Dimethyl branched isomers in the products of n-hexane hydroisomerization on modified mordenite-containing rock

Voloshyna Yu.*, Pertko O., Povazhnyi V., Patrylak L., Yakovenko A.

V.P Kukhar Institute of Bioorganic Chemistry and Petrochemistry of the NAS of Ukraine,

*Murmanska Str., 1, Kyiv-02094, Ukraine, *E-mail: yule.v444@gmail.com*

Introduction

Dimethylbutanes (DMB), having the highest octane numbers among hexane isomers, are the most valuable products of isomerization of the pentane-hexane fraction of oil, so a study of factors determining the selectivity of their formation is topical. In particular, there is no consensus as for the influence of the open areas of zeolite: mesopores, external surface etc. DMB can either be formed selectively in mesopores, or the latter can have a positive effect only as transport routes.

The aim of the work was to determine the effect of the parameters of porous structure of the catalysts based on modified mordenite-containing rock of Transcarpathia on the DMB formation in n-hexane hydroisomerization. To exclude the possible effect of mesopores as transport pores, the reaction was carried out in a micro pulse mode, when reagents were dozed into reaction space in small portions , and the presence of conducting pathways does not matter.

Experimental methods

H-form of the rock was obtained by calcination of NH_4-form at 873 K for 3 h. In turn, NH_4-form was obtained by ion exchange of the original rock with 3 mol/l NH_4NO_3 solution. Synthesis specifics are detailed in **Table 1**. Acid treatment of the samples was realized at 358 K for 2 h in solid to liquid ratio of 1:5. Then they were washed with distilled water and dried in air. After that dehydrated samples of rock (653 K, 2 h) were impregnated with a calculated amount of $PdCl_2$ solution in 0.5 mol/l HCl or aqueous $Ni(NO_3)_2$ solution and dried in air at room temperature. The metal component of the catalysts was reduced in a flow of hydrogen on a flow-through unit at 653 K for 6 h.

Micrographs of the samples were obtained using a transmission electron microscope JEM-1230 (JEOL) with a resolution of 0.2 nm at an accelerating voltage of 80 kV. Samples were prepared by suspending in water with ethyl alcohol for 20 minutes using an ultrasonic bath.

Table 1. Synthesis of the catalysts based on mordenite-containing rock (MR), Lipcha, Transcarpathia.

Catalyst	Specifics of synthesis	
	HCl (mol/l)	Metal component (wt%)
MR-0	-	-
MR-A5/0.5	5	Pd (0.5)
MR-A5/0.7	5	Pd (0.7)
HMR-A5/1	5	Ni (1)
HMR-A3/1	3	-"-
HMR-A1/1	1	-"-
HMR-A1/1.5	-"-	Ni (1.5)
HMR-A1/2	-"-	Ni (2)
HMR-A1/2.5	-"-	Ni (2.5)

Isotherms of low-temperature (T = 77 K) nitrogen ad(de)sorption were measured on a Quantachrome® NOVA-1200e automatic sorbtometer after calcination of the samples in a muffle furnace at 653 K (2 h) and subsequent in situ evacuation at 568 K (10 h). The NovaWin 11.04 software was used to calculate the parameters of a porous structure (**Table 2**).

The catalysts were characterized also using IR-spectroscopy and XRD diffraction.

Catalytic experiments were carried out in a micropulse unit with stainless steel reactor with an inner diameter of 8 mm and a height of 175 mm at atmospheric pressure using H_2 as a carrier gas. The samples were activated at 623 K, the reaction was carried out in the temperature range of 473-623 K with a step of 25 degrees.

Results

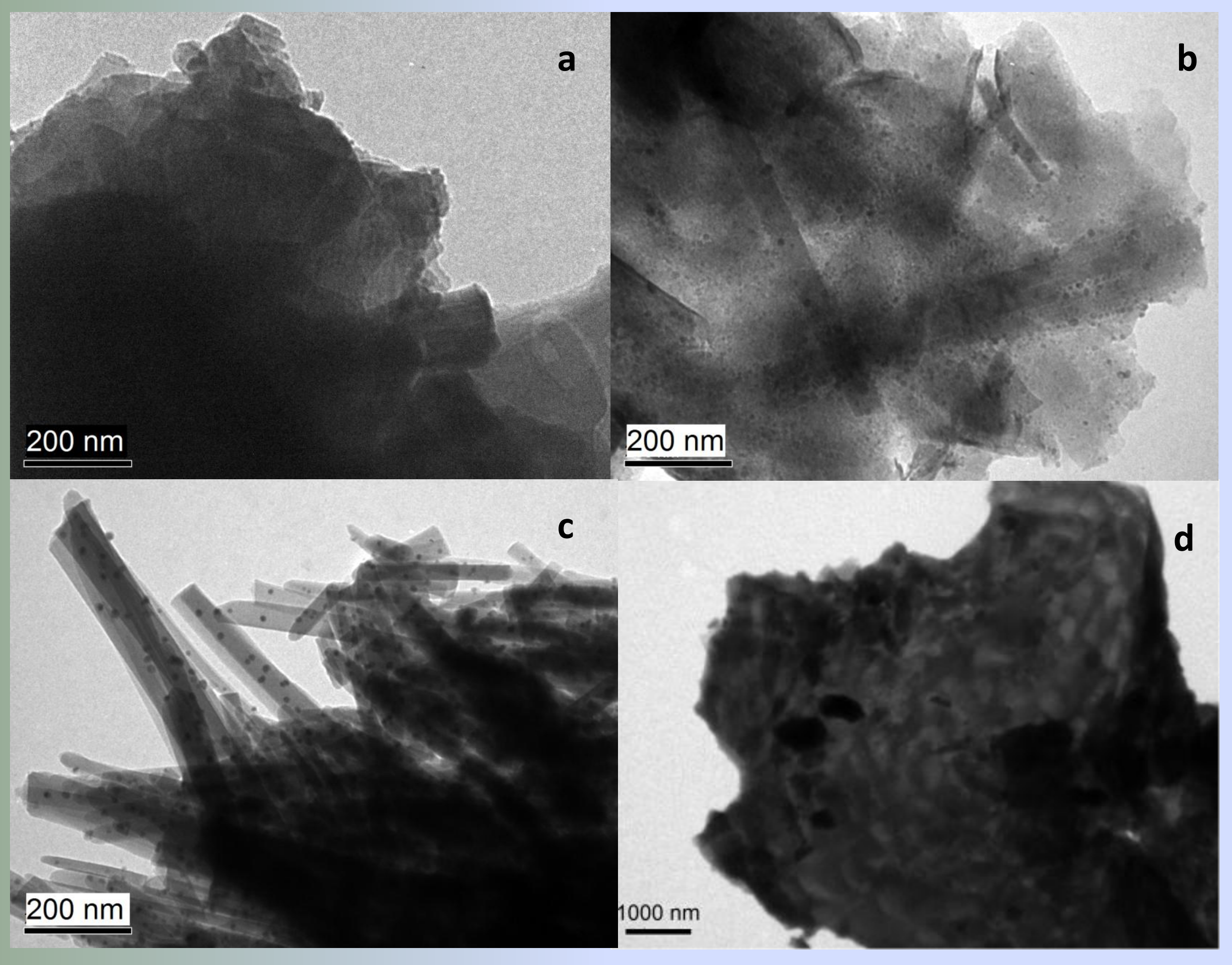

Figure 1. TEM microgfaphs of the catalysts HMR-A1/1 (**a**), HMR-A1/2 (**b**), HMR-A1/2.5 (**c**), MR-A5/0.5 (**d**).

Figure 1 demonstrates that nickel at a content of 1-2wt% forms small particles up to 5 nm, which are located mainly in the micropores, and then on the outer surface of the crystallites. Starting with 2.5%, Ni localize on the external surface as well-defined particles with a size of about 10 nm. Pd, together with clearly delineated metal particles of about 15–30 nm in size, also forms a massive metal phase that covers large areas of the outer surface of the zeolite. It follows that at a content of 2wt% the maximum possible amount of nickel is in close proximity to the acid sites, and therefore the efficiency of such a catalyst in isomerization should be the highest.

Table 2. Parameters of porous structure of the synthesized samples according to low-temperature (T = 77 K) nitrogen ad(de)sorption

Catalyst	S^{BET}, m²/g	S^t, m²/g	S^t_{micro}, m²/g	V, cm³/g	V^t_{micro}, cm³/g	V_{micro}/V, %	$V_1=V-V^t_{micro}$, cm³/g	R^{DFT}, nm	$V[R^{DFT}]$, cm³/g	$V[R^{DFT}]/V_1$, %	R, nm
MR-0	95,3	25,4	69,9	0,099	0,032	32,3	0,067	1,17	0,043	65	2,09
MR-A5/0.5	241	29,4	211	0,163	0,096	58,9	0,067	1,25	0,013	19	1,35
MR-A5/0.7	147	34,3	113	0,131	0,061	46,6	0,070	1,17	0,016	23	1,78
HMR-A5/1	322	37,9	284	0,212	0,113	53,3	0,099	1,25	0,084	85	1,32
HMR-A3/1	292	33,1	259	0,186	0,117	62,9	0,069	1,17	0,040	58	1,27
HMR-A1/1	330	32,0	298	0,204	0,133	65,2	0,071	1,17	0,029	41	1,24
HMR-A1/1.5	304	30,1	274	0,189	0,121	64,0	0,068	1,17	0,037	54	1,24
HMR-A1/2	287	30,2	257	0,182	0,116	63,7	0,066	1,17	0,047	72	1,27
HMR-A1/2.5	278	50,6	228	0,215	0,116	54,0	0,099	1,17	0,046	47	1,54

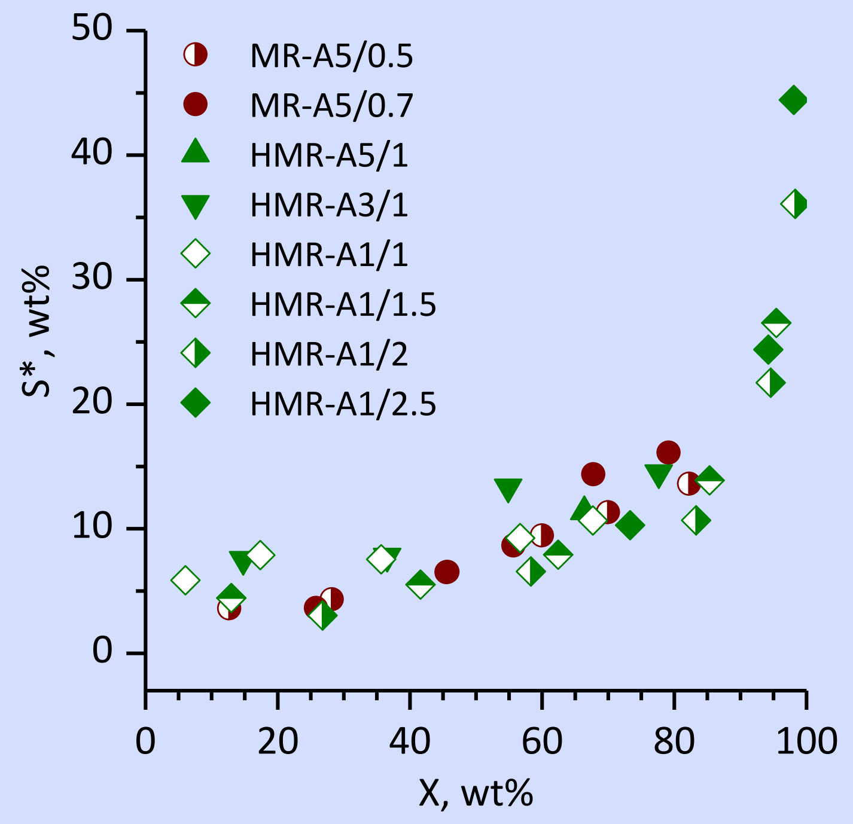

Figure 2. Dependence of DMB content in isohexanes (S*) on n-hexane conversion (X).

For isomerization catalysts of different mesoporosity, S* on the whole increases with X (**Fig. 2**). Therefore, DMB formation is independent of the porous structure of the catalysts and is governed only by kinetic factors.

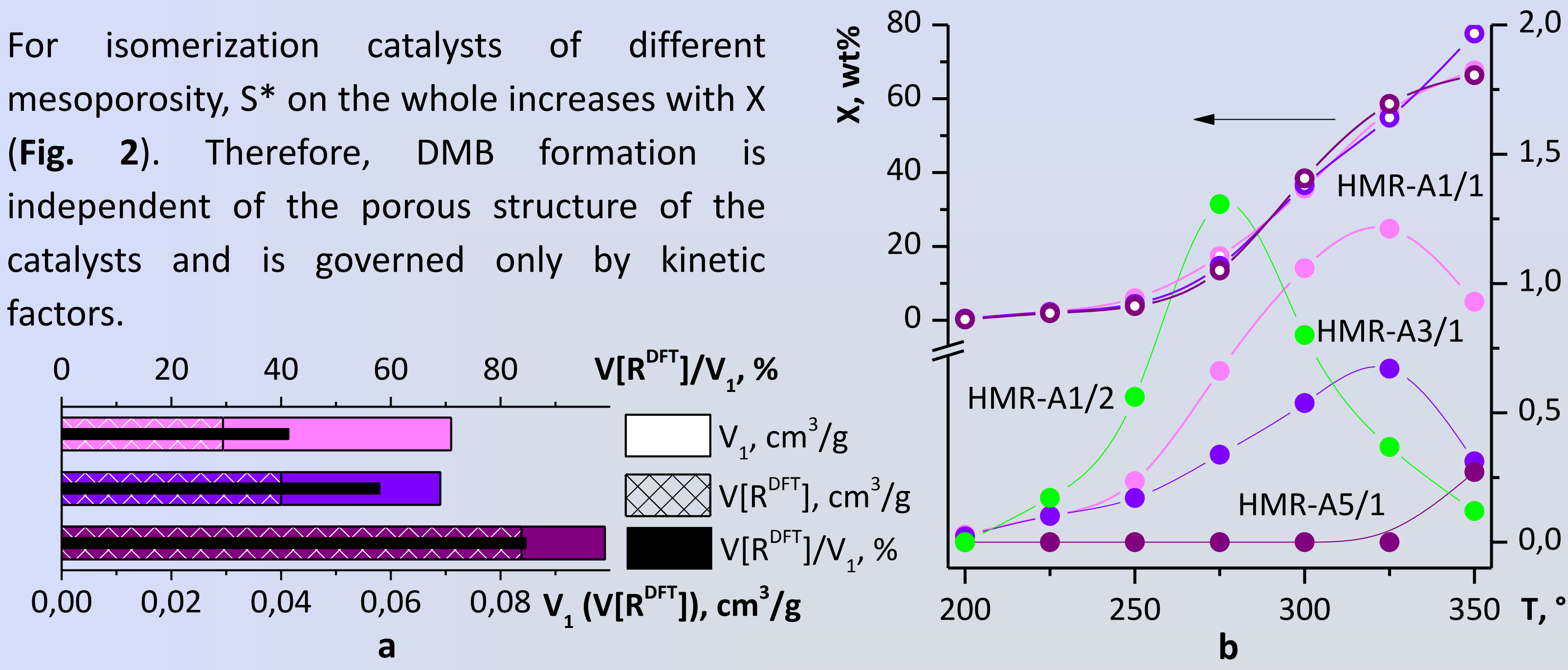

Figure 3. Porous characteristics of acid-treated catalysts (**a**) in comparison with n-C_6 conversion (X) and the yield of DMB (Y_{DMB}) (**b**)

In the series of the samples with the same metal content, the increase in the volume of mesopores does not affect the conversion of n-hexane and does not increase the yield of branched isomers of hexane. The sample HMR-A1/1, which is characterized by the lowest mesoporosity and the highest relative number of micropores, is the most selective for DMB (**Table 2**, **Fig. 3**).
On the sample HMR-A1/2 with optimal Ni content, the higher DMB yield is observed at a temperature 50 K lower than on the HMR-A1/1.

Conclusion

It was found that on the n-hexane isomerization catalysts based on mordenite-containing rock MR, despite the larger kinetic diameter of molecules of dimethyl branched isomers compared to monobranched, DMB formation is not regulated by shape-selectivity. DMB formed more selectively inside zeolite micropores than in mesopores due to the steric hindrance to diffusion of reagent molecules in micropores, which prolongs their contact with the active surface and increases the probability of secondary transformations towards DMB. In the MR-based catalysts, 2wt% was found to be the maximum Ni content, necessary to ensure the maximum yield of i-C_6. This, in turn, has a positive effect on the formation of dimethyl branched isomers of hexane. The highest DMB yield is observed on the sample with a such Ni content.

Acknowledgments

The authors express their gratitude to Candidate of biological Sciences S.M. Scherbakov (M.G. Kholodny Institute of Botany of the National Academy of Sciences of Ukraine) for assistance in obtaining the microphotographs of the samples. The publication contains the results of research carried out under the grant from the National Research Foundation of Ukraine (Project 2020.01/0042).