

PHYSICO-CHEMICAL, TEXTURAL AND OPERATIONAL PROPERTIES OF CATALYSTS OBTAINED FROM LOCAL MINERAL RAW MATERIALS AND INDUSTRIAL TECHNOGENIC WASTE

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Abstract:

The physico-chemical, textural, mechanical and operational properties of catalysts prepared from local mineral raw materials Oltintog' and Angren kaolins, various grades of Navbahor bentonite, and Karmana opaque zeolite-bearing rocks together with industrial technogenic waste (metal-oxide active components) were studied. The supports were modified thermally, by acid treatment and hydrothermally; CuO, Bi₂O₃, NiO, CoO, ZnO, Cr₂O₃ and CdO were used as active components. The samples were characterized by IR spectroscopy, X-ray phase analysis (Rietveld method), scanning electron microscopy (SEM-EDS), a Shimadzu AGS-X mechanical testing machine, and water- and benzene-vapour adsorption isotherms (BET) measured on a McBain–Bakr balance. The results showed that the catalysts possess both Brønsted and Lewis acid sites, exhibit type IV adsorption isotherms, and have specific surface areas of 180–198 m²/g and crushing strengths of 44–60 kg/cm². Bentonite-supported catalysts were distinguished by relatively higher specific surface area, mechanical strength and resistance to poisoning. The study substantiates the feasibility of converting cheap local raw materials and technogenic waste into value-added catalysts (a resource-efficient, circular approach).

Key words: Aluminosilicate, Kaolin, Bentonite, Zeolite, Catalyst, Local Raw Material, Technogenic Waste, Brønsted and Lewis Acid Sites, Adsorption Isotherm, Specific Surface Area, Rietveld Analysis, Mechanical Strength

Introduction

Owing to their unique acid–base and textural properties, aluminosilicates are an important constituent of modern industrial catalysts. Their catalytic activity originates from the excess negative charge generated by the isomorphic substitution of silicon by aluminium in the crystal lattice and from the protons or metal cations that compensate it. Bridging Si–O(H)–Al hydroxyl groups form Brønsted acid sites, whereas coordinatively unsaturated aluminium centres form Lewis acid sites [1][2][3][4]. The

nature, number and strength of these sites govern the adsorption of substrate molecules and their subsequent catalytic transformation.

Natural layered (kaolinite, montmorillonite) and framework (zeolite-type) aluminosilicates are cheap, renewable and environmentally benign materials whose specific surface area, porosity and acid-site concentration can be deliberately increased by thermal and acid activation [5][6][7]. Acid treatment widens the interlayer spacing, partially removes structural water and foreign oxides, increases the SiO₂/Al₂O₃ ratio and amorphizes the surface, thereby improving sorption–catalytic performance [8][9][10]. Therefore, processing local mineral resources and industrial technogenic waste as catalyst supports and active components, instead of expensive synthetic carriers, is topical from the standpoint of resource efficiency and the circular economy.

Uzbekistan possesses industrially significant deposits of Oltintog' and Angren kaolins, various grades of Navbahor bentonite, and Karmana zeolite-bearing rocks. The aim of this work is to comprehensively characterize catalysts prepared from these local raw materials and metal-oxide technogenic components, to determine their acid–base, textural, mechanical and operational properties, and to substantiate their suitability for processes involving acetylene, acetylenic alcohols, carbonyl and carboxyl compounds[11][12][13].

Materials and methods

Supports and modification. Oltintog' kaolin (OK), Angren kaolin (AK), grades of Navbahor bentonite (NB, including PBG and PBV) and Karmana opaque zeolite-bearing rocks (KTJ) were used as catalyst supports. The supports were modified in three stages: (a) thermal treatment to remove organic matter; (b) acid treatment to increase the interlayer space, specific surface area and acid sites; and (c) hydrothermal treatment to increase the surface area of micro- and mesopores and the framework Si/Al ratio. Dehydroxylation above 650–700 °C, which reduces the number of proton acid sites, was taken into account.

Catalyst preparation. CuO, Bi₂O₃, NiO, CoO, ZnO, Cr₂O₃ and CdO were introduced into the modified supports in various ratios as active components (the compositions and their properties are given in Fig. 11). Mineral and organic acids were used as peptizers to enhance the interaction between the active component and the support.[14]

Characterization. The phase composition was determined by X-ray phase analysis and semi-quantitative Rietveld refinement. Surface functional groups and acid sites were studied by IR spectroscopy. Morphology and elemental composition were obtained on a Zeiss SEM EVO MA 10 scanning electron microscope (with EDS). The crushing mechanical strength was determined on a Shimadzu Autograph AGS-X (50 kN) machine. The strength and concentration of acid–base sites were assessed by a visual express method using Hammett-type colour indicators and by reflectance spectra on a Hitachi-330 spectrophotometer; the sample was calcined at 500 °C and treated with 0.005% indicator solutions in benzene, and the colour change was observed. Water- and benzene-vapour adsorption isotherms were measured on a high-vacuum McBain–Bakr (quartz-spring) balance; the specific surface area was calculated using the BET equation. The isotherms were classified according to IUPAC recommendations [15][16].

Results

Phase composition. Semi-quantitative X-ray Rietveld analysis showed that the kaolin mineral consists mainly of kaolinite (Al₄[Si₄O₁₀](OH)₈) and microcline (KAlSi₃O₈); the bentonite mineral of montmorillonite ((Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀)(OH)₂·nH₂O), muscovite (KA₂[AlSi₃O₁₀](OH)₂) and palygorskite; and the Karmana rock of heulandite ([Al₂Si₆O₁₆]·5H₂O), calcite (CaCO₃), quartz

(SiO₂) and sodium chloride (NaCl).

Si/Al ratio. The acidic properties of aluminosilicates depend on the nature and concentration of exchangeable cations and on the SiO₂/Al₂O₃ (Si/Al) molar ratio; the values determined for the studied supports are presented in Fig. 2. The lowest ratio was observed for Angren kaolin (1.2/1) and the highest for the Karmana rock (8.06/1). Exchange of alkaline cations for H⁺ increases the concentration of strong acid sites.

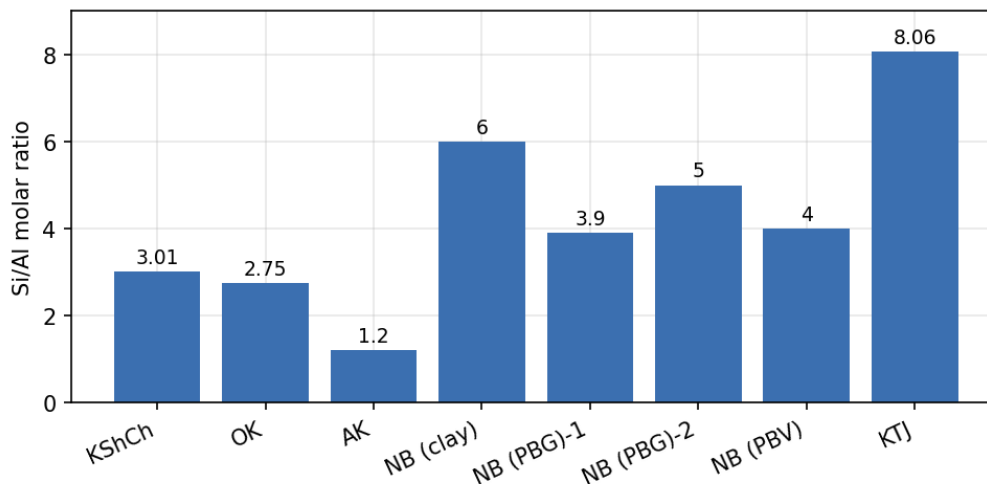


Figure 1. Si/Al molar ratio of the supports

IR spectroscopy. The IR spectra of the catalysts showed valence vibrations at 1000–1114 cm⁻¹ (Si–O), 912 cm⁻¹ (Al–OH), 468 cm⁻¹ (Si–O–Si and Si–O–Al) and 538–914 cm⁻¹ (Cd–O and Cr–O). The valence vibrations of OH groups were observed in the 3691–3750 cm⁻¹ range; absorption near 3712 cm⁻¹ corresponds to silanol groups, the 3620–3651 cm⁻¹ range to Brønsted sites formed upon decationization, and 700–800 cm⁻¹ to Lewis acid sites (Fig. 1). Thus, both Brønsted and Lewis acid sites are present on the catalyst surface.

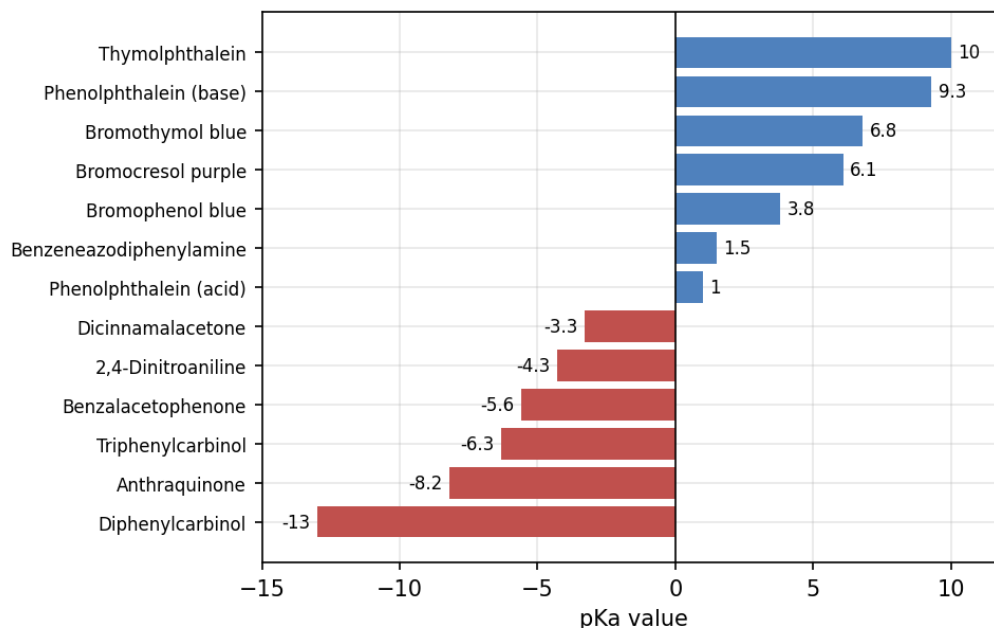


Figure 2. Distribution of acid–base sites on the KNB (PBG)-13 catalyst surface by indicator pKa values

Acid–base sites. The colour-indicator express method revealed acid and base sites of widely varying strength (pKa –13 to +10) on the surface of the KNB (PBG)-13 catalyst (Fig. 2). Very strong acid sites were detected with diphenylcarbinol (pKa –13), anthraquinone (–8.2) and triphenylcarbinol (–6.3), whereas basic sites were detected with thymolphthalein (pKa 10) and phenolphthalein (pKa 9.3). Such a broad spectrum of site strengths gives the catalyst the ability to activate diverse substrates.

Mechanical strength. The crushing mechanical strength was determined on the Shimadzu AGS-X machine (Fig. 3). In all samples, a decrease in the maximum force and stress and a slight increase in strain were observed after synthesis, indicating increased flexibility of the catalyst under operating conditions.

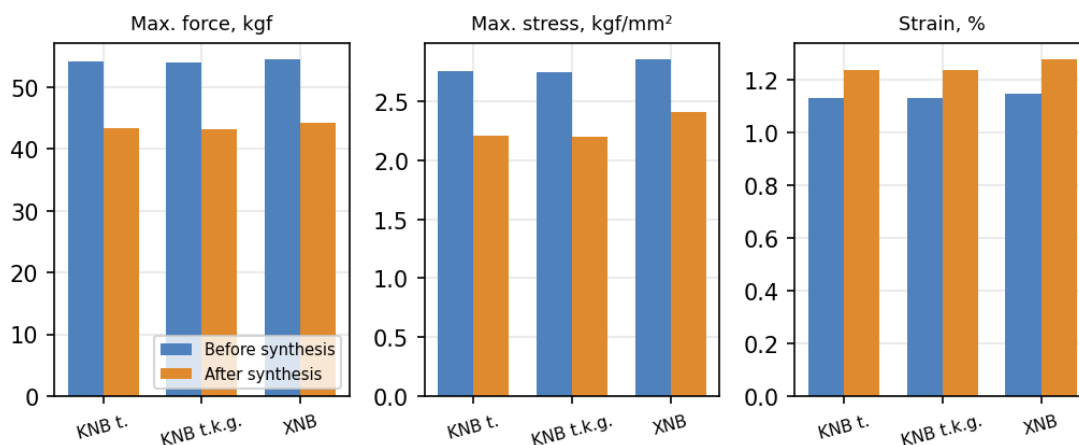


Figure 3. Crushing mechanical parameters of the catalysts before and after synthesis

Morphology and elemental composition (SEM-EDS). SEM images (20 μm) before and after synthesis showed sufficient porosity for sorption on the catalyst surface (Fig. 6). According to EDS analysis, the active-component content decreased as a result of the reaction (Fig. 7): chromium from 3.0% to 1.6% in XNB (PBG)-20; cadmium from 2.5% to 1.6% in KNB (PBG.t.k.g.)-13; and cadmium from 5.1% to 4.5% in KNB (PBG.t.)-13. This is explained by the transition of Cr₂O₃ to an amorphous state above 350–400 °C and the partial reduction of cadmium to the metallic state above 440 °C. In bentonite-supported catalysts, the active component was stable against poisoning.

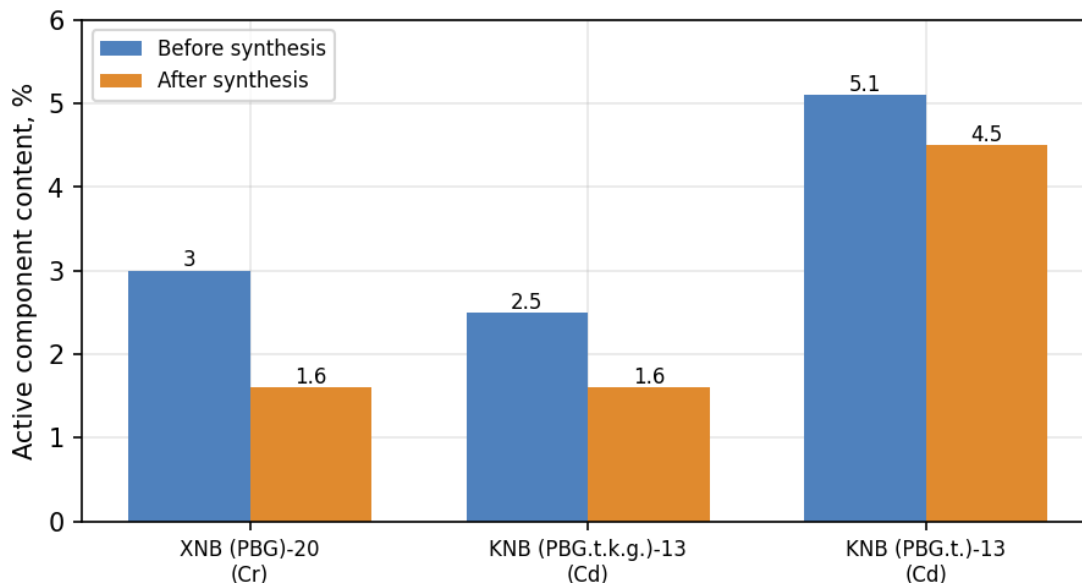


Figure 4. Change in active-component content before and after synthesis (EDS)

Adsorption isotherms. According to the Brunauer and IUPAC classification, the studied supports exhibit type IV isotherms, characteristic of multilayer adsorption and capillary condensation in mesopores [6] (Fig. 4). Owing to the polar nature of the bentonite surface and the presence of interlayer spaces, water vapour was sorbed better than benzene vapour: on the Navbahor bentonite support the specific surface area was 243.66 m²/g for water vapour and 101.72 m²/g for benzene vapour (Fig. 4).

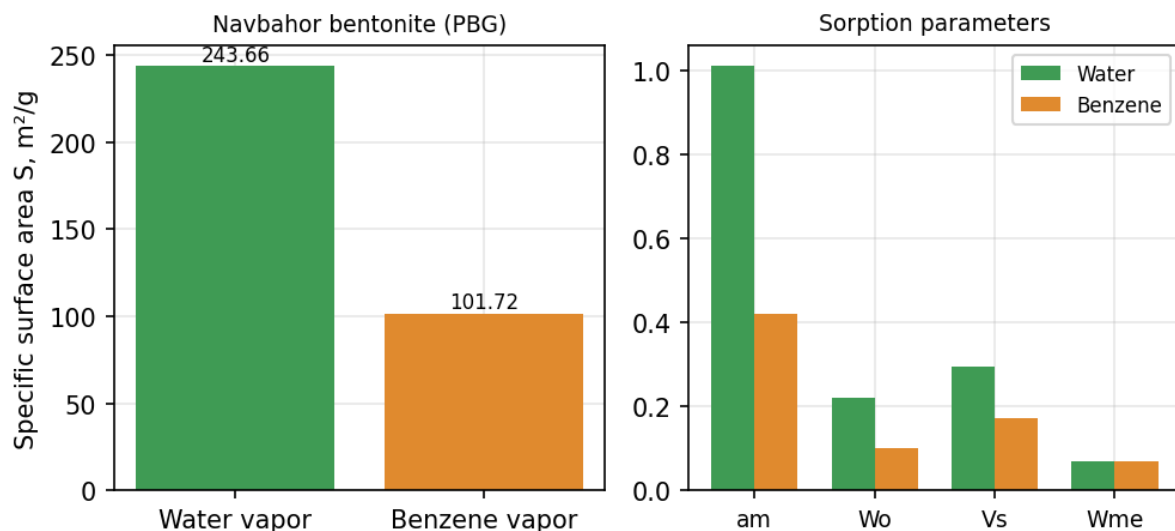


Figure 5. Structure–sorption parameters of the Navbahor bentonite (PBG) support

The specific surface areas of the thermally, acid- and hydrothermally activated KNB (PBG)-13 and XNB (PBG)-20 catalysts for water and benzene vapour were compared before and after synthesis (Fig. 5). The sharp rise of the isotherm at low relative pressure for the pre-synthesis samples confirms the presence of surfaces with high adsorption potential.

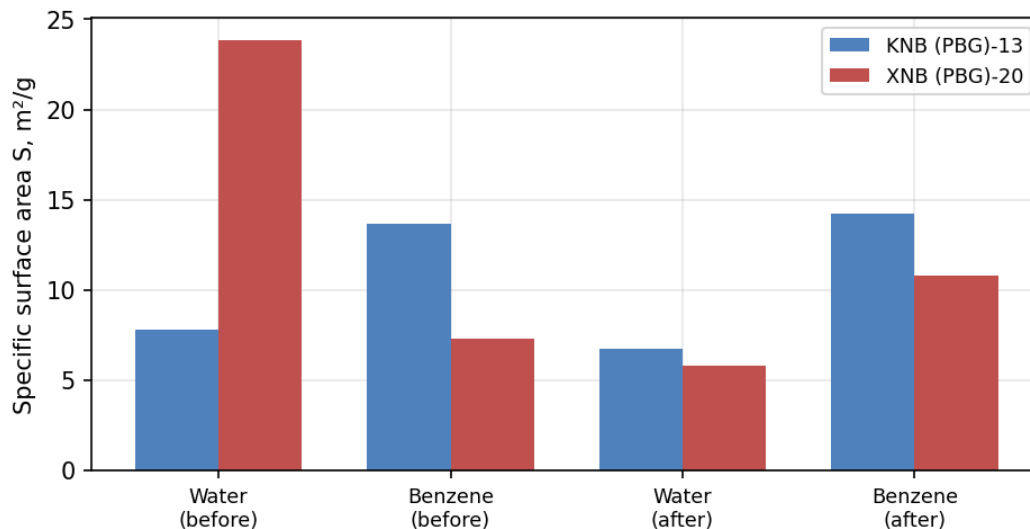


Figure 6. Specific surface area of the KNB (PBG)-13 and XNB (PBG)-20 catalysts (water and benzene vapour, before/after synthesis)

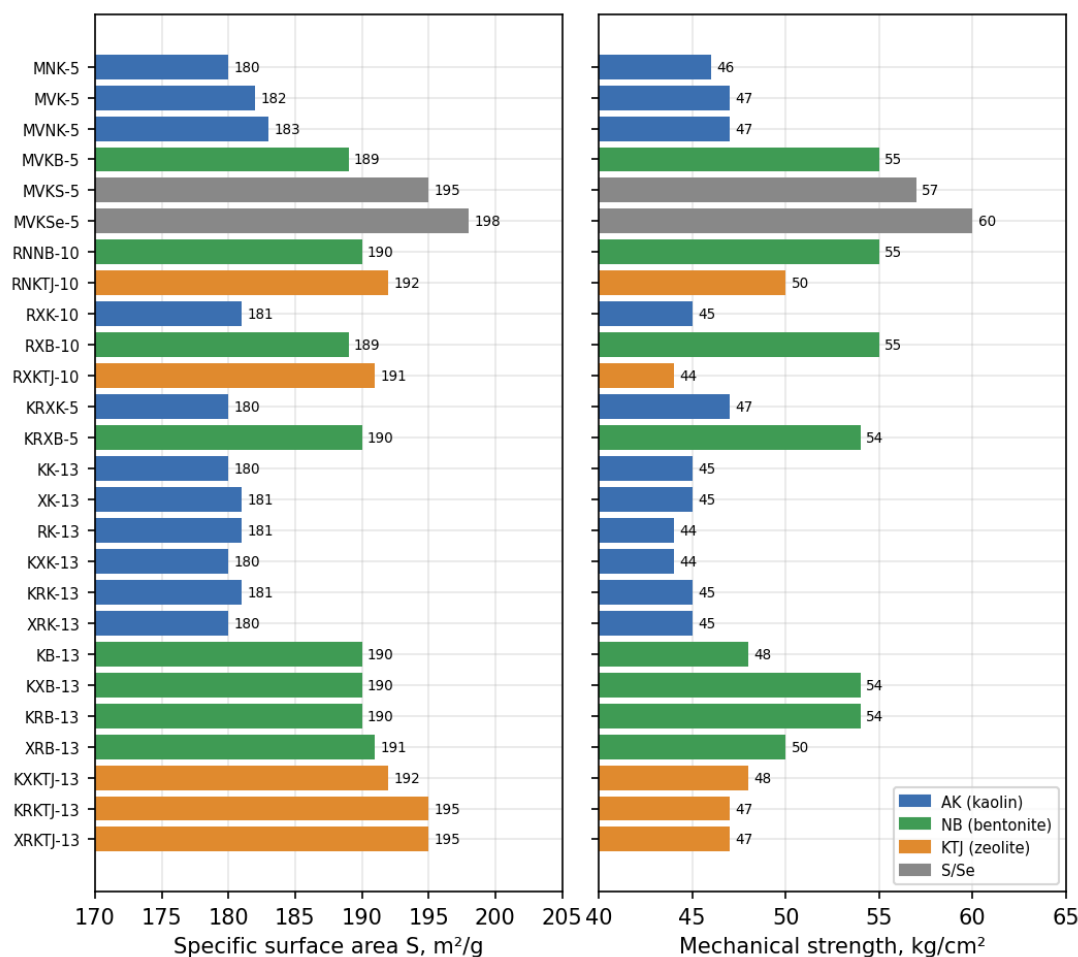


Figure 6. Specific surface area (left) and mechanical strength (right) of the catalysts, by support type

Generalized physico-chemical and operational properties. The specific surface area and mechanical strength of the 26 prepared catalysts are presented in Fig. 11, colour-coded by support type. The specific surface area ranged from 180 to 198 m²/g and the mechanical strength from 44 to 60 kg/cm²; the average pore size was 40–48 Å and the bulk density 716–748 g/cm³. As the figure shows, bentonite (NB) and zeolite (KTJ) supported samples have higher values than kaolin (AK) supported samples. The data obtained confirm that local mineral raw materials and technogenic metal-oxide components can be converted into effective catalysts. The characteristic absorption bands in the IR spectra (3620–3651 cm⁻¹ for Brønsted sites and 700–800 cm⁻¹ for Lewis sites) and the broad pKa range determined by the indicator method (–13 to +10) show that the catalysts possess both protic and aprotic acidic properties. This conclusion is consistent with the general understanding of the nature of active sites in acidic aluminosilicates [1, 2].

Stepwise thermal, acid and hydrothermal modification increased the sorption capacity of the supports while preserving their meso- and micropore structure: in the activated samples the isotherms saturated at lower P/Ps values and retained high adsorption capacity even at high relative pressures. This agrees with literature reports that acid treatment increases the specific surface area and porosity [4, 5]. The better sorption of water vapour than benzene is associated with the degree of surface polarity and the presence of interlayer spaces.

The nature of the support significantly affected the operational parameters (Fig. 11). Bentonite (NB) and zeolite-bearing (KTJ) supported samples were distinguished by a higher specific surface area (190–198 m²/g) and often higher mechanical strength (50–60 kg/cm²) than kaolin (AK) supported samples. SEM-EDS results showed that the active component is more resistant to poisoning in bentonite-

supported catalysts. The decrease in active-component content after synthesis (Cr: 3.0→1.6%; Cd: 2.5→1.6% and 5.1→4.5%) is explained by the amorphization of Cr₂O₃ at high temperature and the partial reduction of cadmium, indicating the need to optimize regeneration regimes.

The variation of the Si/Al ratio (from 1.2/1 for AK to 8.06/1 for KTJ) explains the differences in acid-site distribution and surface activity of the supports: a higher Si/Al ratio increases surface activity. The mechanical tests showed that, together with a decrease in maximum force after synthesis, the deformation capacity increased slightly. Overall, the results substantiate that catalysts based on cheap local raw materials possess the textural and acid–base properties required for processes involving acetylene, acetylenic alcohols, carbonyl and carboxyl compounds, and ammonia.

Conclusions

1. Catalysts were prepared by thermal–acid–hydrothermal modification based on Oltintog'/Angren kaolins, Navbahor bentonite and Karmana zeolite-bearing rocks together with metal-oxide technogenic components (CuO, Bi₂O₃, NiO, CoO, ZnO, Cr₂O₃, CdO).
2. IR spectroscopy and the indicator method confirmed the presence of both Brønsted and Lewis acid sites (pK_a –13...+10); Rietveld analysis established the phase composition of the supports.
3. The samples exhibited type IV isotherms according to IUPAC; water vapour was sorbed better than benzene ($S = 243.66 \text{ m}^2/\text{g}$ on the NB support).
4. Generalized parameters: specific surface area 180–198 m^2/g , pore size 40–48 Å, mechanical strength 44–60 kg/cm^2 , bulk density 716–748 g/cm^3 . Bentonite- and zeolite-supported samples had the highest values.
5. The results substantiate that processing local raw materials and industrial technogenic waste into value-added catalysts is resource-efficient and environmentally expedient.

References

- [1] W. O. Haag, R. M. Lago, and P. B. Weisz, "The active site of acidic aluminosilicate catalysts," *Nature*, vol. 309, pp. 589–591, 1984, doi: 10.1038/309589a0.
- [2] G. J. Kramer *et al.*, "Understanding the acid behaviour of zeolites from theory and experiment," *Nature*, vol. 363, no. 6429, pp. 529–531, 1993.
- [3] J. Klinowski *et al.*, "Monitoring of structural changes accompanying ultrastabilization of faujasitic zeolite catalysts," *Nature*, vol. 296, no. 5857, pp. 533–536, 1982.
- [4] G. T. Kokotailo *et al.*, "Structure of synthetic zeolite ZSM-5," *Nature*, vol. 272, no. 5652, pp. 437–438, 1978.
- [5] V. Verdoliva, M. Saviano, and S. De Luca, "Zeolites as acid/basic solid catalysts: Recent synthetic developments," *Catalysts*, vol. 9, no. 3, Art. no. 248, 2019.
- [6] J. M. Thomas, "Design, synthesis, and in situ characterization of new solid catalysts," *Angewandte Chemie International Edition*, vol. 38, no. 24, pp. 3588–3628, 1999.
- [7] P. Munnik, P. E. De Jongh, and K. P. De Jong, "Recent developments in the synthesis of supported catalysts," *Chemical Reviews*, vol. 115, no. 14, pp. 6687–6718, 2015.
- [8] W. Bing and M. Wei, "Recent advances for solid basic catalysts: Structure design and catalytic performance," *Journal of Solid State Chemistry*, vol. 269, pp. 184–194, 2019.
- [9] P. V. Kumar and G. Madhumitha, "Clay based heterogeneous catalysts for carbon–nitrogen bond formation: A review," *RSC Advances*, vol. 14, no. 7, pp. 4810–4834, 2024.
- [10] B. S. Kumar, A. Dhakshinamoorthy, and K. Pitchumani, "K10 montmorillonite clays as environmentally benign catalysts for organic reactions," *Catalysis Science & Technology*, vol. 4, no. 8, pp. 2378–2396, 2014.

- [11] D. P. Narayanan *et al.*, “A facile synthesis of clay–graphene oxide nanocomposite catalysts for solvent-free multicomponent Biginelli reaction,” *Arabian Journal of Chemistry*, vol. 13, no. 1, pp. 318–334, 2020.
- [12] T. Chellapandi and G. Madhumitha, “Montmorillonite clay-based heterogeneous catalyst for the synthesis of nitrogen heterocycle organic moieties: A review,” *Molecular Diversity*, vol. 26, no. 4, pp. 2311–2339, 2022.
- [13] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, and K. S. W. Sing, “Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report),” *Pure and Applied Chemistry*, vol. 87, nos. 9–10, pp. 1051–1069, 2015, doi: 10.1515/pac-2014-1117.
- [14] G. Nagendrappa and R. R. Chowreddy, “Organic reactions using clay and clay-supported catalysts: A survey of recent literature,” *Catalysis Surveys from Asia*, vol. 25, no. 3, pp. 231–278, 2021.
- [15] M. A. D. Fard, H. Ghafuri, and A. Rashidizadeh, “Sulfonated highly ordered mesoporous graphitic carbon nitride as a super active heterogeneous solid acid catalyst for Biginelli reaction,” *Microporous and Mesoporous Materials*, vol. 274, pp. 83–93, 2019.
- [16] M. M. H. Al-Abayechi *et al.*, “Organic synthesis via renewable heterogeneous nanocatalysts based on montmorillonite clay,” *Current Organic Chemistry*, vol. 28, no. 3, pp. 213–221, 2024.