Industry Day Theme # Emerging Nano and Advanced Materials

HMCM-22 zeolite with different Si/Al_2 ratios: Synthesis and Catalytic Properties in Methane Dehydroaromatization

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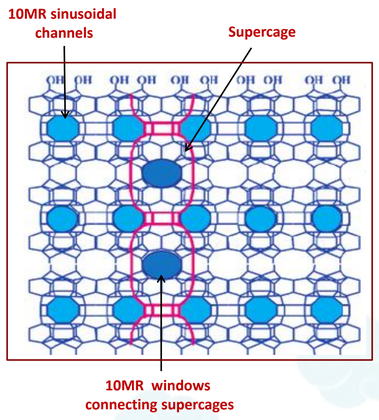
Chemical Engineering

Abstract

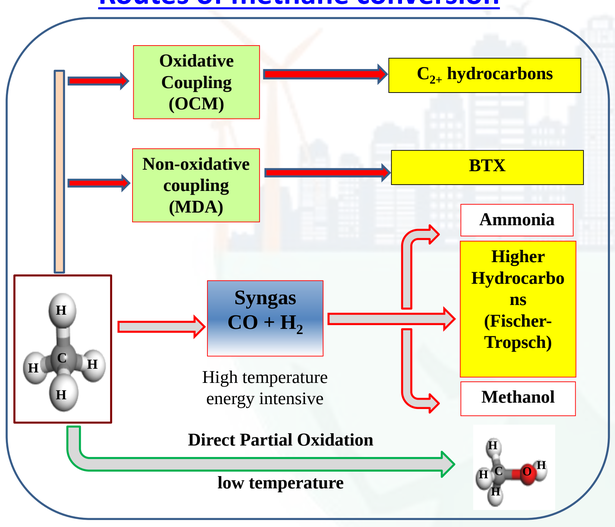
- HMCM-22 zeolite is a potential catalyst for petrochemical industries
- Key catalyst for different aromatic alkylation and isomerization reactions
- Highly effective in Methane dehydroaromatization (MDA) process than the conventional ZSM-5 catalyst with molybdenum (Mo)



Introduction

- Natural gas availability at remote locations imparts high transportation cost
- Current commercial processes via indirect path require economy of scale
- Direct conversion of methane into higher hydrocarbons is an efficient process for natural gas upgradation
- Zeolite supported molybdenum catalysts are among the most promising catalysts for this process.

Routes of methane conversion



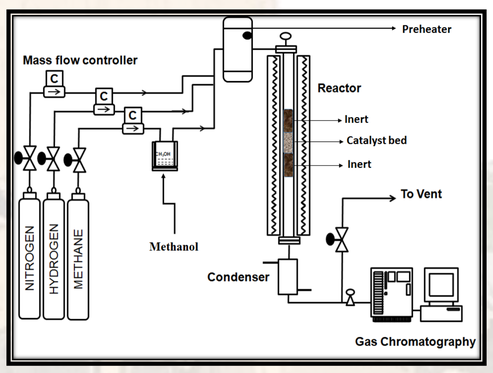
Syngas step accounts for 60% of the capital cost

$$CH_4 \xrightarrow{Active\ Metal\ site} CH_3{*} + H{*}$$
$$2CH_3{*} \xrightarrow{Active\ Metal\ site} C_2H_4 + H_2$$
$$3C_2H_4 \xrightarrow{Support\ site} C_6H_6 + 3H_2$$

Materials and Methods

- Molar gel composition for HMCM-22 zeolite: **0.30 NaOH: SiO_2: xAl_2O_3: 0.35 HMI: 45 H_2O** where x (0.033, 0.025, 0.0182) varies for different SiO_2/Al_2O_3
- Mo loading over HMCM-22 support was done by conventional wet impregnation methods

Existing reactor setup



Reaction conditions

Parameters	Values
Temperature (°C)	700
Pressure	1 atm
$GHSV_{CH4}$ (mL/g-h)	1500

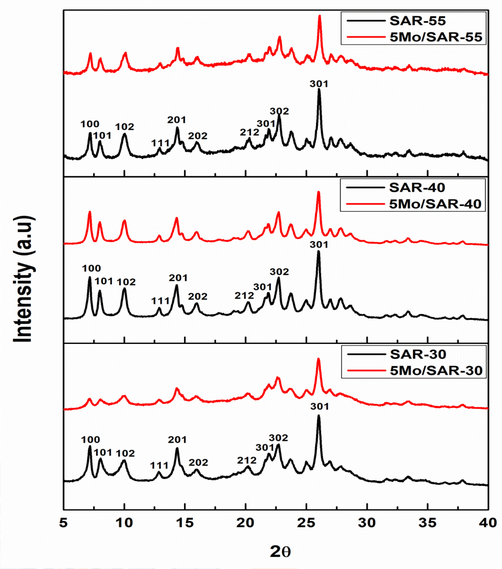
***Before activity test, catalyst was pre-treated with 25% CH_4/H_2 for carburization step**

Conclusions

- HMCM-22 (SAR-30) with high BAS (exchangeable) concentration results high Mo dispersion
- ^{27}Al MAS NMR confirms the strong interaction with HMCM-22 having SAR-30
- 5%Mo/HMCM-22 with SAR-30 is the most active catalyst for MDA reaction in terms of high methane conversion, high benzene formation rate with lower coke deposition

Results

Textural properties: XRD & BET analysis

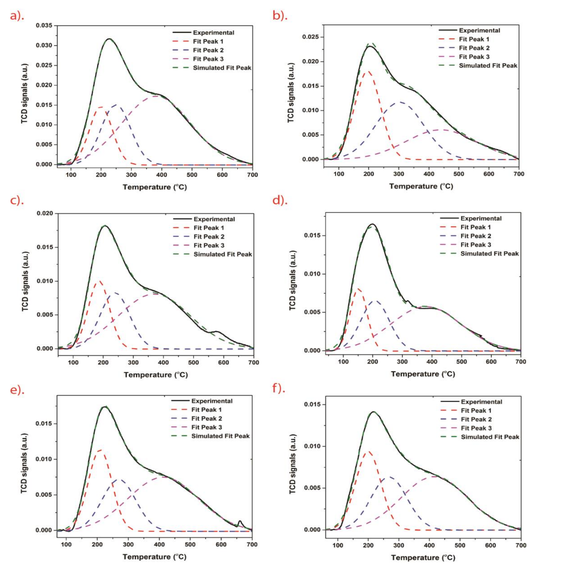


Catalyst	BET surface area (m^2/g)	Micropore Pore Volume (cm^3/g)	Crystallinity (%)
HMCM-22 (SAR-30)	585	0.16	100
HMCM-22 (SAR-40)	458	0.13	84
HMCM-22 (SAR-55)	377	0.12	79
5Mo/HMCM-22 (SAR-30)	447	0.14	74.5
5Mo/HMCM-22 (SAR-40)	334	0.10	64.6
5Mo/HMCM-22 (SAR-55)	314	0.11	68

NH_3-TPD analysis

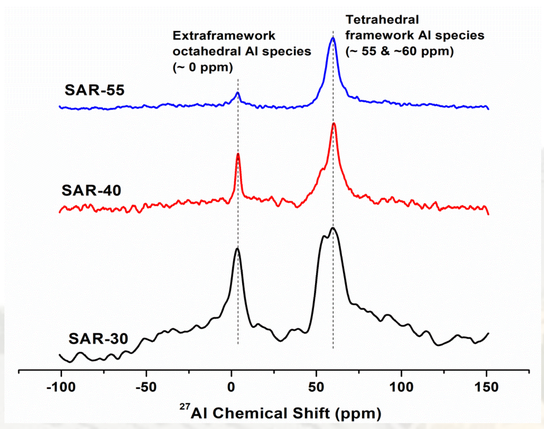
SAR	NH_3 consumption, mmole/g_{cat} (Temperature, °C)			
	Peak 1	Peak 2	Peak 3	Total
30	0.29 (199)	0.38 (248)	1.02 (381)	1.69
40	0.33 (185)	0.38 (238)	0.91 (370)	1.62
55	0.35 (208)	0.32 (269)	0.69 (412)	1.36
5Mo/SAR-30	0.44 (195)	0.52 (302)	0.39 (439)	1.35
5Mo/SAR-40	0.14 (151)	0.59 (207)	0.65 (379)	1.38
5Mo/SAR-55	0.34 (199)	0.31(268)	0.59(415)	1.24

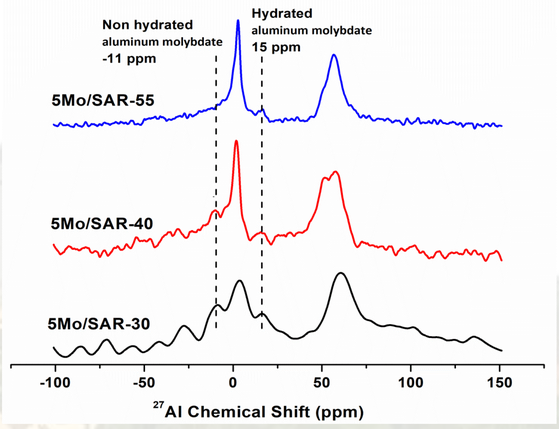
Maximum BAS (exchangeable) concentration was observed in HMCM-22 with SAR-30 resulting high Mo dispersion



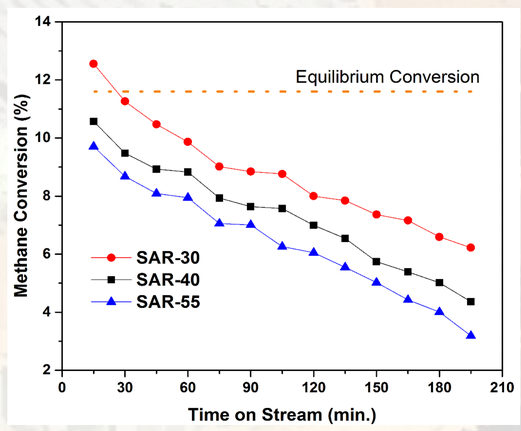
(a) SAR-30 (b) 5Mo/SAR-30 (c) SAR-40 (d) 5Mo/SAR-40 (e) SAR-55 (f) 5Mo/SAR-55

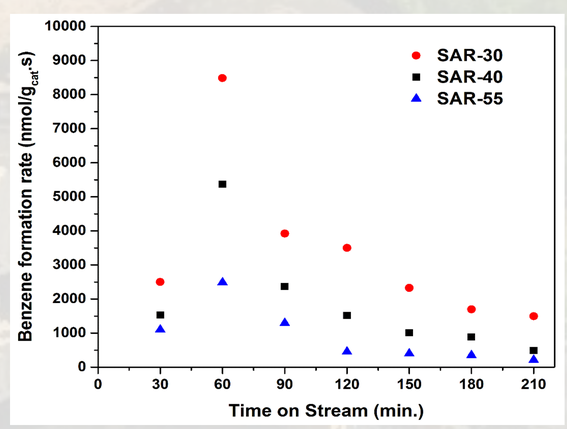
^{27}Al MAS NMR analysis





Activity test





Industrial Significance

- HMCM-22 zeolite is the key catalyst for aromatic alkylation and isomerization reactions
- Tuning of the framework structure significantly improves the yield of desired products
- For MDA process, which is an efficient technology for direct natural gas utilization, it results higher benzene yield (key chemical of petrochemical and polymer industries) in comparison with the conventional ZSM-5 catalyst

References

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2. Mishra S, Balyan S, Haider M A, Pant K K., *J. Chem. Sci.* 129, 2017, 1705
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