

Catalytic activity and isomerizing ability of multicomponent skeletal nickel catalysts in the hydrogenation reaction of hexene-1 and cyclopentadiene

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Abstract: This study investigates the hydrogenation of cyclopentadiene and 1-hexene over skeletal nickel catalysts modified with various metallic additives. The results demonstrate the high catalytic activity of skeletal nickel in promoting the migration of the $\text{C}=\text{C}$ bond during the hydrogenation of 1-hexene. It was found that the addition of Fe, Pd, Sn, and Ag enhances the migration coefficient (K_{migr}), while Ti, Mo, and Ti-Mo exert little to no influence on this process. The catalytic performance in the hydrogenation of cyclopentadiene is strongly affected by the nature of the modifying elements incorporated into the initial alloy. Additives such as Cu, Zn, Mo-Cu, Bi, and Mo significantly improve both the activity ($W = 73\text{--}158 \text{ cm}^3/\text{min} \cdot \text{g Ni}$) and selectivity ($K_{\text{sel}} = 0.93\text{--}0.98$) of the reaction, facilitating the selective conversion of cyclopentadiene to cyclopentene. In contrast, Ti, Sn, and Cr-Cu additives do not substantially enhance either the activity or selectivity of the catalyst. The study highlights that the electronic and structural effects introduced by the modifying elements play a crucial role in determining the catalytic behavior of skeletal nickel systems. These findings provide valuable insights into the design of efficient nickel-based catalysts for selective hydrogenation processes and underline the potential of multi-component catalytic systems in optimizing reaction pathways. Overall, the research expands the understanding of structure-activity relationships in skeletal metal catalysts and demonstrates how tailored additive selection can improve both hydrogenation efficiency and product selectivity.

Keywords: hydrogenation reaction, hexene-1, cyclopentadiene, catalytic activity, isomerizing ability

1. Introduction

Catalytic hydrogenation is one of the most important and widely applied processes in modern chemical technology. The improvement of motor fuels, refined kerosenes, and hydrocarbon solvents is closely related to the need to reduce the content of unsaturated compounds, including aromatic hydrocarbons. The application of highly active transition metal complexes with various ligands provides an effective means of achieving this goal (Kravchenko et al., 1994; Cabrero-Antonino et al., 2020). Catalytic hydrogenation also plays a central role in the upgrading of biomass-derived feedstocks, the stabilization of pyrolysis oils, and the synthesis of fine chemicals. In these transformations, the removal or saturation of unsaturated and oxygenated functional groups is crucial for improving the quality and stability of the final products. From a mechanistic standpoint, hydrogenation proceeds through the adsorption and activation of H_2 on metal surfaces, followed by substrate chemisorption and stepwise hydrogen addition. Therefore, catalyst design has increasingly focused on controlling the electronic structure, dispersion, and coordination environment of active metal sites.

In industrial practice, hydrogenation processes are typically carried out under severe conditions—at elevated temperatures and high hydrogen pressures—using metal-oxide catalysts based on transition metals such as Co, Mo, Ni, Cu, and W. Among these, alloy-modified nickel catalysts have recently attracted significant

attention as efficient, readily available, and cost-effective alternatives in hydrogenation reactions (Aitmukhanbetov et al., 2015). Recent developments in catalyst engineering have demonstrated that electronic modification of nickel through alloying can fine-tune hydrogen adsorption energy, enhance resistance to poisoning, and improve selectivity toward specific reaction pathways. Such tenable catalytic systems are increasingly viewed as promising substitutes for precious-metal catalysts. Previous studies have reported the synthesis and catalytic performance of mono- and bimetallic Rh- and Rh-Co complexes containing oligoallenic ligands in the hydrogenation of unsaturated compounds such as isoprene, 1-hexene, and toluene (Kharkova et al., 2010). It has been shown that the catalytic activity of Rh(DMA)ol and Rh-Co(DMA)ol in the hydrogenation of 1-hexene reaches 16,800 and 23,000 mol/g-at h, respectively, while in the hydrogenation of toluene the activity is 72 and 90 mol/g-at h. Complete hydrogenation of isoprene occurs through two successive stages corresponding to the reduction of both double bonds. Furthermore, the catalytic activity of oligodimethylallenic palladium complexes supported on mineral carriers (e.g., Al_2O_3) strongly depends on the preparation method, particle size, and metal dispersion. The heterogenization of homogeneous Rh and Pd complexes has been shown to enhance their catalytic activity in hydrogenation reactions.

Alternative approaches have focused on the hydrogenation of cyclic unsaturated hydrocarbons using nickel nanoparticles deposited on various supports, such as Tseokar-2, activated carbon (BAU-A), alumina, and NaX zeolite (Alonso et al., 2011). These studies highlight the crucial role of metal-support interactions, which can modulate the oxidation state of active sites, influence hydrogen spillover, and alter particle size distribution factors that significantly affect catalytic performance. More recently, supported catalytic systems of the Me/CeO_x type (Me = Pt, Pd, Ru) have attracted attention due to their unique structural and catalytic properties (Mamad Zaera, 2014). Their high activity and thermal stability are associated with synergistic effects between the active metal and cerium oxide support, including the formation of mixed oxide phases and dynamic oxygen-hydrogen exchange at the interface (Sun et al., 2020). Such systems exemplify broader trends in modern catalysis, where strong metal-support interactions, redox-active oxides, and dynamic surface restructuring contribute to improved activity and resistance to deactivation. Similar phenomena are being exploited in nanostructured catalysts, alloy nanoparticles, and emerging single-atom catalysts, which offer highly tenable reactivity.

In industrial hydrogenation, catalysts based on platinum group metals (Pt, Pd, Ru, Rh) are often used for the selective hydrogenation of pyrolysis products. However, their high cost, sensitivity to catalytic poisons, and the need for harsh reaction conditions significantly limit their practical applicability. Therefore, the development of new, low-cost, highly active, and selective catalysts for the hydrogenation of individual unsaturated hydrocarbons and their mixtures remains an important research direction.

Nickel-based catalysts are particularly promising in this respect, offering high activity, selectivity, and stability at relatively low cost compared to noble metal systems (Aitmukhanbetov et al., 2015). Multicomponent skeletal nickel catalysts have demonstrated excellent performance in various hydrogenation processes due to their high activity and selectivity, ease of preparation and regeneration, operational stability over extended cycles, and resistance to poisoning [7]. It has been shown [8] that the modification of skeletal nickel with different metals enables precise control of catalytic properties across a wide range. These modifications allow tuning of the electronic density at Ni sites, changes in surface acidity/basicity, and alterations in hydrogen activation pathways—key parameters determining the balance between hydrogenation and isomerization reactions.

In contrast to the work of Jeldybayeva et al. (2022), which focused primarily on the catalytic behavior of mono- and bimetallic Ni systems, the present study systematically investigates a broader spectrum of alloying additives, including new combinations such as Ti-Mo, Mo-Cu, and Cr-Cu. These systems have not been previously evaluated with respect to their influence on C=C bond migration during the hydrogenation of 1-hexene and cyclopentadiene.

The present work investigates the effect of the amount of catalyst and the nature of modifying additives on the catalytic and isomerization activity of skeletal nickel in the hydrogenation of 1-hexene and cyclopentadiene.

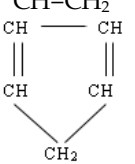
2. Materials and methods

2.1. Preparation of catalysts

A weighed portion (0.4–0.8 g) of crushed and powdered Ni-Al alloy, with particle sizes ranging from 0.06 to 0.20 mm (the alloy compositions are listed in Table 2), was subjected to activation by treatment

with a 20% KOH solution at 96 °C in a boiling water bath for 2 hours. The resulting product was repeatedly washed with distilled water (4–5 times) by decantation until no alkaline reaction to OH[−] ions was detected in the washings. Subsequently, the catalyst was rinsed with the solvent used in the hydrogenation process (ethanol) to remove residual moisture and prepare the sample for further experiments.

Table 1. The physicochemical characteristics of hexene-1 and cyclopentadiene

Compound	Structural formula	Molecular mass, g/mol	Boiling point, °C	Density d_4^{20} g/cm ³	Refractive index n_D^{20}	Solubility in:		
						water	ethanol	hexanes
hexene-1 butylethylene	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH=CH ₂	84.16	63.5	0.6732	1.3821	does not dissolve	∞	∞
cyclopentadiene -1,3		66.11	42.5	0.8048	1.4446	does not dissolve	∞	∞

2.2. Experimental methods

Hydrogenation experiments were conducted in a thermostated catalytic apparatus ("duck" type) [9] under atmospheric pressure and at a temperature of 20 °C. During the reaction, the hydrogen uptake rate (expressed as the volume of hydrogen absorbed per unit time, cm³/min) and the catalyst potential (mV) were continuously recorded relative to a saturated calomel reference electrode, following the procedure described in [9]. Prior to the reaction, the catalyst was pre-treated with hydrogen in the reaction solvent (V = 25 cm³) until the reversible hydrogen potential was established. The hydrogenation process was carried out in kinetic mode, with a stirring rate of 700–800 rpm.

$$K_s = \frac{\text{the yield of alkene, \%}}{\text{the yield (of alkene+alkane), \%}} \quad (1)$$

$$K_{\text{migr}} = \frac{\text{the yield (of cis-alkene-2+trans-alkene-2)}}{\text{the yield (of alkene-1+cis-alkene-2+trans-alkene-2)}} \quad (2)$$

$$K_{\text{isomer}} = \frac{\text{the yield of trans-alkene-2, \%}}{\text{the yield (of cis-alkene-2+trans-alkene-2), \%}} \quad (3)$$

$$S_t = \frac{\text{cis-alkene}}{\text{trans-hexene}} \quad (4)$$

The selectivity coefficient for the hydrogenation of 1-hexene and cyclopentadiene was calculated according to Equation (1); the migration coefficient of the -C=C- bond was determined using Equation (2); the isomerization coefficient and stereospecificity were evaluated using Equations (3) and (4), respectively. Chromatographic analysis of the reaction mixtures was performed using a Khromos GC-1000 gas chromatograph (Khromos, Russia) equipped with a flame ionization detector operating in isothermal mode. A BP21 (FFAP) capillary column (50 m × 0.32 mm i.d.) with a polar stationary phase (polyethylene glycol modified with nitroterephthalate) was employed. The column temperature was maintained at 90 °C, while the injector temperature was set to 200 °C. Helium was used as the carrier gas, and the injected sample volume was 0.2 × 10^{−6} m³. During each experiment, 2–3 aliquots of the liquid reaction mixture were collected for chromatographic analysis.

3. Results and discussion

3.1. Hydrogenation of hexene-1

Analysis of the data presented in Table 2 shows that the yield of hydrogenation products is strongly influenced by the amount of catalyst introduced into the reaction medium. For instance, the yield of 2-hexene increases linearly with the catalyst mass up to 0.5 g of nickel, reaching 67% at the initial stage of

the reaction. However, a further increase in catalyst loading (up to 0.75–1.0 g Ni) results in a decrease in the yield of 2-hexene. It is evident from Table 2 that the amount of catalyst significantly affects the ratio between the hydrogenation of 1-hexene and the migration of the $-C=C-$ bond. The migration coefficient (K_{migr}) and selectivity coefficient according to Bond G.C. (K_{sel}) [10], which characterize these processes, depend on the catalyst content in the reaction mixture. At the initial reaction stage, K_{migr} (the ratio of 2-hexene yield to the total yield of hexenes) increases from 0.29 to 0.98 as the catalyst mass rises from 0.05 to 1.0 g. Similarly, K_{sel} (the ratio of 2-hexene yield to hexane yield) increases from 0.36 to a maximum value of 1.01, then slightly decreases to 0.86. Recent data indicate that when a small amount of catalyst is used, the migration process proceeds approximately twice as slowly as the hydrogenation of 1-hexene. Conversely, at higher catalyst loadings (1.0 g Ni), the formation of 2-hexene occurs about twice as fast as the hydrogenation of 1-hexene. During the hydrogenation of 1-hexene over skeletal nickel, the trans-isomer of 2-hexene is formed preferentially at the early reaction stages. The isomerization coefficient (K_{iz}), defined as the ratio of the trans-isomer yield to the total yield of 2-hexene, ranges from 0.72 to 0.84. This value remains nearly constant throughout the reaction until 1-hexene is completely converted and is practically independent of the catalyst amount. After the disappearance of 1-hexene, K_{iz} increases slightly, which can be attributed to the different hydrogenation rates of the trans- and cis-isomers to hexane. Thus, when hydrogenation of 1-hexene is carried out using 0.15–0.5 g of skeletal nickel catalyst, the K_{migr} values (at 0.5 mol of hydrogen absorbed) vary within the range of 0.38–0.95. These results are consistent with previously reported data [8], where migration coefficients were found to fall within similar limits. Based on the obtained results, it can be concluded that skeletal nickel exhibits a high isomerizing ability, second only to palladium among known hydrogenation catalysts [11].

Table 2. Composition of the hydrogenation product obtained by hydrogenation of hexene-1 on skeletal nickel from a Ni : Al (1 : 1) alloy (the amount of absorbed hydrogen is given per 0.5 mol of H_2)

Catalyst weight, g	Reaction products, %				K_{migr}	K_{sel}	K_{isom}
	Hexane	Hexene-1	Hexene -2				
			trans	cis			
0.05	45.0	39.3	11.3	4.4	0.29±0.05	0.36±0.02	0.72±0.03
0.15	51.1	29.8	13.8	5.3	0.38±0.03	0.58±0.04	0.74±0.04
0.25	46.5	7.3	33.5	12.7	0.88±0.04	1.01±0.09	0.74±0.04
0.50	50.1	2.5	33.9	13.5	0.95±0.08	0.78±0.05	0.76±0.03
0.75	51.1	2.3	34.2	12.4	0.96±0.07	0.96±0.06	0.73±0.03
1.00	53.3	1.4	37.5	7.8	0.98±0.07	0.86±0.05	0.84±0.02

However, if we calculate the migration coefficient of skeletal nickel with a catalyst weighed of 0.05 g (i.e., on the same catalyst weighed on which hydrogenation is carried out on Pd, Rh, Pt and other catalysts), then K_{mig} will be equal to 0.29. Consequently, skeletal nickel, in terms of isomerizing ability, belongs to a number of metals Pd, Rh, Pt, etc., which weakly catalyze the migration of the $-C=C$ bond [7, 11, 12]. Modification of skeletal nickel with various metals has a significant effect on the catalytic activity and isomerizing ability of a skeletal nickel catalyst during the hydrogenation of hexene-1 (Table 3), which may be associated with a change in the energy state of adsorbed hydrogen on the surface of the catalyst. The results of chromatographic analysis (Table 3, Fig. 1) indicate the high activity of modified skeletal nickel catalysts in the migration reaction of the $-C=C$ bond during the hydrogenation of hexene-1.

Modification of Ag, Pd and Sn increases K_{migr} from 0.68 to 0.71–0.75, and additions of Ti, Mo and Ti-Mo practically do not change it. The introduction of Cr-Cu, Cu, Zn, Ti-Mo and Mo-Cu into the catalyst composition reduces the ability of the catalyst to move the $-C=C-$ bond ($K_{migr} = 0.47$ –0.63). Additive modifiers almost do not change the ratio of cis/trans isomers of hexene-2 ($K_{isom} = 0.75$ –0.81). The activity of the catalyst increases with the introduction of the metals Cu, Zn, Ti-Mo, Mo, Bi, Ag and Mo-Cu into the initial alloy ($WC\equiv C = 125$ –250 cm^3/min g Ni), and the addition of Pd reduces it ($WC\equiv C = 68$ cm^3/min g Ni). The influence of Ti and Sn on the change in $WC\equiv C$ is insignificant ($WC\equiv C = 119$ cm^3/min g Ni). The strongest adsorption of hexene-1 is observed on catalysts containing Mo, Ti, Bi and

Sn ($\Delta E_{\text{start}} = 210\text{--}290$ mV). Alloying the alloy with Cu and Mo-Cu, Cr-Cu leads to a decrease in ΔE_{start} up to 90–170 mV.

Table 3. Hydrogenation of hexene-1 on multicomponent skeletal nickel catalysts (conditions: $m_{\text{cat}} = 0.4$ g, $T = 20^\circ\text{C}$, $P_{\text{H}_2} = 0.1$ MPa, $V_{\text{sol}} = 25$ cm³ (ethanol))

Alloy composition	Ni-Al-Me content, wt. %	$W_{\text{C=C}}$	ΔE_{start}	K_{migr}	S_t
Ni-Al	50-50	120	210	0.68	0.76
Ni-Al-Cu	40-55-5	150	150	0.53	0.75
Ni-Al-Ag	48-50-2	135	185	0.71	0.76
Ni-Al-Zn	43-44-13	250	140	0.59	0.75
Ni-Al-Ti	47-50-3	119	290	0.66	0.76
Ni-Al-Sn	45-50-5	119	230	0.75	0.75
Ni-Al-Bi	45-50-5	125	210	0.70	0.78
Ni-Al-Mo	45-50-5	125	290	0.67	0.75
Ni-Al-Pd	48-50-2	68	260	0.75	0.79
Ni-Al-Ti-Mo	44-50-3-3	155	210	0.63	0.81
Ni-Al-Mo-Cu	42-50-3-5	130	90	0.63	0.76
Ni-Al-Cr-Cu	42-50-3-5	115	170	0.47	0.77

* $W_{\text{C=C}}$ – specific activity of the catalyst for the hydrogenation of hexene-1, cm³ H₂/min g Ni; ΔE_{start} – initial displacement of the catalyst potential, mV; S_t – stereospecificity (cis-hexene-2/ trans-hexene-2)

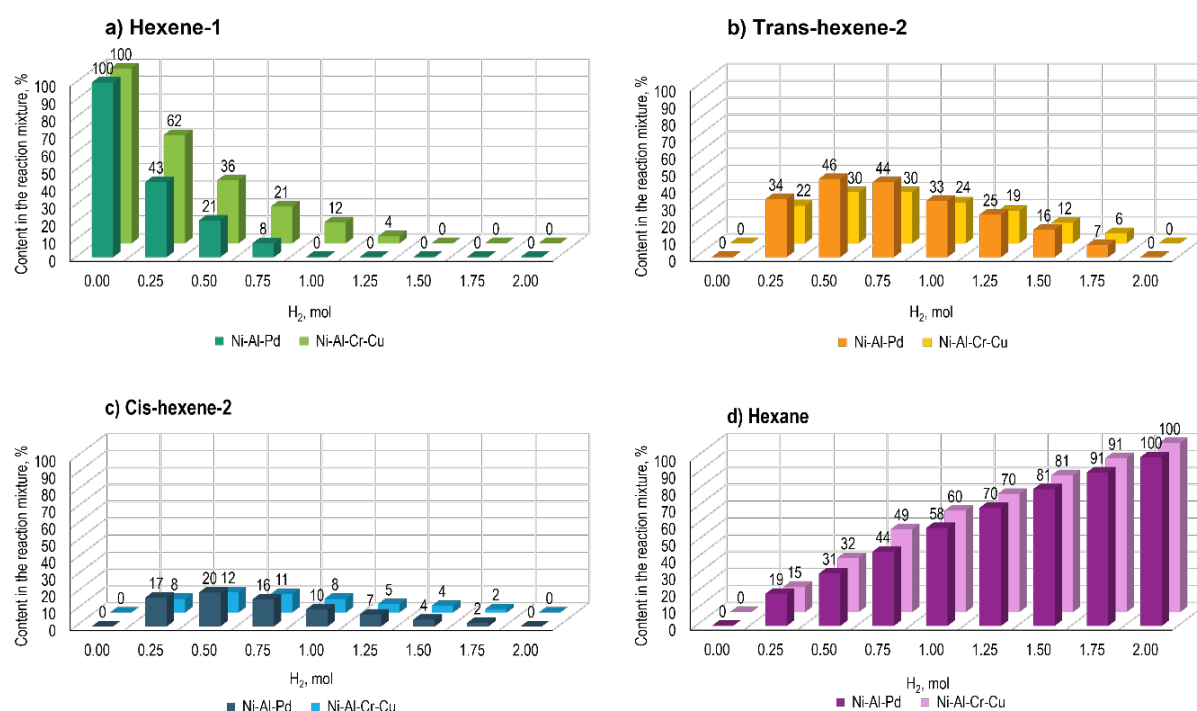
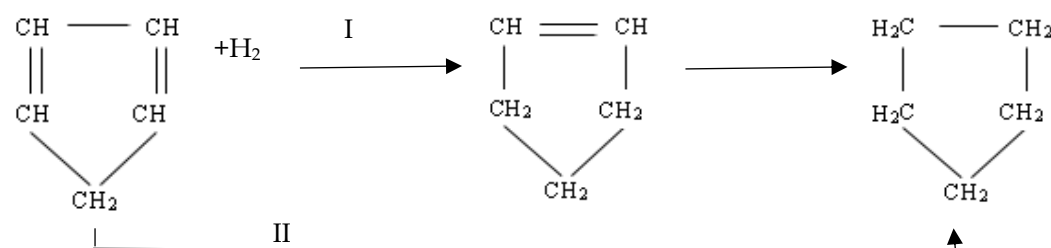


Fig. 1. Comparison of the reaction mixture content: a) hexene-1, b) trans-hexene-2, c) cis-hexene-2, d) hexane during the hydrogenation of hexene-1 on skeletal nickel from Ni-Al-Pd and Ni-Al-Cr-Cu alloys (conditions: $m_{\text{cat}} = 0.4$ g, $T = 20^\circ\text{C}$, $p_{\text{H}_2} = 0.1$ MPa, $V_{\text{sol}} = 25$ ml (ethanol))

3.2. Hydrogenation of cyclopentadiene

Hydrogenation reactions of cyclopentadiene can proceed in two directions (see scheme 1). The hydrogenation curves of cyclopentadiene (Fig. 2) obtained over modified skeletal nickel catalysts exhibit a distinct “stepwise” character, which reflects the sequential nature of the reaction. The hydrogenation of cyclopentadiene proceeds at an approximately constant rate until one mole of hydrogen is absorbed, at which point a turning point appears on the curve. Beyond this stage, the

hydrogenation of the intermediate cyclopentene occurs at a noticeably slower rate. The ratio of the hydrogenation rates $W_{C=C=C}/W_{C=C}$ ranges from 1.43 to 2.6, depending on the type of modifying additive used (Table 4). The highest ratios (1.73–2.5) were observed for catalysts containing Cu, Mo–Cu, and Bi additives. The stepwise character of cyclopentadiene hydrogenation is also confirmed by the potentiometric measurements. The initial potential shift of the catalyst, which depends on the nature of the modifying additives introduced into the Ni–Al alloy, ranges from $\Delta E = 180$ to 340 mV. The subsequent hydrogenation of cyclopentene takes place at more cathodic potentials ($\Delta E = 52$ –84 mV). The catalytic activity of multicomponent skeletal nickel systems is strongly influenced by the type of modifying elements incorporated into the parent alloy. The introduction of Cu, Zn, Mo–Cu, Bi, or Mo significantly enhances catalytic activity, with hydrogenation rates $W_{C=C=C}$ in the range of 73–158 $\text{cm}^3 \text{min}^{-1} \text{g}^{-1} \text{Ni}$. In contrast, the addition of Ti, Sn, or Cr–Cu has little to no effect on the activity of the catalyst (Table 4).



Scheme 1. Directions of hydrogenation reactions of cyclopentadiene

Table 4. Hydrogenation of cyclopentadiene on multicomponent skeletal nickel catalysts in ethanol (conditions: $m_{\text{cat}} = 0.4 \text{ g}$, $T = 20^\circ \text{C}$, $P_{\text{H}_2} = 0.1 \text{ MPa}$, $V_{\text{solv}} = 25 \text{ cm}^3$ (ethanol))

Alloy composition	Content Ni–Al–Me wt. %	Cyclopentadiene			
		$W_{C=C=C}$	$W_{C=C}$	ΔE_{start}	K_{sel}
Ni–Al	50–50	100	52	270	0.92
Ni–Al–Cu	40–55–5	145	58	180	0.98
Ni–Al–Ag	48–50–2	136	76	260	0.97
Ni–Al–Zn	43–44–13	158	84	200	0.97
Ni–Al–Ti	47–50–3	102	60	310	0.96
Ni–Al–Sn	45–50–5	105	66	290	0.93
Ni–Al–Bi	45–50–5	158	77	260	0.98
Ni–Al–Mo	45–50–5	144	72	340	0.98
Ni–Al–Pd	48–50–2	83	58	280	0.93
Ni–Al–Cr	47–50–3	110	99	240	0.94
Ni–Al–Ti–Mo	44–50–3–3	120	65	260	0.97
Ni–Al–Mo–Cu	42–50–3–5	73	42	210	0.94
Ni–Al–Cr–Cu	42–50–3–5	169	65	300	0.97
Ni–Al–Ti–Cu	42–50–3–5	93	4.	210	0.94

* $W_{C=C=C}$ – specific activity of the catalyst for the hydrogenation of cyclopentadiene, $\text{cm}^3 \text{H}_2/\text{min g Ni}$; $W_{C=C}$ is the specific activity of the catalyst during the hydrogenation of cyclopentene, $\text{cm}^3 \text{H}_2/\text{min g Ni}$; ΔE_{start} – initial displacement of the catalyst potential, mV

The introduction of the vast majority of alloying elements into the initial alloy leads to an increase in the selectivity of cyclopentadiene hydrogenation: K_{sel} increases to 0.98 (Fig. 3, Table 4).

When cyclopentadiene is hydrogenated, one intermediate alkene (cyclopentene) is formed (Fig. 3). This is due to the cyclic structure of cyclopentadiene, which determines the formation of identical cycloalkene molecules upon addition of hydrogen to any position. The saturation of cyclopentadiene almost completely ends when 1 mole of hydrogen is absorbed, and cyclopentene can be obtained in good yield (Fig. 3). The petrochemical industry is very interested in the synthesis of this cycloalkene. Polypentenamer, which has technically valuable elastomeric properties, is synthesized by ring-opening polymerization of cyclopentene [7, 8, 10, 13]. In this regard, an increase in the selectivity coefficient of

cyclopentadiene hydrogenation from 0.92 to 0.98 when modifying skeletal nickel with the metals Zn, Cu, Mo, Bi, Mo-Cu, Ag, Ti-Mo, Cr-Cu, Pd and Sn (Table 4) is important practical significance.

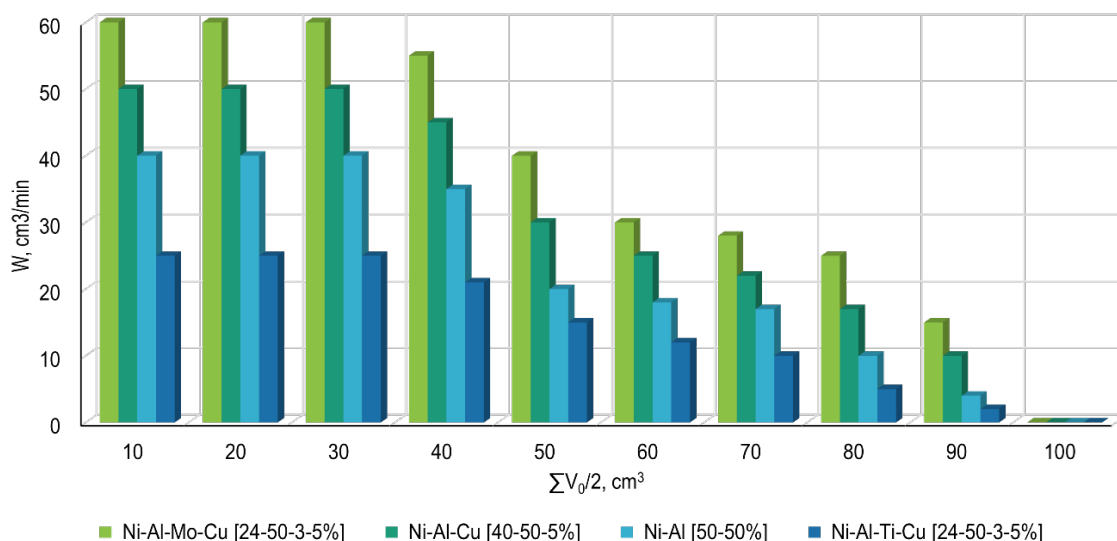


Fig. 2. Curves of cyclopentadiene hydrogenation ($A_{H_2}=100 \text{ cm}^3$) in ethanol on multicomponent skeletal nickel alloy catalysts ($m_{\text{alloy}}=0.8 \text{ g}$)

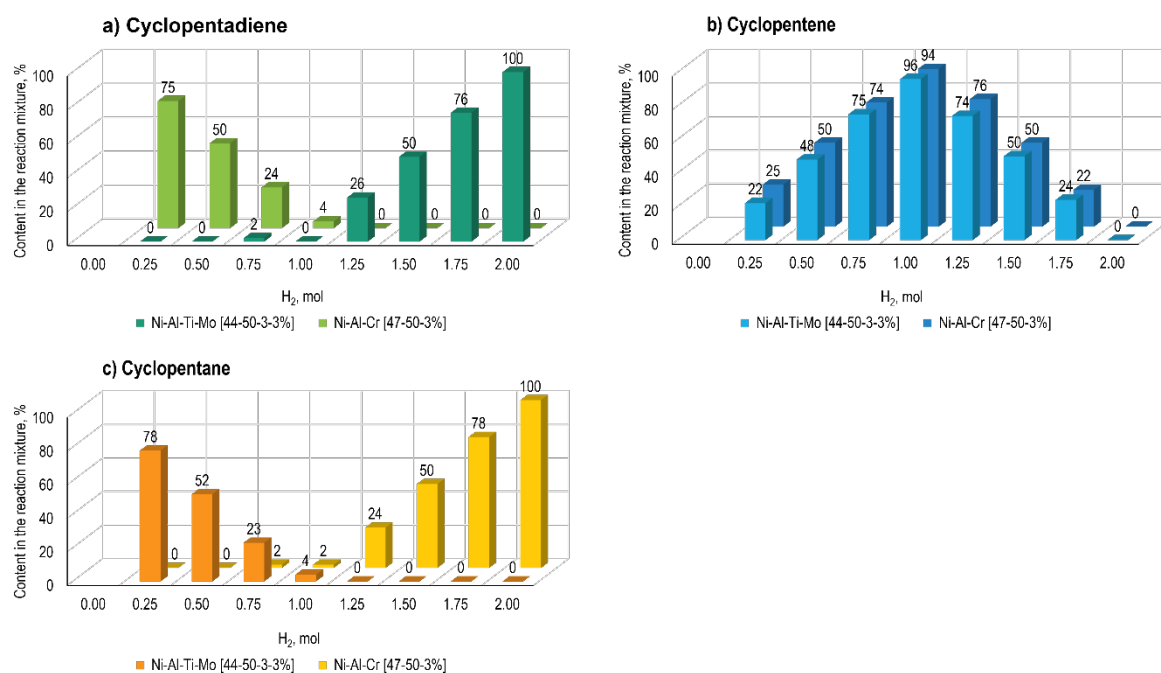


Fig. 3. Changes in the composition of the reaction mixture: a) cyclopentadiene, b) cyclopentene, c) cyclopentane during the hydrogenation of cyclo-pentadiene on skeletal nickel from Ni-Al-Ti-Mo and Ni-Al-Cr alloys (conditions: $m_{\text{cat}}=0.4 \text{ g}$, $T=20^\circ\text{C}$, $p_{H_2}=0.1 \text{ MPa}$, $V_{\text{solv}}=25 \text{ ml}$ (ethanol))

Although some general trends in hydrogenation activity resemble those described by Yermoldina et al. [14], the present study reveals new mechanistic insights arising from the introduction of novel alloying systems. For example, the enhanced K_{migr} values obtained for Fe-, Pd-, Sn- and Ag-modified catalysts, compared with the suppressed migration observed for Mo-Cu or Ti-Mo compositions, indicate significant changes in the preferred adsorption geometry of the olefin. This finding suggests that the interplay between π -complex formation and allylic rearrangement steps differs fundamentally from previously reported systems.

It is worth emphasizing that although the obtained results clearly indicate a differential effect of individual alloying additions on the direction of bond migration and the activity of the studied catalysts, a complete interpretation of the observed relationships requires consideration of electronic and structural effects occurring in the modified Ni framework. The literature indicates that metal additions can modify the surface electron density, the energy and mode of alkene adsorption, and the stability of the transitional π -complex and allyl forms. The mechanism of $-C=C-$ bond migration under hydrogenation conditions is most often described using the classical Horiuti–Polanyi model, in which the order and strength of adsorption of both hydrogen and the substrate, as well as the equilibrium between the σ - and π -adsorbed forms, play a key role. However, this paper does not present detailed adsorption models or a schematic isomerization mechanism, which limits the possibility of fully explaining the role of individual alloying additions in stabilizing the transitional reaction states. Taking these aspects into account, both in the form of surface analyses and computational mechanistic models, is an important direction for further research on nickel framework catalysts.

4. Conclusions

In summary, the conducted studies demonstrated that for all catalysts examined, the product yields in migration and isomerization processes are strongly dependent on the amount of catalyst introduced into the reaction mixture. Specifically, the yield of 2-hexene increases linearly with catalyst mass up to 0.5 g of nickel, reaching 67% at the initial stage of the reaction, but decreases when the catalyst weight is further increased up to 1.0 g Ni. Chromatographic analysis confirmed the high activity of modified skeletal nickel catalysts in promoting the migration of the $-C=C-$ bond during 1-hexene hydrogenation. Additions of Fe, Pd, Sn, and Ag enhanced the migration coefficient (K_{migr}) from 0.66 to 0.71–0.75, whereas Ti, Mo, and Ti–Mo had negligible effect. In contrast, the incorporation of Cu, Ti–Mo, and Mo–Cu decreased the catalyst's ability to induce bond migration ($K_{migr} = 0.53$ –0.63). The activity of multicomponent skeletal nickel catalysts in cyclopentadiene hydrogenation was found to be strongly influenced by the nature of the alloying additives. Introduction of Cu, Zn, Mo–Cu, Bi, and Mo significantly improved both catalytic activity ($W_{\{C=C-C=C\}} = 73$ –158 cm³ min⁻¹ g⁻¹ Ni) and selectivity ($K_{sel} = 0.93$ –0.98) in the hydrogenation of cyclopentadiene. By contrast, Ti, Sn, and Cr–Cu had little effect on either the activity or selectivity of the catalyst.

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