comparison, C free membrane layer (ZWC) was also investigated by TEM analysis. Fig. 7f shows the TEM micrograph of ZWC

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membrane (powder obtained from membrane layer by the same procedure), while inset of Fig. 7f shows the EDAX analysis of the corresponding area.

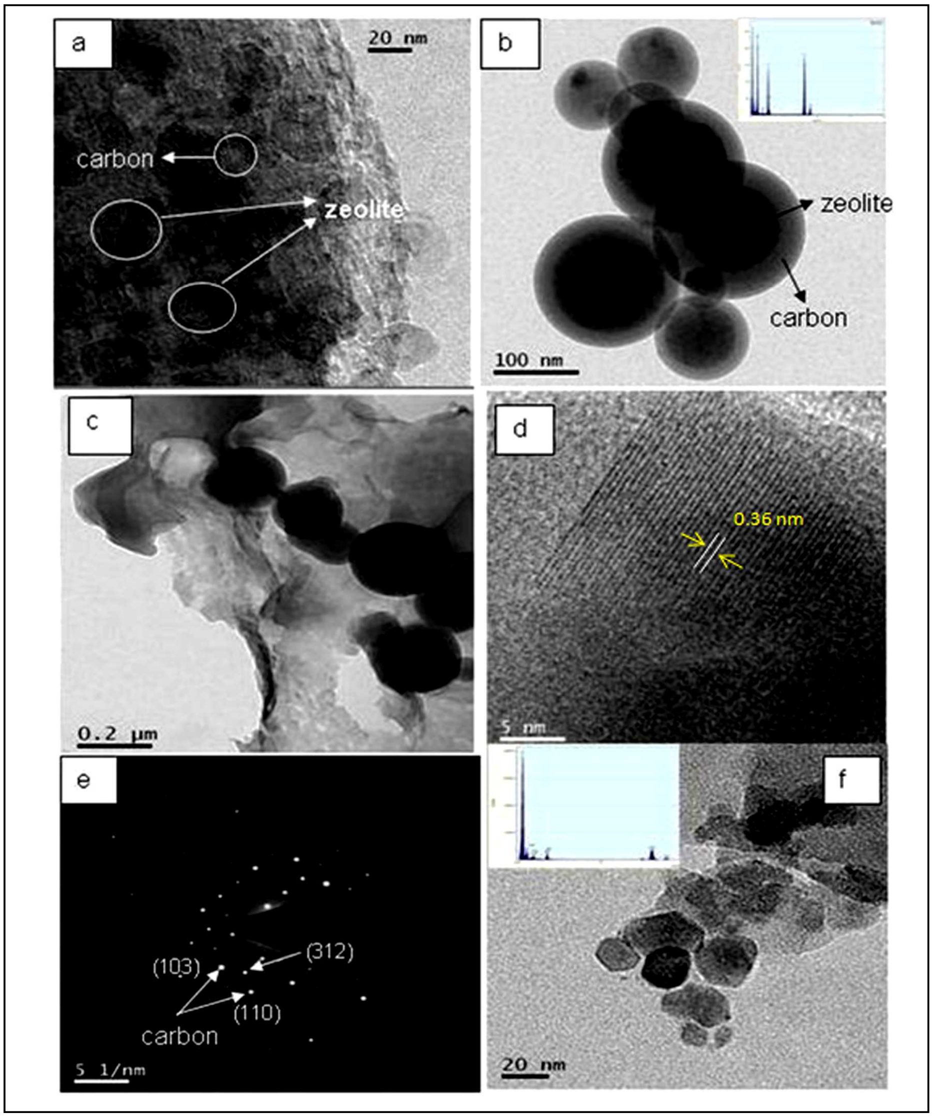

Fig. 7 TEM micrograph of (a) Carbon loaded zeolite membrane layer (ZC); (b) images of zeolite core shell structures along with amorphous carbon after carbonisation;(c) Bright field (BF) image of ZC shows the regular pattern of zeolite -carbon core shell structure; (d) HRTEM images of C-loaded zeolite membrane; (e) SAED pattern of C loaded membrane;(f) BF image of ZWC membrane (inset EDAX pattern of ZWC zeolite membrane)

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Raman spectroscopy, a powerful technique was used to study the presence of C loaded materials for ZWC and ZC membranes.

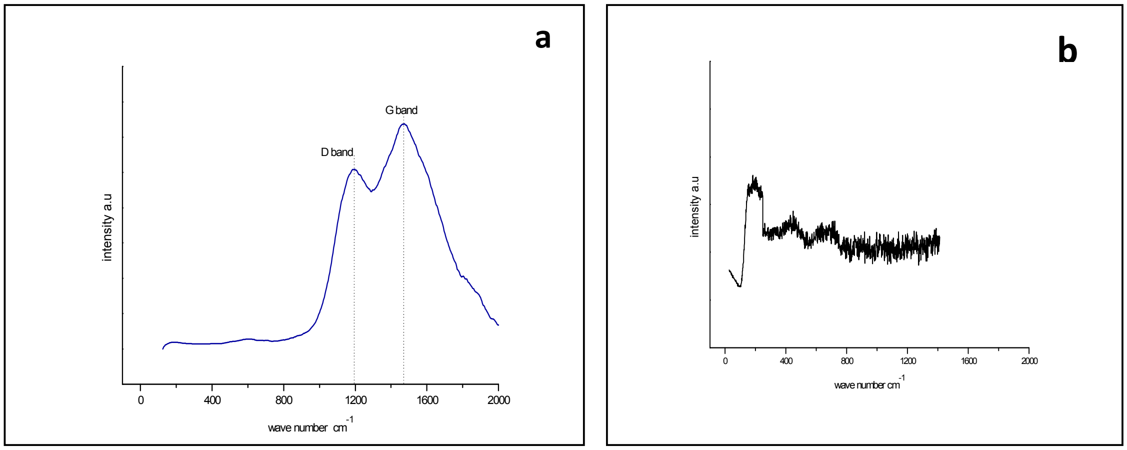

Fig. 8 Raman spectra of (a) C-loaded membrane (ZC).), and (b) calcined membrane (ZWC) (514.5 nm LASER as excitation source is used for the collection of Raman spectra).

The spectra were recorded using a 514.5 nm LASER as excitation source. The spectrum in Fig. 8a shows peaks at 1200 and 1480 cm^{-1} for ZC. The peak at 1480 is the D peak of amorphous carbon. The peak at 1200 cm^{-1} has been attributed to nanocrystalline carbon. The 1200 cm^{-1} mode always has a companion mode at 1480 cm^{-1} [24, 25]. But in case of ZWC membrane, no such peaks could be seen confirming the absence of C as shown in Fig. 8b.

In order to understand the presence of C in the membrane layer after heat treatment, X-ray photoelectron spectroscopy (XPS) analysis was carried out. Fig. 9 shows the XPS pattern of ZC membranes and their related binding energies. The XPS study was performed to ascertain the compositional information as well as the electronic state of the C present in the membrane after calcinations. The XPS of C 1s shows the peak located at 283.6 that corresponds to the graphitic carbon, [26] and confirms the presence of C in ZC membrane matrix. In addition, one peak was observed at 282.2 which corresponds to the signal from C- zeolite surface. [27].

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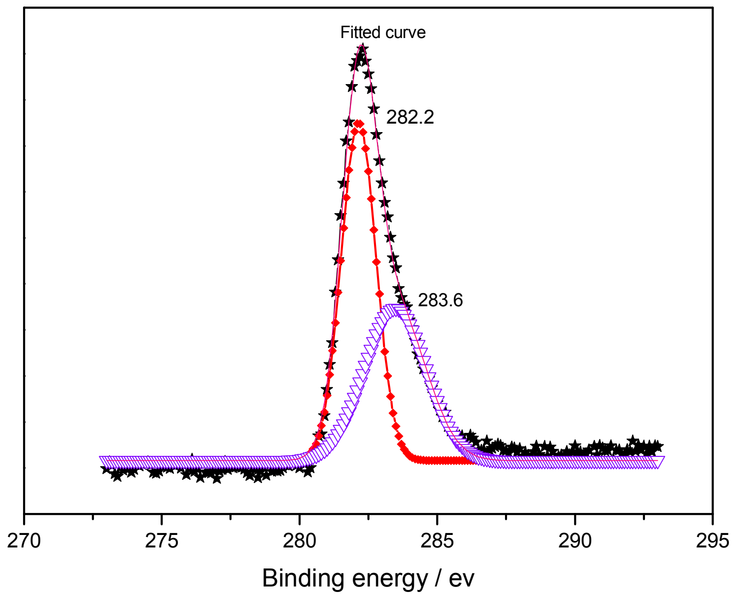

Fig. 9 Fitted and deconvoluted XPS spectra for the C 1s region of the C loaded DDR (ZC) membrane.

To evaluate the presence of zeolitic and non zeolitic pores in the developed membrane, pore size distribution was measured by N_2 adsorption desorption method. Fig. 10 a and b show the pore size distribution and average pore size of the ZC and ZWC membrane respectively. Here the pore size distribution has been calculated by Horvath- Kawazoe (HK) method. This technique has been successfully used for the determination of the pore size distribution of zeolites, activated carbon and other mesoporous materials[28] .The micropore size and its distribution for both the membranes ZC and ZWC are shown in Fig 10. Each figure shows sharp peaks in two regions, which indicates that each membrane contains monodisperse pores of zeolitic and non zeolitic in nature . Fig. 10 a and b shows that ZWC membrane contains pores with diameter of 3. 68 Å and 6.68 Å whereas ZC membrane contains pores having diameter 4.09 Å and 7.08 Å respectively. In case of C-loaded membrane, the pore sizes are of slightly larger values. The difference may be due to the variation of the interaction potential between adsorbate and pore wall. Due to the presence of quadrupole moment of N_2 molecule, the interaction between polar ZWC membrane (

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usually zeolite pore wall contains surface charges) and nitrogen might be different from that of between ZC and nitrogen which ultimately results the difference in pore size.

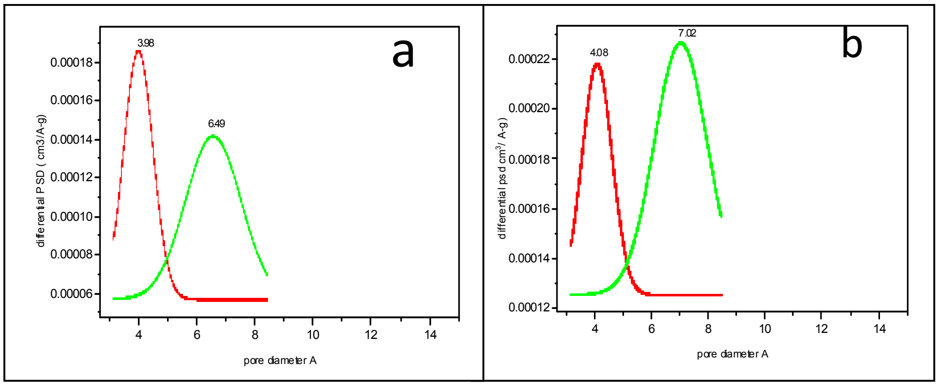

Fig. 10 Pore size distribution of (a) ZWC membrane (b) ZC membrane by N_2 adsorption desoption method using HK technique

Finally, in order to assess the membrane quality, gas permeation studies were carried out at room temperature in different feed pressures. The flow rate of different gases was controlled by a mass flow controller (MFC). Fig. 11 describes the single gas permeance of H_2 and CO_2 gases through ZC and ZWC membranes prepared on clay alumina supports with and without C loading at 30 °C and different feed pressure. It is interesting to note that single-gas permeance through the ZC membrane at room temperature changed drastically in comparison to ZWC membrane. The rate of increase of H_2 permeance through carbon loaded membrane (ZC) is much higher than that of CO_2. It could be attributed due to the fact that the deposition of C layer makes the pore surface

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non wettable which restricts the moisture absorption to the pore surface and as the kinetic diameter of H_2 (0.29 nm) is less than CO_2 (0.33 nm), H_2 permeates faster than CO_2 through the channel of DDR zeolite having pore size 0.36 nm.

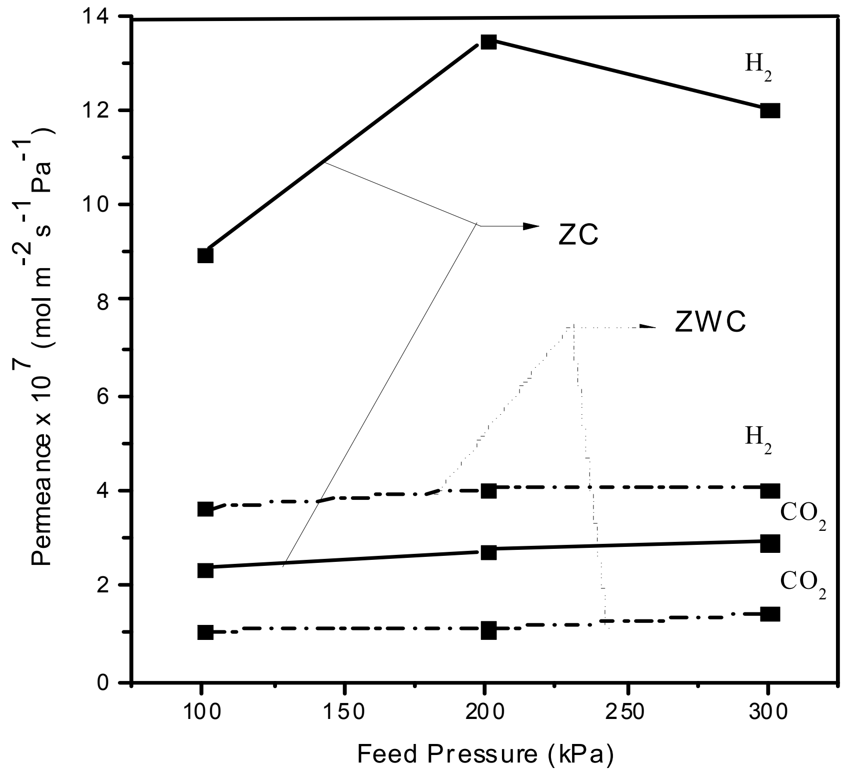

Fig.11 Single gas permeance of H_2 and CO_2 for ZWC (dotted line) and ZC (solid line) at 30 ^{0}C as a function of different feed pressure.

The ZWC membrane, did not impart any non wettable charcter on the membrane pore surface and thus shows no influence on the permeability characteristics. So, the permeance of H_2 was higher than that of CO_2, because of the lower kinetic diameter of H_2 as usual. But the single gas permeation for both the gases increased for ZC membrane. Usually, after pore modification and removal of non zeolitic pores, the permeability decreases drastically. But in the present investigation, the permeability increased abruptly after pore modification and removal of defects, especially in case of H_2. In addition, the non wettable character of the membrane pore surface

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influences more for H_2 permeation than that of CO_2. The presence of the quadrupole moment of CO_2 molecule results in the strong interaction with the membrane pore surface which may be predominant over the influences of the non wettable character of the membrane pore on permeation, and ultimately lowers the permeation rate through zeolitic pores. So the difference in permeability between H_2 and CO_2 gas through ZC is much more than that of ZWC membrane.

The increased permeability would be explained by the presence of C layer. The non wettable character of the C layer inhibit moisture (present in the gas mixture as well as in the environment) to come in contact with the membrane layer making the membrane pore available for gas diffusion. As a result, permeability increased for both H_2 and CO_2. In contrast, pores of ZWC membrane might be partially occupied by the moisture resulting in lower value of permeance. The rate of increase of permeability of H_2 was more than CO_2. Here the permeability of CO_2 was increased due to non wettability of the pore surface. On the other hand, the permeability of CO_2 decreased because with increasing pressure the desorption rate became lower (due to the presence of quadrupole moment of CO_2, it may adsorbed on the zeolite pore surface during permeation followed by desorption and diffusion). The combined effect resulted into relatively lower permeability values. In the light of these observations, it can be concluded that the pore sizes of zeolitic and non-zeolitic pores are minimum in case of ZC membrane.

The effects of feed pressure on the selectivity of the single gas permeation of H_2 and CO_2 are shown in Fig. 12a. for ZC and ZWC membranes. It can be seen from the figure that the selectivity was gradually increased with increasing feed pressure up to 200 kPa beyond which the selectivity was decreased. It could be perhaps due to the higher permeance values of H_2 as compared to CO_2 at different feed pressure. The highest H_2/CO_2 selectivity observed was 3.7 in case of ZWC membrane however, it reached a value of 4.9 in case of ZC membrane. The enhancement of the separation performance could be attributed due to the reduction of non zeolitic pores as well as the non wettability characteristics of the zeolitic pores of the membrane.

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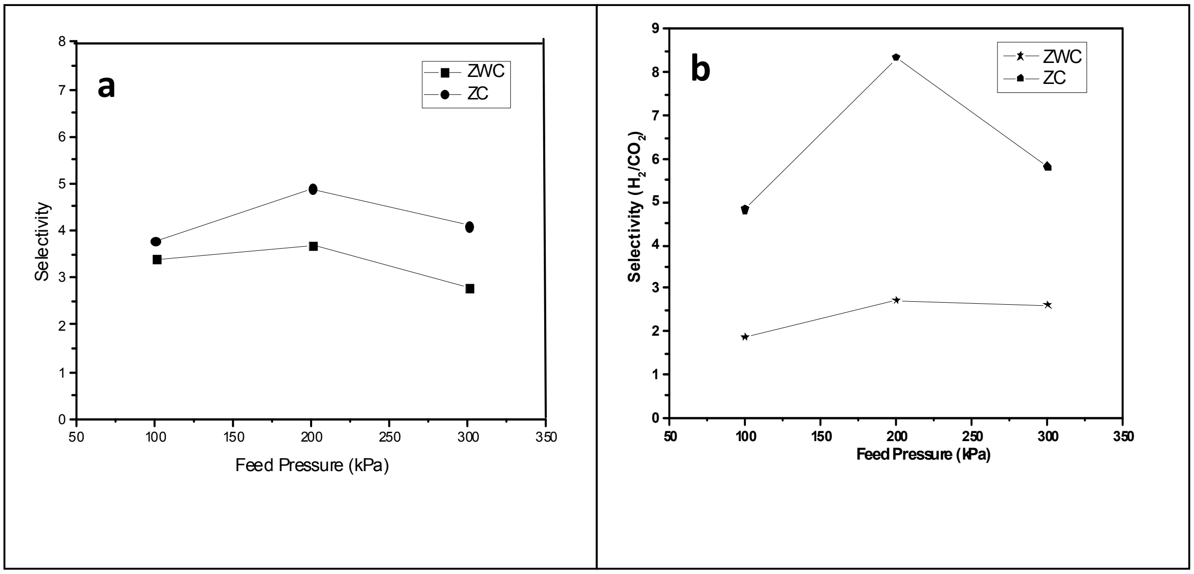

Fig. 12 Effect of feed pressure on the selectivity of H_2 and CO_2 for ZWC and ZC membranes based on (a) single gas permeation, and (b) mixture of H_2 and CO_2 (1:1).

The real performance of the membrane for separating H_2 from a mixture of H_2 and CO_2 can be evaluated from the studies of separation of this gas mixture. Fig. 12b compares the selectivity of the ZC and ZWC membrane for a binary gas mixture (1:1) of H_2 and CO_2 with varying feed pressure. In case of gas mixture, the interaction of each component ultimately influences the performance of the membrane. With increasing feed pressure, CO_2 adsorbs preferentially onto the membrane than H_2 because of its strong electrostatic quadruple moment which reduced its permeability to a little extent. But permeability of H_2 through the zeolite pores increases, and as a result, the overall separation factor increases with respect to different feed pressure. The highest mixture gas separation factor achieved by ZC membrane was 8.5. However, the mixture separation factor in case of ZWC membrane was 2.8.

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Table 1 describes the single gas permeability and selectivity of both the gases H_2 and CO_2 for ZC membranes compared to the values reported in the literature. The permeability of H_2 was increased up to 13. 47x 10 $^{-7}$ for ZC membrane.

Table 1. Comparison of observed values of single gas permeance and selectivity of H_2-CO_2 with those reported in the literature. Study temperature = 30^0C

Membrane/support	**Permeance [mol/m^2 s^1 Pa^1]**		**Selectivity**	**References**
	H_2	**CO_2**		
DDR/Alumina support	15.2×10^{-7}	40.7×10^{-7}	0.37	[12]
DDR/Ceramic support	0.5×10^{-7}	1.0×10^{-7}	0.5	[29]
DDR/Disk shaped α alumina support	0.3×10^{-7}	0.42×10^{-7}	0.7	[30]
Low cost clay alumina support	4.04 X 10 $^{-7}$	1.10 X10^{-7}	3.7	[31]
Porous support	--	0.3 X 10^{-12}	--	[32]
ZC/Low cost clay alumina support	**13.47×0^{-7}**	**2.756×10^{-7}**	**4.9**	**Present study**

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4. Conclusions

The main objective of the current investigation was to modify the DDR zeolite pore followed by removing defects. In this work, C loaded zeolite membranes were prepared by a controlled decomposition of structure directing agent (1-adamantanamine) into the zeolite pores in a single step process. DDR zeolite has the pore size of 0.36nm. To increase the separation efficiency of H_2 / CO_2, the pore size of the DDR pores were constricted, so that the diffusion rate of one component should be higher than that of other component. The presences of non zeolitic pores were also reduced by deposition of C layer. The ZC and ZWC membranes were finally evaluated for binary gas permeations of H_2/CO_2. The membrane was demonstrated the high separation factor of 8.5. The permeation behaviours of H_2 and CO_2 through the membranes were investigated and it shows increased permeance for H_2 together with a high separation factor. Interestingly, the membrane performance revealed the ability to restrict the permeation of CO_2 from H_2-CO_2 mixture, which in turn purifies the CO_2 in the retentate side. This aspect assumes significant importance from the perspective of CO_2 enrichment or capture as one of the GHG mitigation options.

Usually, after pore modifications and defect repairing, gas permeabilities were reported to decrease drastically with increasing separation factor. To overcome these difficulties, pores were modified by C deposition followed by the removal of the defects. The proposed modification is conceived to enhance the separation factor as well as gas permeance simultaneously. In fact, the pore modification and removal of defect increase the separation factor by restricting the diffusion of one component compared to the other. But in case of higher permeability, the non wettability character of C loaded pore increases the overall permeability. To deposit C, multiple stages of membrane modification were replaced by a single stage in the present investigation. According to literature, pores were modified in polycrystalline zeolite membranes by post-synthetic treatments. As the utilisation of the template used for synthesis of zeolite may be a challenging task for making the zeolite synthesis process cost effective, C deposition by decomposition of template in

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a single stage makes the process easy, time saving and cost effective. The present article elucidated such a unique method for modification of zeolitic and non zeolitic pores that does not seem to have been reported earlier in the literature. Furthermore, this process reduces the pollutants released to the environment as the carbon remains occluded into the membrane pores.

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