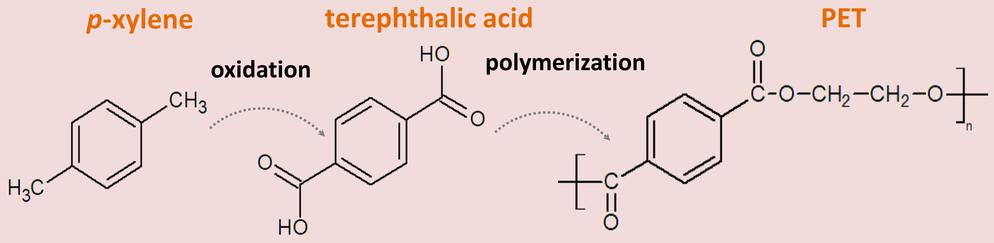
MICRO-MESOPOROUS PT-CONTAINING CATALYSTS FOR XYLENES HYDROISOMERIZATION

Gubkin Russian State University of Oil and Gas, Moscow, Russia

N. Demikhova, M. Rubtsova, A. Glotov, D. Tsaplin, E. Ivanov, V. Vinokurov

1 BACKGROUND

The naphtha fraction from reforming units is rich in aromatic compounds of C_8H_{10} composition (*p*-, *o*-, *m*-xylenes and ethylbenzene), which are widely used in petrochemical industry for producing synthetic resins, fibers, and plasticizers. For instance, oxidation of the most demanded isomer, *p*-xylene, yields terephthalic acid, which is used in production of textile fibers.



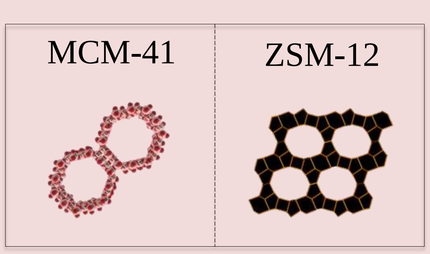
Objectives

In this work new functional materials based on microporous ZSM-5 zeolite in conjunction with mesoporous ZSM-12 and MCM-41 aluminosilicates were synthesized and investigated as catalyst components for the isomerization process.

2 MATERIALS AND METHODS

In this work new functional materials based on microporous **ZSM-5** zeolite in conjunction with mesoporous **ZSM-12** and **MCM-41** aluminosilicates were synthesized and investigated as catalyst components for the isomerization process. Micro-mesoporous **MCM-41/ZSM-5** composite was synthesized by a double-template method using TPAOH and CTAB as templates. Zeolite of ZSM-12 was prepared with TEABr as a template and then mechanically mixed with commercial ZSM-5 zeolite. The resulting material is referred to as **ZSM-12/ZSM-5**.

ZSM-5	
Pore diameter, Å	6
Wall thickness, Å	2
Surface area, m^2/g	380
Pore volume, cm^3/g	0.28



Functional materials ZSM-5:MCM-41, ZSM-5:ZSM-12 → **Carriers** ZSM-5:MCM-41/Al_2O_3, ZSM-5:ZSM-12/Al_2O_3 → **Catalysts** Pt/ZSM-5:MCM-41/Al_2O_3, Pt/ZSM-5:ZSM-12/Al_2O_3

The resulting composites **ZSM-5:ZSM-12, ZSM-5:MCM-41** were mixed with bohemite in 60:40 % wt. ratio and extruded, then Pt was deposited over the extrudates by incipient wetness impregnation method in the amount of 0.5 % wt.

3 EXPERIMENTAL

The catalytic activity of the prepared materials was investigated in isomerization of C_8 aromatic fraction supplied from catalytic reforming unit. The catalytic experiments were performed in a flow-type reactor with a fixed-bed catalyst (5 µL) under hydrogen pressure 1.0 MPa in a temperature range from 350 to 400°C, volume hourly space velocity (VHSV) 1-6 h^{-1}, H_2:feed volume ratio of 1200.

Feedstock composition

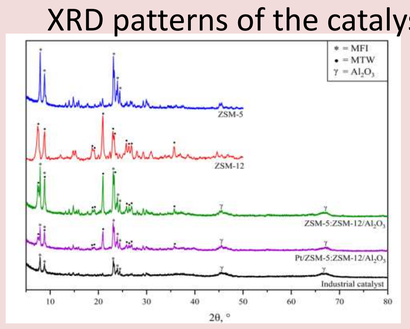
Component	Content, wt. %
Toluene	0.38
Ethylbenzene	10.00
p-Xylene	3.04
m-Xylene	66.12
Isopropylbenzene	0.03
o-Xylene	16.04
Other	4.39

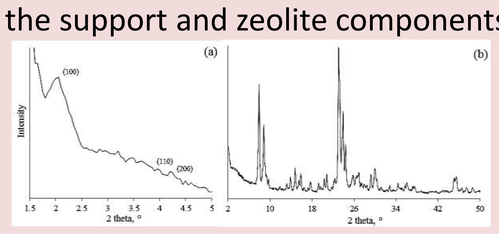
4 RESULTS

All resulting materials and catalysts were investigated by XRD, TEM, SEM, N_2 adsorption/desorption and ammonia temperature programmed desorption (NH_3-TPD).

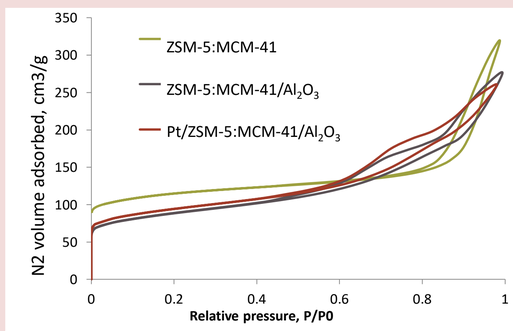
Sample	Acidity (µmol NH_3/g)			Strong/ weak	BET surface area, m^2/g	Microporous surface area, m^2/g	Pore volume, cm^3/g		Average pore diameter, Å	
	Weak (<300°C)	Strong (>300°C)	Total				meso-	micro-	meso-	micro-
ZSM-5:MCM-41	866	355	1220	0.41	366	229	0.15	0.13	43	7
ZSM-5:MCM-41/Al_2O_3	465	566	1031	1.22	304	134	0.31	0.08	61	8
Pt/ZSM-5:MCM-41/Al_2O_3	598	815	1413	1.36	301	135	0.31	0.07	61	7
ZSM-5	724	740	1465	1,02	364	244	0,10	0,13	33	9
ZSM-12	174	193	367	1,11	279	212	0,04	0,10	40	6
ZSM-5:ZSM-12/Al_2O_3	354	485	839	1,37	268	132	0,19	0,07	16	7
Pt/ZSM-5:ZSM-12/Al_2O_3	424	649	1073	1,53	272	130	0,19	0,07	15	7
Industrial catalyst	259	1318	1577	5.09	313	54	0.60	0.03	65	7

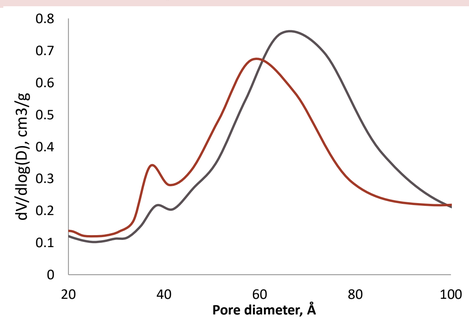
XRD patterns of the catalysts, the support and zeolite components

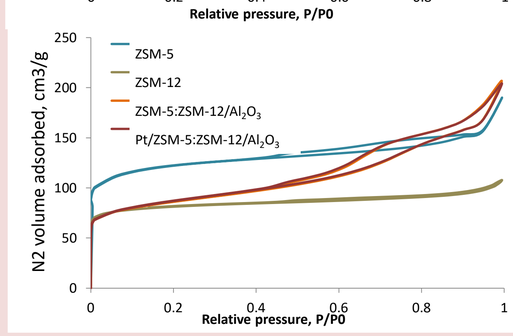


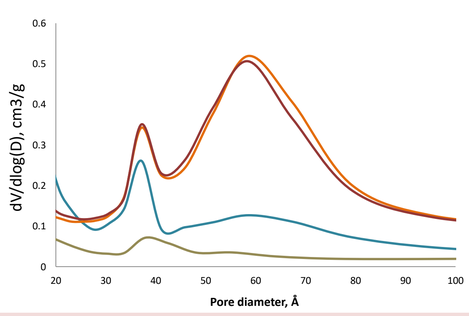


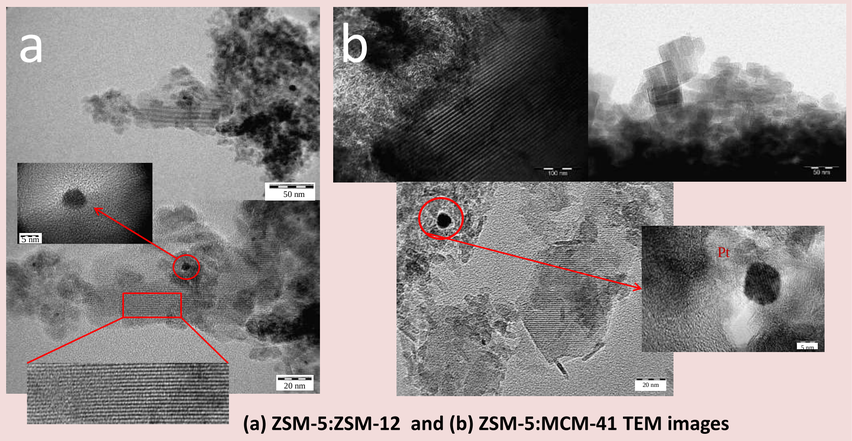
(a) Low- and (b) wide-angle XRD patterns for MCM-41/ZSM-5 micro-mesoporous composite



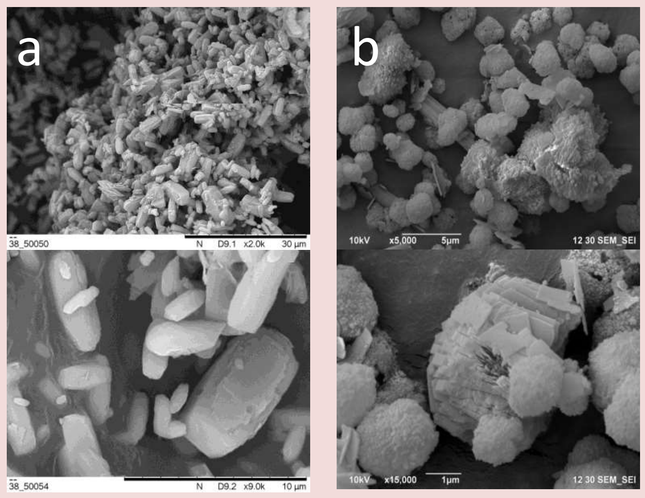






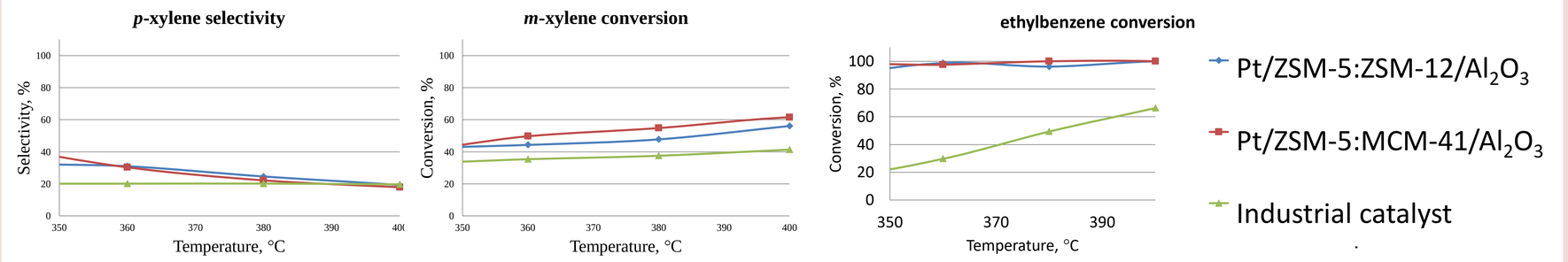


(a) ZSM-5:ZSM-12 and (b) ZSM-5:MCM-41 TEM images



(a) ZSM-5:ZSM-12 and (b) ZSM-5:MCM-41 SEM images

CATALYTIC TESTING



5 CONCLUSION

- ✓ New functional micro-mesoporous materials were synthesized, characterized and tested as components of catalysts for isomerization of aromatic compounds.
- ✓ The operating characteristics of the developed catalysts exceeded the same of the industrial analog.
- ✓ The obtained catalysts based on cheap and environmentally friendly materials can be easily scaled up for industrial applications.

ACKNOWLEDGEMENTS

This work was supported by the Russian Science Foundation (Grant №19-19-00711).