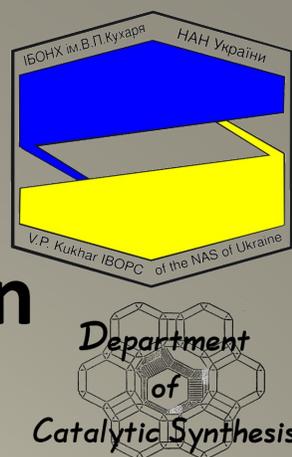


Evaluation of the catalytic efficiency of metal-containing zeolite composites with separated phases in the conversion of n-hexane



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Introduction

Traditionally, zeolites are widely used as a basis of catalysts for various types of reactions. One of the ways to increase their effectiveness is to change the properties of the zeolite component. In particular, different combinations of zeolites can be used. The combination of zeolites of various types and other materials into composite catalytic systems allows of optimal use

of their structural and acid-base characteristics, thus regulating the content and strength of active sites and their availability in the resulting material, which opens broad prospects for the use of such systems in catalysis. Procedures for the synthesis of true zeolite composites are quite complex. In this work, composite catalytic systems with a natural mordenite component and a

synthetic MFI zeolite phase were obtained by mechanical mixing. The samples were modified with Pd and Ni nanoparticles.

The aim of the study was to evaluate such metal-containing zeolite composites with separated phases as catalysts for the hydroisomerization of n-hexane.

Experimental

Table 1. Two-phase composite catalysts for linear hexane hydroisomerization.

Catalyst	MFI-component ¹	MOR-component ²	Total content of a metal component (wt%)
#L1	(I)HMFI-1Pd	(II)HR	0,5Pd
#L2	(I)HMFI-1Pd	(II)HR-2Ni	0,5Pd/1Ni
#L3	(II)HMFI-1Pd	(I)HR-2Ni	0,5Pd/1Ni
#C	HMFI-1Pd	HR-2Ni	0,5Pd/1Ni
#C-B α ³	HMFI-1Pd	HR-2Ni	0,35Pd/0,7Ni
#C-B γ ³	HMFI-1Pd	HR-2Ni	0,35Pd/0,7Ni

¹Based on the synthetic MFI type powdered zeolite, SiO₂/Al₂O₃=41; the number in parentheses – see in the text below.

²Based on the Transcarpathian mordenite-containing rock with a mordenite content of 72 wt% and SiO₂/Al₂O₃ ratio of 9.5.

³The samples containing 30 wt% α -Al₂O₃ or γ -Al₂O₃ as a binder.

Firstly, the H-form was obtained by exchanging the cations of the initial zeolites for NH₄⁺ cations followed by calcination of the NH₄-form at 873 K. Then, the MFI-component and the MOR-component (Table 1) were obtained, introducing 1 wt% Pd into the HMFI zeolite and 2 wt% Ni into the dealuminated H-form of rock (HR), respectively. Dealumination aimed at adjusting the SiO₂/Al₂O₃ ratio in rock was carried out by modifying the samples with a 5 mol/L HCl solution; the dealumination degree determined by chemical analysis has amounted to 40 %.

The L-series samples are catalytic systems consisting of separate layers of the MFI- and MOR-components with a fractional composition of 0.063-0.1 mm; the number in parentheses (Table 1) indicates the order in which the reagent enters the corresponding layer during the reaction.

The samples of C-series are composite catalytic systems with isotropic component distribution, obtained by mechanical mixing (1:1).

The reduction of metals in the composites was carried out in a flow of hydrogen (50 cm³/min) at a temperature of 653 K for 6 h.

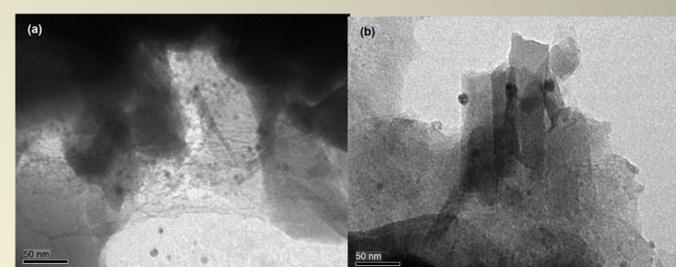


Fig. 1 TEM micrographs of the metal containing components of zeolite composites: (a) HMFI-1Pd, (b) HR-2Ni. The metal phases are presented by the nanosized particles of Pd (7–12 nm) and Ni (~5 nm), respectively.

The samples were examined using IR spectroscopy, X-ray diffractometry, transmission electron microscopy, low-temperature nitrogen ad(de)sorption, and tested in the hydroisomerization of n-hexane in a micropulse mode at atmospheric pressure using H₂ as a carrier gas.

Results

XRD, IR spectroscopy

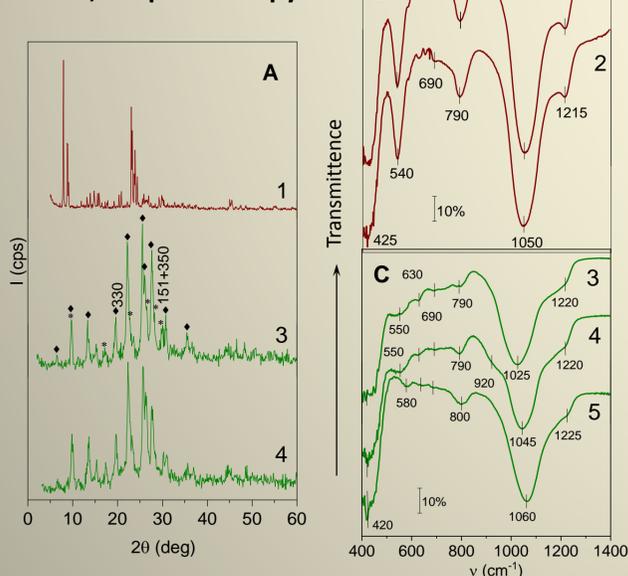


Fig. 2 (A) X-ray powder diffraction patterns and (B, C) FTIR spectra in the region of framework vibrations of the initial materials and the components of the composite catalysts: (1) HMFI, (2) HMFI-1Pd, (3) original rock, (4) dealuminated rock, (5) HR-2Ni; \blacklozenge – mordenite phase, \blacklozenge – clinoptilolite phase

- The MFI-component contains only this type of a zeolite.
- The incorporation of Pd nanoparticles does not affect the MFI zeolite structure.
- The MOR-component consists of two phases, mordenite and clinoptilolite, with the predominance of the former.
- A degree of crystallinity of the clinoptilolite phase after acid treatment decreases to 73%. Partial destruction of clinoptilolite may contribute to the formation of mesoporosity in the MOR-component.
- A high-frequency shift of the a.b. at 550 cm⁻¹ in the spectrum of the HR-2Ni sample confirms the existence of metal particles in the zero-valent state.

N₂ adsorption

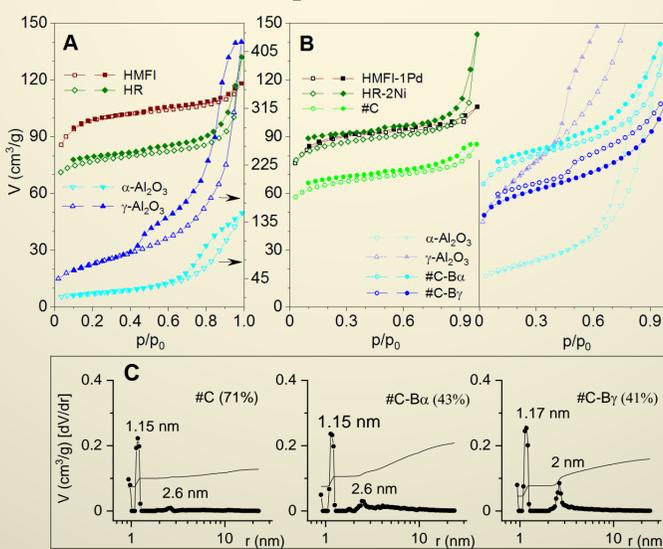


Fig. 3 N₂ ad(de)sorption isotherms (T = 77 K, blank symbols – adsorption, filled symbols – desorption): (A) initial materials, (B) composite catalysts and their components apart, and (C) pore size distribution in the composites with the proportion of micropores (in parentheses)

- The MFI-component of the catalysts has a microporous structure (84%), and the MOR-component is micro-mesoporous (55%).
- The composite without a binder remains mostly microporous (71%).
- The use of a binder (α -Al₂O₃ or γ -Al₂O₃) significantly increases the external surface of the catalysts and contributes to the appearance of mesopores with a radius of 2–10 nm and 2 nm, respectively.

Catalysis

(A), (B) Separation of zeolite phases in the composites made it possible to identify differences in the role of Pd and Ni nanoparticles in the C₆ conversion.

(A)–(D) The formation of C₆ isomers revealed a synergy of the two zeolite components. The synergy is more effective in the samples of C-series.

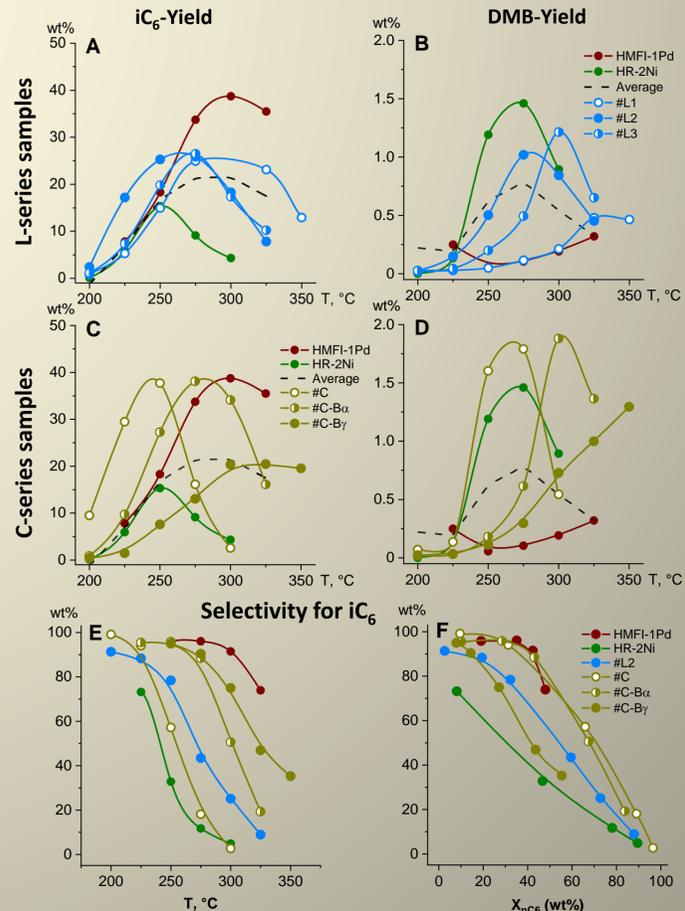


Fig. 4 Notes: iC₆ – C₆ isomers, DMB – dimethylbutanes, T – temperature and X_{nC₆} – conversion of n-hexane

(E), (F) The selectivity of all C-series samples, except for the low-activity #C-B γ , is on a par with the HMFI-1Pd. The addition of Ni and the specifics of sample preparation affect only the catalyst activity.

Conclusion

In the conversion of n-hexane, the role of palladium is to provide an initial efficient alkane dehydrogenation, which facilitates further isomerization. The hydrogenation of the formed isomers to the final products can occur on less efficient hydrogenating-dehydrogenating sites, such as nickel nanoparticles.

In the formation of C₆-isomers, the studied composites with separated zeolite phases demonstrate a synergy of the two zeolite components.

The highest efficiency in the formation of hexane isomers in general as well as valuable dimethyl-branched isomers was shown by the predominantly microporous composite catalyst. The reduced catalytic performance of the composite catalysts with developed mesoporosity is explained by their insufficient activity due to the lower nickel content.