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Mechanistic Studies on the CVD Modification of Zeolitic Pores In MFI Membranes

Zhong Tang[1], Seok-Jhin Kim[1], Junhang Dong[1,*], Tina M. Nenoff[2]

[1]Department of Chemical & Materials Engineering, University of Cincinnati, Cincinnati, Ohio 45221

[2]Surface and Interfacial Science, Sandia National Laboratories, PO Box 5800, MS 1415, Albuquerque, New Mexico 87185

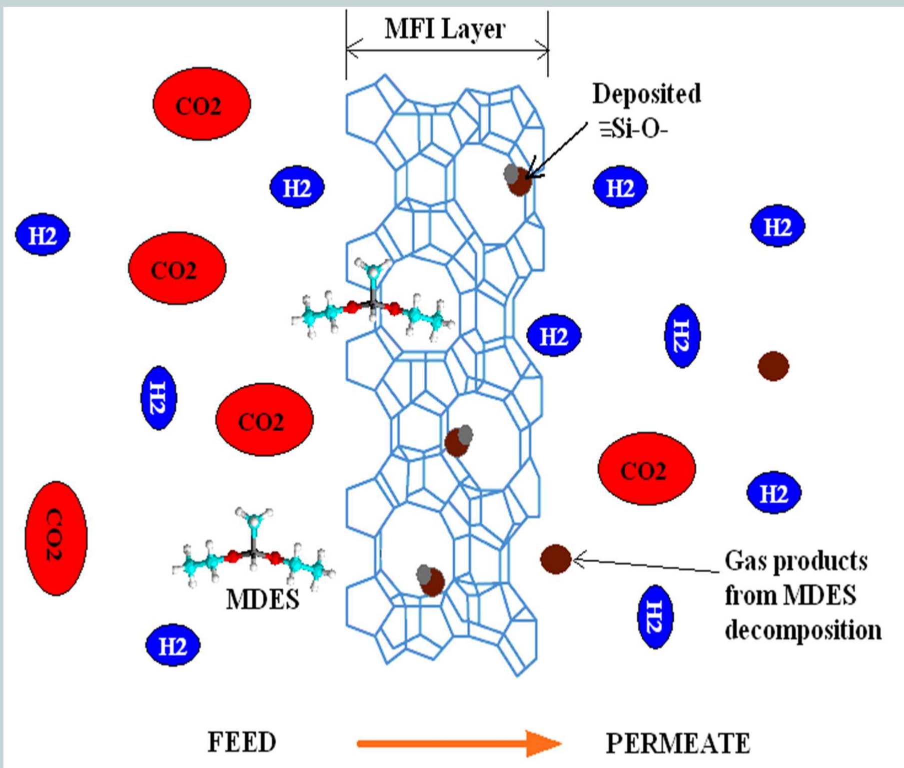
*Phone: (513) 556-3992; Email: junhang.dong@uc.edu.

1. INTRODUCTION

MFI membrane modification by catalytic thermal cracking deposition (CTCD) of silane in the zeolitic pores can dramatically enhance high temperature H_2/CO_2 separation[1,2]. In this research, we study the mechanisms of this new CVD modification process.

2. APPROACH

Modification was conducted at 450°C during the permeation of a 50/50 H_2/CO_2 gas mixture, with continuous online monitoring of the modification effect. Si modification of zeolite pore, reduces the pore size such that transport of H_2 and CO_2 is changed to **configurationally diffusion** mechanism, resulting in a dramatic enhancement of H_2 selectivity. H_2 permeance is only moderately affected because deposition occurs to only a small depth of the channel length.

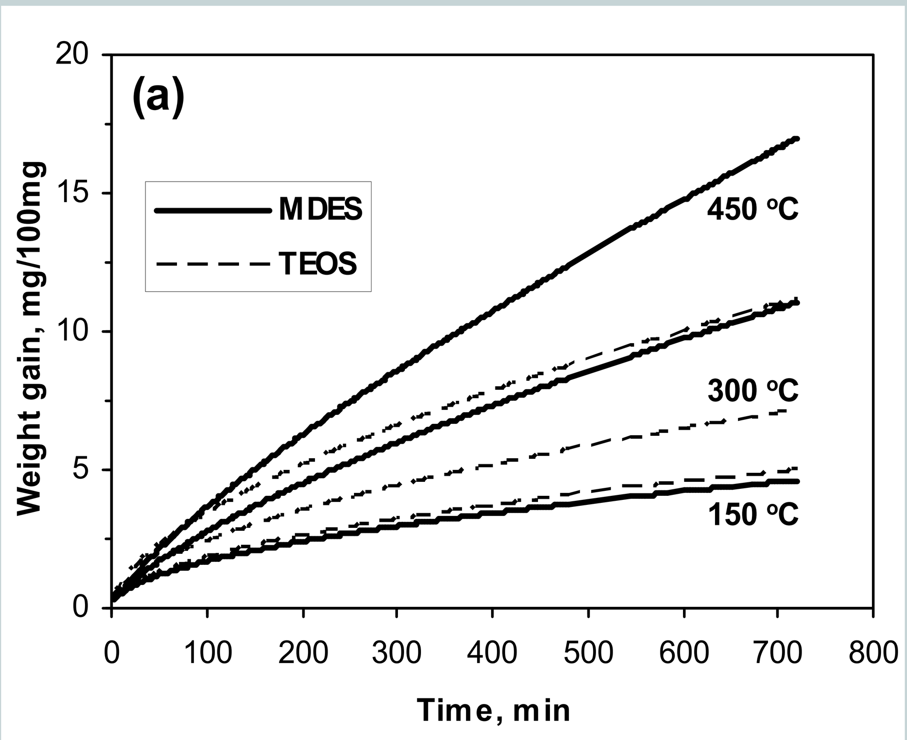


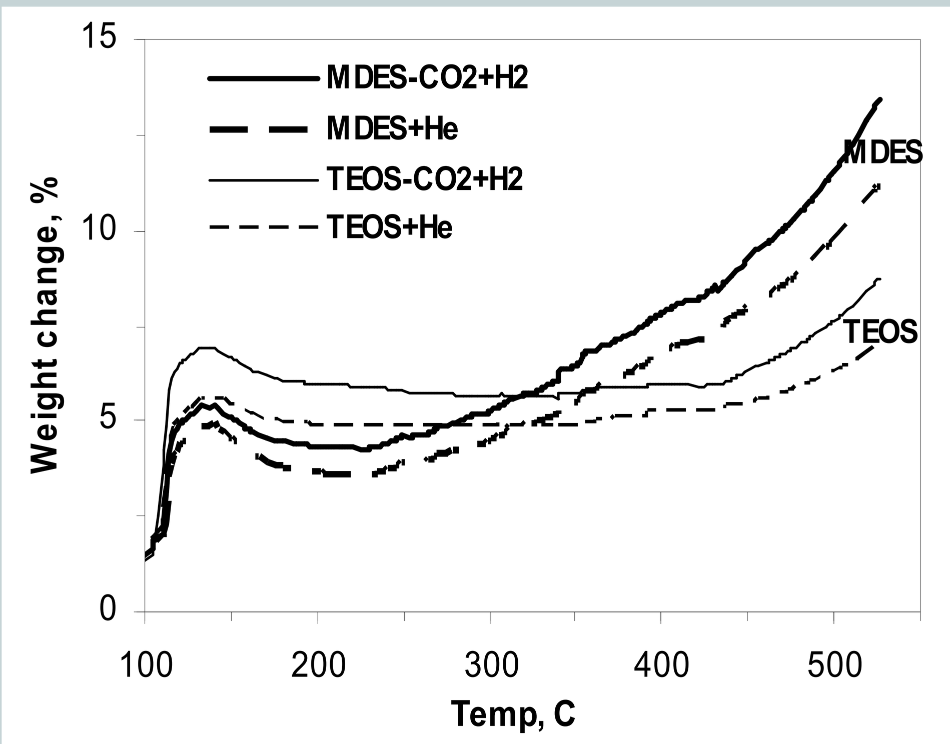
3. EXPERIMENTAL

3.1 Zeolite membranes and modification

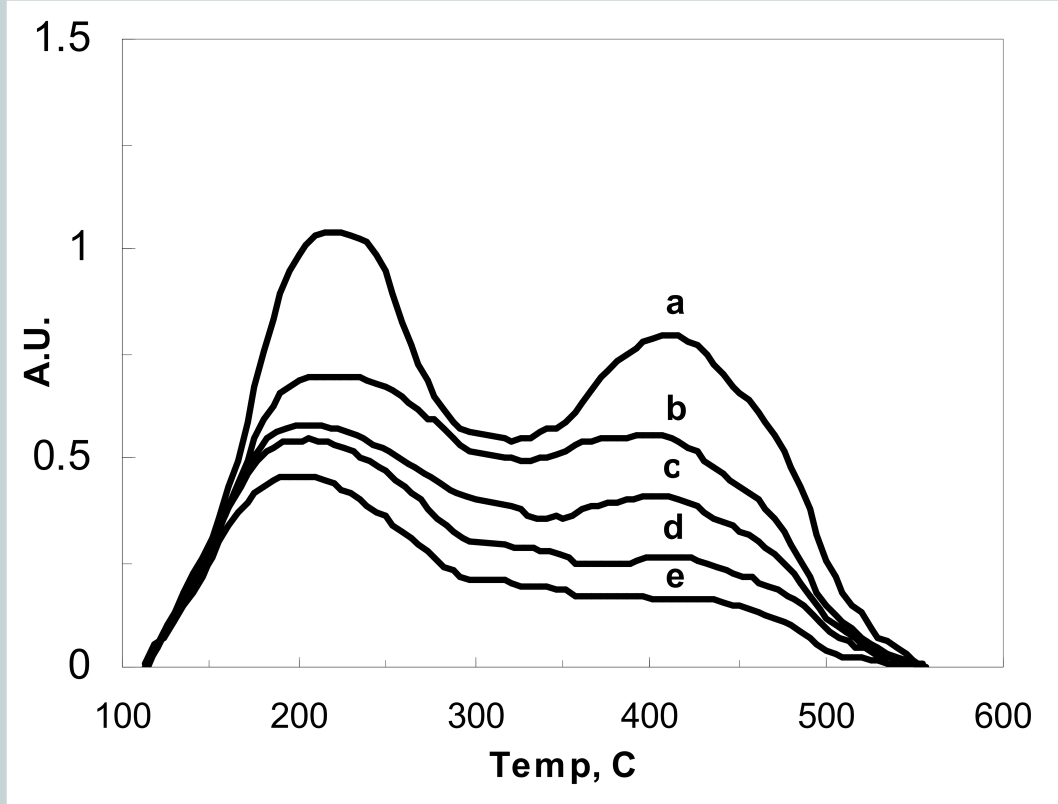
MFI zeolite particles were obtained by hydrothermal synthesis; **Zeolite membranes** were synthesized on alumina supports by microwave heating[3]. **CTCD** was studied for both MDES (methyldiethoxysilane, 0.4x0.9nm) and TEOS (tetraethyl orthosilicate, 0.96x0.96nm).

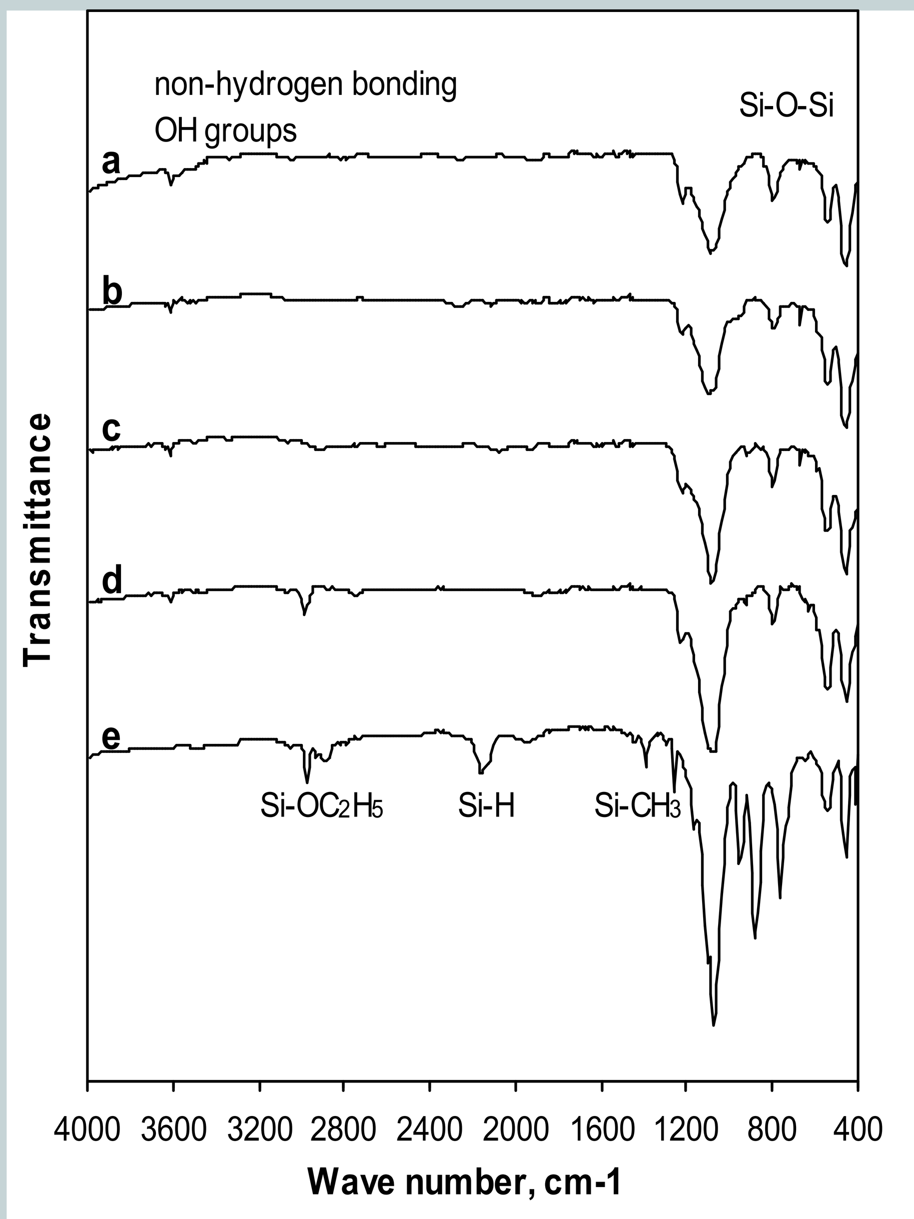
3.2 Characterization





TGA tests showed that large TEOS was unable to enter and deposit in side the zeolitic pores while the **smaller MDES was able to modify the international surface of MFI zeolites**. The CTCD modification was more effective in H_2/CO_2 carrier gas than in inner He carrier because the former generates H_2O which can facilitate the catalytic thermal cracking.





NH_3-TPD results indicated that the deposition occurred inside zeolite pores: (a) sample S-1, (b) 150°C, (c) 300°C, (d) 450°C, (e) 23~450°C

FTIR spectra showing that SiO_2 was the final deposit: (a) sample S-1, (b) modified from 150~450°C, (c) 450°C, (d) 300°C, (e) 150°C

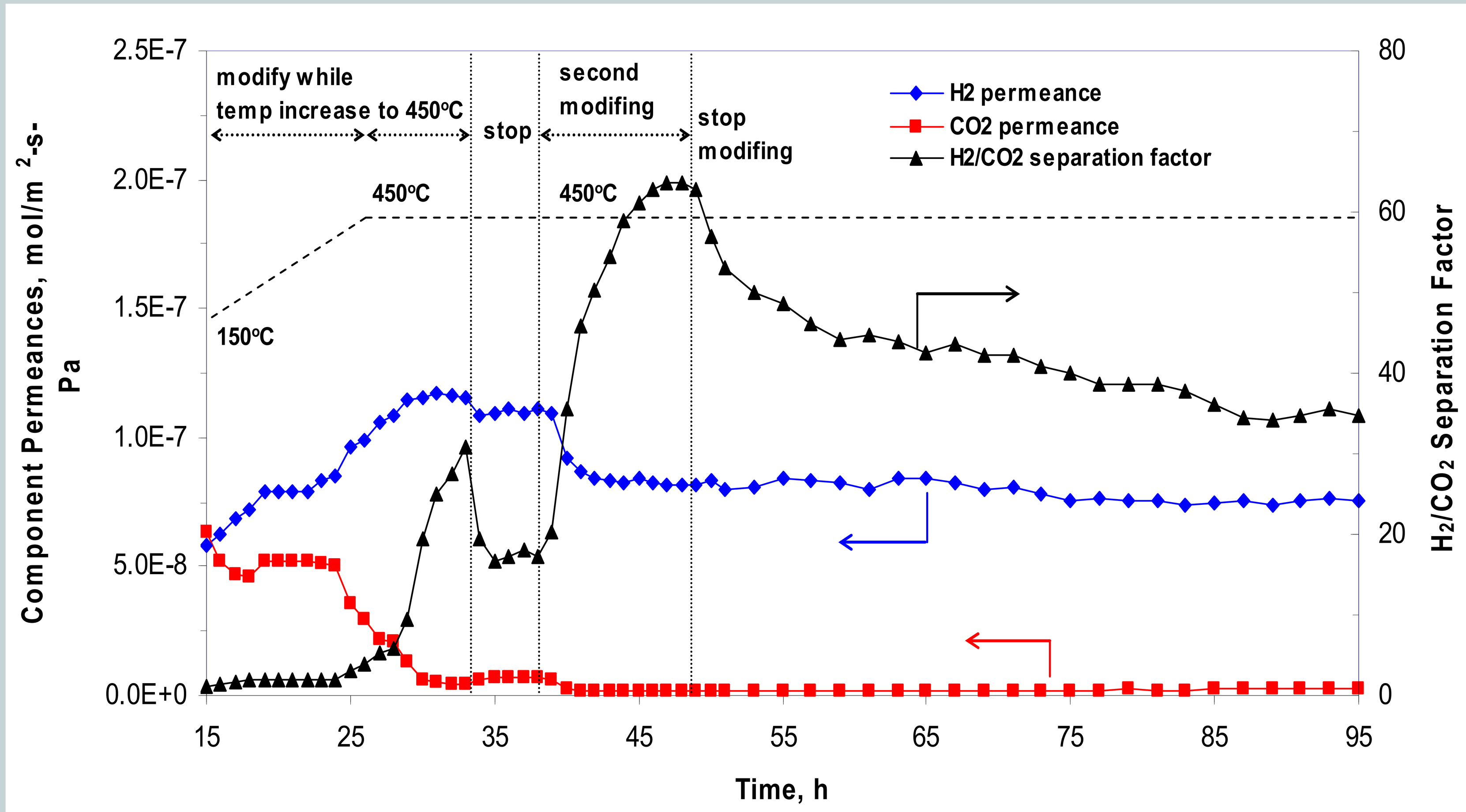
Key Reactions of CTCD for MDES

$CH_3(C_2H_5O)_2$Si-O-Si≡ + $2H_2O$ ⟶ $2C_2H_5OH$ + $CH_3(OH)_2$Si-O-Si≡

$CH_3(OH)_2$Si-O-Si≡ + H_2O ⟶ C_2H_5OH + $(OH)_3$Si-O-Si≡

CO_2+H_2 ⟶ H_2O+CO (reverse water-gas-shift reaction)

3.3 H_2 separation enhancement



H_2/CO_2, 450°C	Separation Factor
Before modification	3.8
1st round	15
2nd round	34

Results of online monitoring of membrane modification showing elimination of intercrystalline pores by CTCD of TEOS and zeolitic pore reduction by CTCD of MDES.

4. CONCLUSIONS

MFI zeolite channels can be effectively modified by CTCD of MDES to achieve high selectivity for H_2 from CO_2. The CTCD of MDES resulted in SiO_2 deposition in side the zeolitic channels. Using H_2/CO_2 as carrier gas not only allows for great process control but facilitates the CTCD process.

References: [1] T. Masuda, N. Fukumoto, M. Kitamura, *Micropor Mesopor. Mat.* 48 (2001) 239; [2] X. Gu, Z. Tang, J. Dong, *Micropor. Mesopor. Mat.* 111 (2008) 411; [3] X. Gu, J.Dong, T.M. Nenoff, D.E. Ozokwelu, *J. Member. Sci.* 280 (2006) 624.

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