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Transition Metal Sulfides- and Noble Metal-Based Catalysts for N-Hexadecane Hydroisomerization: A Study of Poisons Tolerance

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Abstract: Bifunctional catalysts on the base of transition metal sulfides (CoMoS and NiWS) and platinum as noble metal were synthesized via wetness impregnation of freshly synthesized Al_2O_3 -SAPO-11 composites, supported with favorable acidic properties. The physical-chemical properties of the prepared materials were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), low-temperature N_2 adsorption and high resolution transmission electron microscopy (HR TEM) methods. Catalytic properties were studied in n-hexadecane isomerization using a fixed-bed flow reactor. The catalytic poisons tolerance of transition metal sulfides (TMS)- and Pt-catalysts has been studied for sulfur and nitrogen, with the amount of 10–100 ppm addition to feedstock. TMS-catalysts show good stability during sulfur-containing feedstock processing, whereas Pt-catalyst loses much of its isomerization activity. Nitrogen-containing compounds in the feedstock has a significant impact on the catalytic activity of both TMS and Pt-based catalysts.

Keywords: hydroisomerization; n-alkanes; bifunctional catalysts; stability; CoMoS; NiWS; Pt; catalytic poisons

1. Introduction

Nowadays, transformation of n-alkanes to corresponding branched forms by hydroconversion, i.e., hydrocracking or hydroisomerization, is becoming more important for the petroleum refinery and petrochemical industry [1–5]. This process plays a significant role in the production of high-quality gasoline and diesel fuels, as well as motor oils. Diesel and gasoline oil fraction treatment transforms the high freezing long-chain n-paraffins, and contributes to the improvement of the octane number of gasoline and the low-temperature performance of diesel or lubricating oils [6–10]. One of hydroisomerization's advantages is the high yield of liquid products. These light fractions do not have any sulfur, but contain branched alkanes with high octane numbers, which causes isomerization products to be the most valuable component of gasoline. Hydroisomerization of linear long-chain hydrocarbons is becoming more important considering ecological restrictions [11,12].



Hydroisomerization catalysts are bifunctional systems, containing metal particles acting as hydrogenation/dehydrogenation sites and acidic mesoporous support, providing acid sites for isomerization [13,14]. The hydrogenation/dehydrogenation activity of hydroisomerization catalysts is provided by the metallic sites, typically Pt, supported on acidic mesoporous carriers [13,15–17]. Different kinds of zeolites, natural clays and aluminosilicates are widely used as supports for bifunctional catalysts [18–24].

According to widely acknowledged hydroisomerization mechanisms, n-alkanes are dehydrogenated on metallic active sites to form alkene intermediates. The resulted olefins are protonated and isomerized mainly on Brønsted acid sites, followed by rapid hydrogenation over metal sites to the corresponding branched iso-alkanes (Figure 1) [25,26]. Besides, the length of the hydrocarbon chain is considered to be correlated with the reactivity thereof [27]. Thus, the acidity properties are inversely proportional to the chain length [1]. Therefore, the selectivity of the catalyst towards isomerization is affected by a proper balance between metallic and acidic sites.



Figure 1. Scheme of n-hexadecane hydroisomerization. **a**—Hydrogenation-dehydrogenation on metallic sites; **b**—Protonation-deprotonation on acid sites; **c**—Addition of proton to form alkylcarbonium ion on acid; **d**—Dehydrogenation to form alkylcarbenium ion; **e**—Competitive adsorption–desorption of alkene and carbenium ion on acid sites; **f**—Rearrangement of alkylcarbenium ion; **g**—Cracking of alkylcarbenium ion; **h**—Hydrogenation to form alkane on metallic sites.

The structural properties of the support also affect the shape-selectivity of molecular sieves. In general, the smaller the zeolite pore size, the lower the methyl branching [28,29]. While for microporous molecular sieves methyl branching takes place, for wide pore openings and large cavities, ethyl and propyl branched isomers are obtained [7,30]. Multibranched isomers formed during n-paraffins isomerization are more susceptible to hydrocracking, which leads thereby to lower isomerization selectivity [31]. The support structure and textural properties are also crucial for long-chain isomerization from the point of view of diffusion limitations, due to the transformation of linear alkanes occurring in the micropores: the rapid diffusion of molecules to the bulk phase should be provided before the undesired cracking reactions occur.

The hydrogenation/dehydrogenation activity of hydroisomerization catalysts is provided by metallic sites, typically Pt, supported on acidic mesoporous carriers [13,15]. Different kinds of zeolites, natural clays and aluminosilicates are widely used as supports for bifunctional catalysts [18–24]. The most significant characteristic for these catalysts from an industrial viewpoint is stability to poisons [32,33]. Noble metal-based catalysts stand out as more active for hydroisomerization when the content of the active metals is higher than 0.5 wt %, which makes them very expensive [34–37]. Moreover, catalyst poisoning by nitrogen- and sulfur-containing compounds leads to dramatic decreases in activity [38–41]. Metal active sites poisoning by sulfur involves hydrogen sulfide adsorption followed

by its dissociation, leading to rearrangement of the metal surface, wherein the polysulfide layer forms, and catalyst deactivation is reversible. When the S/Pt ratio is higher than 0.4, the poisoning becomes irreversible. This may also be caused by strong Pt–S covalent bonding [42]. The deactivation of the noble metal-based catalysts by nitrogen-containing compounds takes place due to their strong adsorption on the acid sites of the support. As a result, the content of available active sites decreases, which has a negative influence on catalytic activity [43]. Therefore, the industrial application of noble metal-based catalysts for hydroisomerization is limited, and research focuses shift towards novel low-cost bifunctional catalysts with sufficient activity and stability. As such, the development of transition metal-containing catalysts for hydroisomerization of linear alkanes is of both scientific and industrial interest [44–47].

The most promising sulfur tolerance catalysts are transition metal sulfides. The transition metal sulfides providing high catalytic activity are widely used for hydrotreatment processes [44,48–51]. CoMo bimetallic catalysts have been investigated for ethylbenzene hydrogenation [34]. Appropriate acidity of the support favors the hydrogenation/isomerization activity of the catalysts, which allows the performance of ultra-deep sulfur removal from oil fractions [52–54].

A number of microporous zeolites, such as ZSM-22, ZSM-23 and ZSM-48, were used as functional supports for hydroisomerization catalysts. Among one-dimensional porous materials, structured SAPO-11 exhibits appropriate acidity and shape-selectivity, making it one of the more promising supports for hydroisomerization catalysts. This silicoaluminophosphate, consisting of Al₂O₃, SiO₂ and P₂O₅ as the main components, has a one-dimensional, 10-membered ring channel system, with an elliptical pore opening of 0.44 × 0.64 nm [55]. Thanks to moderate acidity and shape-selectivity, the medium-pore SAPO-11 acts as a functional support for isomerization catalysts, favoring selective isomerization of long-chain alkanes (for monomethyl isomers) [56]. Thus, SAPO-11-supported Pt-catalysts were found to exhibit high selectivity to skeletal isomers in n-dodecane hydroisomerization at 300 °C and hydrogen pressure of 1 bar (weight hourly space velocity (WHSV) = 2 hr⁻¹) [57]. Similar results were obtained in [58], when 1 wt % of Pt was loaded on SAPO-11 and tested at 307 °C under higher hydrogen pressure (20 bar). Ni-Mo-SAPO-11-catalysts have demonstrated a high selectivity to C₁₈ hydrocarbons (57%) at 350 °C under 30 bar [45]. More recently, the SAPO-11-supported CoMo-catalyst has been applied in n-hexadecane hydroisomerization, and exhibited comparable activity with noble metals-based catalysts [59].

Herein, we examined the stability of transition metal-containing catalysts in terms of the isomerization function of n-alkanes to poisoning by nitrogen and sulfur compounds. This investigation also includes calculations of kinetic parameters, evaluating the n-paraffin isomerization selectivity depending on sulfur and nitrogen influence.

2. Results

The key factor, from the industrial viewpoint, in catalyst application, is mechanical stability, provided by supports. In general, hydroisomerization catalysts are formed into pellets by the extrusion of functional acidic components mixed with boehmite. The latter provides γ -Al₂O₃ formation after calcination at 550–600 °C [15,59]. Thus, we here report the examination of pelletized Al₂O₃-SAPO-11-supported Pt and transition metal sulfide catalysts in the hydroisomerization of n-hexadecane in the presence of poisons. The SAPO-11 component in these catalysts has appropriate acidity and provides selectivity in hydroisomerization reactions.

2.1. Physical-Chemical Properties of the Solids

Figure S1 shows the diffraction pattern of synthesized Al_2O_3 -SAPO-11 support. Observed signals on the recorded XRD pattern for Al_2O_3 -SAPO-11 material are consistent with standard SAPO-11 (PDF 047-0614) and Al_2O_3 (PDF 075-0921).

Figure S2 shows the SEM image of the prepared Al₂O₃-SAPO-11 support. SEM images of the composite support surface looks like a mixture of alumina, with a smooth surface and well-dispersed

crystals of silicoaluminophosphate, as can be seen from energy dispersive X-rays analysis (EDX) mapping (Figure 2). SAPO-11 particles (1–5 μ m) are uniformly distributed over the Al₂O₃ surface. The structure of the SAPO-11 crystals does not look damaged by acid.



Figure 2. EDX image mapping of the elements on composite Al₂O₃-SAPO-11 support.

The textural properties of the prepared Al₂O₃-SAPO-11 composite support and bifunctional catalysts were measured by low-temperature N₂ adsorption. The nitrogen adsorption–desorption isotherms and pore size distributions of the support and synthesized catalysts are shown in Figure 3. Synthesized materials exhibited a typical type I–type IV combination of isotherms, indicating a micro-mesoporous starting material. The total nitrogen adsorbed is slightly higher for the support, according to its higher pore volume. In particular, the steep uptake at lower relative pressure (P/P₀ < 0.05) indicates the N₂ filling in the micropores of the SAPO-11 phase. Meanwhile, all the prepared catalysts and composite support's nature, combining the micropores of SAPO-11 and the slit-shaped pores of alumina.

The textural properties of the prepared Al_2O_3 -SAPO-11 composite supports and transition metal sulfide (TMS) catalysts, as well as the reference Pt-catalyst, are listed in Table 1. All the prepared materials offer bimodal characteristics of pore size distribution (Figure 3). Pores with an average diameter about 3.8 nm (*t*-plot) correspond to SAPO-11, and the other ones, with 8.0 nm diameter, are related to alumina. Active metals loading has no significant effect on the textural properties of the supported catalysts. Specific surface area decreases from 268 to about 200 m²/g in the case of sulfide catalysts synthesis, and keeps almost constant for Pt-catalyst. The average pore volume and micropore properties evaluated, by t-plot and density functional theory (DFT) methods, do not change after catalysts' impregnation (Table 1).



Figure 3. N₂ adsorption isotherms (**a**) and pore size distribution curves (**b**) of composite support (curves a) and prepared catalysts (curves b).

	Brunauer–Emmett–Teller (BET)			<i>t</i> -Plot & DFT		
Catalyst (Support)	S _{BET}	D _p avr.	V _{pore}	S _{micro}	D _{micro}	V _{micro}
	(m ² /g)	(nm)	(cm ³ /g)	(m²/g)	(nm)	(cm ³ /g)
Al ₂ O ₃ -SAPO-11 (support)	268	<4.0 & 8.1 *	0.50	69	3.8	0.06
CoMoS/Al ₂ O ₃ -SAPO-11	204	<4.0 & 8.0 *	0.49	66	3.7	0.05
NiWS/Al ₂ O ₃ -SAPO-11	198	<4.0 & 7.9 *	0.47	64	3.8	0.05
Pt/Al ₂ O ₃ -SAPO-11	259	<4.0 & 8.1 *	0.51	59	3.7	0.04

Table 1. Textural properties of the prepared solids.

* bimodal pore size distribution.

Figure 4 shows representative HR TEM micrographs of the prepared catalysts. The active phase of CoMoS- and NiWS-catalysts is preceded by the typically well-dispersed sulfide phase—Hexagonal crystallites of Mo(W)S₂ decorated with Co(Ni) atoms on the edges, as presented in Topsøe's works [44,60,61]. On the HR TEM pictures, the sulfide phase looks like single or stacked dark stripes. The average length of CoMoS sulfide's active phase is 3.6 nm, and a stacking number of 2.1 resulted in dispersion equal to 0.33 (Table 2). NiWS's active phase is characterized by average length of 4.6 nm and stacking number 1.9, resulting in 0.27 dispersion. The active phase of the reference Pt-catalyst is presented by nanosized metal clusters dispersed on the catalyst surface. The average particle size of Pt clusters on the surface of Pt/Al₂O₃-SAPO-11-catalyst is 1.5 nm.

The acidic properties of CoMoS and NiWS-based bifunctional catalysts have been studied with the NH₃-TPD method, and the amounts of desorbed ammonia are presented in Table 2. The measured acidic properties of sulfide catalysts provide very close values of desorbed NH₃ for each type of acid site, and are in accordance with previously obtained results [62]. Sulfide active phase formation leads to an increase in the amount of high-temperature active sites, in comparison with Al₂O₃-SAPO-11 support, from 0.22 up to 0.62 mmol/g. The NiWS-catalyst exhibits slightly higher total acidity evaluated by NH₃-TPD, about 10% relative to CoMoS-catalyst. Catalytic properties of the Pt/Al₂O₃-SAPO-11-catalyst are almost equal to the initial composite support, most likely due to low concentration of platinum.



Figure 4. HR TEM micrographs of the synthesized bifunctional catalysts: (**a**) CoMoS/Al₂O₃-SAPO-11, (**b**) NiWS/Al₂O₃-SAPO-11, (**c**,**d**) Pt/Al₂O₃-SAPO-11.

Parameter		Catalyst					
		CoMoS/	NiWS/	Pt/			
		AI_2O_3 -SAPO-11	Al ₂ O ₃ -SAPO-11	Al ₂ O ₃ -SAPO-11			
Act	ive metals loading (wt %)						
•	Mo(W) or Pt (for ref. catalyst)	10.6	18.5	1.0			
•	Co(Ni)	3.1	3.0	-			
Active phase morphology							
•	Average length, \overline{L} (nm) (diameter for ref. catalyst)	3.6	4.6	1.5			
•	Average stacking number, \overline{N}	2.1	1.9	-			
•	Dispersion of active phase, D	0.33	0.27	0.91			
Acidity—TPD NH ₃ , mmol/g *							
•	Weak	0.421	0.423	0.367			
•	Medium	0.193	0.204	0.261			
•	Strong	0.507	0.616	0.236			
•	Total	1.121	1.243	0.865			

Table 2. Metals content and active phase properties of the prepared catalysts.

* Temperature programmed desorption of ammonia (TPD NH₃), acid sites are classified as weak (100–250 °C), medium (250–400 °C), and strong (> 400 °C).

2.2. Catalytic Properties Examination

It is well-known that Pt-containing bifunctional catalysts are much more active than other ones, nevertheless, several previous studies have shown the possibility of using the transition metal-based catalysts application for n-alkanes hydroisomerization. Figure 5 shows the comparison between the reaction rate constant of n-hexadecane isomerization at various temperatures with CoMoS-, NiWS- and Pt-catalysts, supported with Al_2O_3 -SAPO-11 support. The obtained results correlate with published data [59,62]. The difference in activity between Pt- and TMS-based catalysts gradually decreases as the temperature increases from 300 to 340 °C. The Pt-catalyst demonstrates a reaction rate constant 10 times higher at 300 °C and 4.5 times higher at 340 °C, compared to the NiWS-catalyst (Figure 5). The increased temperature of the process is likely favorable for TMS-catalysts application. Methyl- and ethylpentadecanes were the main products of the isomerization reaction. Coke formation, as well as cracking products, were not observed under the studied conditions for any experiments.



Figure 5. Reaction rate constants of n-hexadecane isomerization at 300–340 °C, versus Al₂O₃-SAPO-11 supported CoMoS-, NiWS- and Pt-catalysts. *—Results adopted from [59,62], **—Results obtained in this work.

feeds at constant reaction conditions. Table 3 summarizes the obtained results of catalytic activity measurements of TMS- and Pt-based catalysts. CoMoS- and NiWS-catalysts demonstrate perfect stability during the experiments with sulfur-containing feedstock. The conversion of n-hexadecane keeps constant, 53% and 59% for CoMoS- and NiWS-catalysts, respectively, while processing feeds with up to 100 ppm of sulfur. Reaction rate constants are comparable for both sulfide catalysts in the experiments with sulfur-containing feedstocks, and equal to the initial values for pure n-C₁₆ processing. Consequently, the inhibiting effect of sulfur on TMS-catalysts is equal to zero. The Pt-based catalyst is exposed to sulfur poisoning more intensively. The addition of 10 ppm sulfur into the feedstock reduces n-C₁₆ conversion from 79% to 52%, which is valued at 53% activity inhibition, but the residual activity nevertheless is higher than for the NiWS- or CoMoS-catalysts. The sulfur concentration increasing up to 100 ppm has a dramatic (77%) inhibiting effect on the Pt-catalyst. The isomerization reaction rate constant is $0.35 \pm 0.006 \times 10^{-4}$ (mol g⁻¹ h⁻¹), which is almost three times lower than NiWS-catalyst's one. For all experiments, hydroisomerization selectivity was almost 100%, and no cracking products were observed.

Table 3. Catalytic performance of TMS-based and reference Pt-catalyst in n-hexadecane hydroisomerization
at 340 °C, 1.5 MPa, 150 nL/L H ₂ to feedstock ratio.

Catalyst & Reaction Parameter		Reaction Conditions (T = 340 $^{\circ}$ C, P = 15 bar, H ₂ /Feedstock = 150nL/L)						
		WHSV (h ⁻¹)	Feedstock: N-Hexadecane 2.9 wt % + Catalytic Poison					
			No Poison	10 ppmS	100 ppmS	10 ppmN	50 ppmN	
Co	MoS/Al ₂ O ₃ -SAPO-11							
•	n- C_{16} conversion (%)	1.0	52.8	53.1	52.0	29.8	12.4	
•	$k_{\rm iso} \times 10^4 \;({\rm mol}\;{\rm g}^{-1}\;{\rm h}^{-1})$		0.76 ± 0.02	0.77 ± 0.02	0.74 ± 0.01	0.36 ± 0.01	0.13 ± 0.003	
•	Inhib. effect		-	-	2%	52%	83%	
Ni	WS/Al ₂ O ₃ -SAPO-11							
•	n- C_{16} conversion (%)	1.0	59.0	59.5	58.8	38.8	18.8	
•	$k_{\rm iso} \times 10^4 \;({\rm mol}\;{\rm g}^{-1}\;{\rm h}^{-1})$		0.90 ± 0.01	0.92 ± 0.02	0.90 ± 0.02	0.50 ± 0.01	0.21 ± 0.005	
•	Inhib. effect		-	-	1%	45%	76%	
Pt/	Al ₂ O ₃ -SAPO-11							
•	n- C_{16} conversion (%)	3.0	78.6	51.8	8.5	9.1	2.9	
•	$k_{\rm iso} \times 10^4 \;({\rm mol}\;{\rm g}^{-1}\;{\rm h}^{-1})$		4.75 ± 0.22	2.2 ± 0.044	0.35 ± 0.006	0.29 ± 0.01	0.09 ± 0.004	
•	Inhib. effect		-	53%	77%	94%	98%	

Figure 6 is used to show, in a graphic outline, the comparison of residual catalytic activity, i.e., the measured activity after the n-hexadecane conversion stopped decreasing, of bifunctional catalysts during sulfur- and nitrogen-containing feedstock processing. Similar reaction conditions can be used in this case due to the higher inhibition effect of catalytic poisons on Pt-containing catalyst. A reaction rate constant more than two times lower was measured for Pt-catalyst in the experiment with 100 ppm sulfur, resulting in residual n-C₁₆ conversion becoming equal to 37%, versus 59% for the NiWS-catalyst, meanwhile, the 10 ppm of sulfur in the feedstock allows the Pt-catalyst to provide higher catalytic activity in n-C₁₆ isomerization (Figure 6a).

The calculated inhibition effect of 10 ppm nitrogen-containing feed on CoMoS- and NiWS-catalysts is about 45–52%, meaning that the reaction rate constant is only half of the initial one and the conversion of n-hexadecane decreases to 30% and 39% for CoMoS and NiWS samples, respectively (Table 3). The Pt-catalyst already demonstrates extremely low n-C₁₆ conversion at studied reaction conditions when 10 ppm of nitrogen is added. The inhibiting effect is 94% in this case. The increasing of the nitrogen content to 50 ppm in the feedstock dramatically drops n-hexadecane conversion measured

for all the prepared catalysts. CoMoS- and NiWS-catalysts lose 83% and 76% of their initial activity, respectively. The observed n-hexadecane conversion over the Pt-catalyst is almost equal to zero; only about 3% of C_{16} isomers are detected in the product. Such low values of n-hexadecane conversion measured for Pt-catalyst in the nitrogen-containing feedstock processing is connected with the high WHSV 3.0 h⁻¹, which was chosen for the Pt-catalyst due to the extremely high catalytic activity in pure n- C_{16} hydroisomerization. However, by paying attention to the isomerization reaction rate constants calculated for all the catalysts (Table 3), it becomes possible to conclude that the catalytic behavior of the studied TMS- and Pt-based bifunctional catalysts is quite similar in nitrogen-containing feedstock processing.



Figure 6. Conversion of n-C₁₆ (with sulfur (**a**) and nitrogen (**b**) poisoning) over TMS- and Pt-catalysts at similar conditions: (T = 340 °C, P = 15 bar, WHSV = 1.0 h^{-1} , H₂/feedstock = 150 nL/L).

The comparison of the n-C₁₆ conversion with the prepared catalysts under the similar reaction conditions (Figure 6b) demonstrates quite clearly that the isomerization activity of synthesized TMS and- Pt-based bifunctional catalysts was inhibited by nitrogen through the similar mechanism, which differs from the one for Pt-catalysts poisoning by sulfur. The residual catalytic activity is the result of a strong limitation of the isomerization reaction in both TMS- and Pt-based catalysts caused by nitrogen in the feedstock. The logical explanation of such catalytic behavior is that nitrogen mostly poisons acid sites of bifunctional catalysts, leading thereby to decreases of acidity and isomerization activity, while the hydrogen sulphide changes the Pt into sulfide form, decreasing thereby its hydrogenation–dehydrogenation activity [7,33]. Since the TMS-based catalysts have already sulfided the active CoMoS or NiWS phase, sulfur in the feedstock has no inhibiting effect. The acid sites deactivating in the bifunctional catalysts is equally undesirable for both TMS- and Pt-containing catalysts.

In addition to the established difference in the inhibition effect of sulfur and nitrogen on Pt-catalyst activity, the rate of catalyst poisoning by the corresponding feedstock's undesired component was studied (Figure 7). The period of catalytic activity stabilization, in hours, required for reaching the steady state of n-hexadecane conversion was different when sulfur and nitrogen components were introduced into the feedstock. It took about 38 h during sulfur-containing feedstock processing to get the stable conversion of n-hexadecane (region "c" on Figure 7a). The inhibiting effect of nitrogen was exhibited not only in a significant degree, but also more rapidly. It takes about 20 h for all the studied catalysts to get almost-steady n-C₁₆ conversion—Region "c", specified in Figure 7b. It is important to point out that catalytic activity stabilization for both TMS- and Pt-based catalysts takes the same period. Almost the same time interval is required to get a steady state when 10 and 50 ppm of nitrogen are introduced into the feedstock.



Figure 7. The dependence of the n-hexadecane conversion in time for sulfur-containing (**a**) and nitrogen-containing (**b**) feedstock processing.

The observed differences in poisoning kinetics are most likely connected with mechanisms focused on metal active sites in the case of sulfur poisoning of Pt-catalyst, and the acid sites of the silicoaluminophosphate component of the composite supports. In view of this, the NiWS-catalyst provides slightly higher tolerance to nitrogen in feedstock in comparison with CoMoS- and Pt-catalysts. NiWS sulfide's active phase exhibits moderate acidic properties, and is probably involved in the isomerization step of the n- C_{16} reaction.

3. Materials and Methods

3.1. Preparation of the Solids

SAPO-11 was hydrothermally synthesized according to the reported procedure [63] from the pseudoboehmite (Sasol Company, Hamburg, Germany), orthophosphoric acid (Merck) and Ludox AS30 colloid silica (Aldrich), used as alumina, phosphorus and silicon sources, respectively. The final molar composition of the prepared gel was: 1.0 Al₂O₃; 1.0 P₂O₅; 0.3 SiO₂; 1.2 DPA; 45 H₂O. The crystallization was performed in a Teflon-lined stainless steel autoclave at 200 °C for 24 h. The product was water-washed, dried and calcined at 600 °C for 6 h to obtain the SAPO-11 material.

Composite Al_2O_3 -SAPO-11 support was prepared by mixing SAPO-11 with AlOOH boehmite followed by incipient wetness impregnation with peptizer (concentrated nitric acid with modulus 0.04) and further molding by extrusion to form pellets with 2 mm diameter [15,59]. Pellets were dried at 80 and 110 °C for 4 h at each temperature followed by calcination in air at 550 °C for 6 h.

The bifunctional catalysts were prepared by incipient wetness impregnation technique. Composite Al₂O₃-SAPO-11 support was crushed and sieved to particles between 0.25 and 0.50 mm. CoMoS-catalyst was synthesized using 12-molybdophosphoric heteropolyacid (HPA) H₃[PMo₁₂O₄₀]·nH₂O and cobalt (II) carbonate (CoCO₃). NiWS-catalyst was prepared from phosphotungstic acid H₃[PW₁₂O₄₀]·nH₂O and nickel (II) carbonate (NiCO₃). Citric acid was used as a chelating agent. An H₂PtCl₆ solution was used to prepare Pt-based catalysts. Aqueous impregnation solutions were prepared by dissolving all listed components in deionized water under continuous stirring at 50 °C. The amount of dissolving precursors and corresponding concentrations of active metals in solutions were calculated from the required metal loadings (Table 2). For example, for CoMoS/Al₂O₃-SAPO-11-catalyst preparation in amount of 50 g, 10.85 g of 12-molybdophosphoric HPA and 3.21 g of cobalt carbonate were dissolved in water with 6.02 g of citric acid. Then 40 g of freshly synthesized Al₂O₃-SAPO-11 carrier was impregnated with 36 cm³ of prepared solution. All impregnated materials were dried at 120 °C for 4 h. Pt-catalyst was further calcined at 450 °C (2 h) and reduced just before catalytic testing in a hydrogen atmosphere at 400 °C. TMS-catalysts were activated by sulfidating with a mixture of 15% H₂S in H₂ at 400 °C, 1.0 MPa for 2 h.

The elemental analysis (Mo, W, Co, Ni and Pt) of the prepared catalysts was performed by Shimadzu EDX800HS analyzer. SEM-EDX analysis was used to confirm the uniform distribution and check the possible agglomeration of active metals on the surface of the catalysts.

3.2. Characterization of Supports and Catalysts

X-ray powder diffraction measurements were performed on a Bruker D2 X-ray Diffraction system using Cu K α radiation (λ = 1.54056 Å) with a scanning speed of 2.0°/min. The powders were loaded on a glass disk by packing the samples into a cavity on the disk. The diffractograms were analyzed using standard JCPDS files.

The surface morphology of the supports was examined by scanning electronic microscopy (SEM) on a Carl Zeiss EVO 50 microscope.

The textural characteristics of the prepared supports and catalysts were measured by low-temperature N₂ adsorption at -196 °C on a Quantachrome Autosorb-1 porosimeter after outgassing procedure under deep vacuum at 350 °C for 4 h. Specific surface area (SSA) was calculated using the Brunauer–Emmett–Teller BET method. The total pore volume and pore size distribution were calculated from the desorption branch of the isotherm using the Barrett-Joiner-Halenda (BJH) model. Properties of micropores were evaluated using the *t*-plot method.

HR TEM images of the catalysts were obtained on a JEOL JEM-2100 microscope with electron tube voltage of 200 kV. To measure the key morphological characteristics at least 500 particles from 10–12 regions of the surface were handled for every sample. The average length of Mo(W)S slabs, as well as average number of slabs per stack, were calculated for TMS-catalysts according to the commonly accepted approach. The average diameter of active phase particles was evaluated in the case of Pt-catalyst. The dispersion (D) of active phase was calculated on the basis of geometric characteristics and evaluated as available atoms on the surface of metal clusters, with assumptions that active particles of metallic catalysts are spherical and $Mo(W)S_2$ slabs are perfect hexagons [64–66].

3.3. Catalytic Activity Examination

The catalytic tests were performed using a fixed-bed flow reactor. A 2.5 cm³ volume of the catalyst was charged into the isothermal region of the reactor as particles of 0.25–0.50 mm. All catalysts were activated before testing directly in the reactor. Pt-based catalyst was reduced in 0.5 MPa hydrogen atmosphere at 400 °C for 2 h, while TMS samples were sulfided at 400 °C in an atmosphere of H₂S/H₂ for 2 h. A mixture of n-hexadecane (2.9 wt %) in n-heptane as a solvent with optional addition of dimethyl disulfide (DMDS) (as sulfur source) and quinolone (as nitrogen source) in 10–100 ppm concentration was introduced into the reactor as a model feedstock for evaluation of hydroisomerization performance and inhibiting effect. N-heptane was not reacted under the experimental conditions.

Catalytic activity was examined under the following conditions: temperature 340 °C, 1.5 MPa H_2 , 1–3 h⁻¹ (weight hourly space velocity (WHSV), and a 150 nL/L volume ratio of H_2 to feedstock. The liquid product compositions of the samples collected every 1.0 h were determined using an Agilent 7890A Gas Chromatograph equipped with a Flame Ionization Detector and 30 m DB-5 Fused Silica capillary column (30 m * 0.32 mm * 0.5 µm). Volume of injection was equal to 1.0 µm, the temperature of the injector and detector was 250 °C. The program of temperature started from 60 °C and was raised to 180 °C with 5 °C/min rate. Helium was used as carrier-gas. An example chromatogram is presented in Figure S3. The identification of the obtained reaction products was performed using gas chromatography/mass-spectrometry analysis and by matching retention times with available commercial standards. Methyl- and ethylpentadecanes were the main products of the reaction. The corresponding peaks on the chromatograms were located in the interval of 7.6–8.4 min retention time.

The hydroisomerization reaction was allowed to proceed for the period of time that provided the steady state of the process. In the case of sulfur and nitrogen addition into the feedstock this period varied from 20 to 38 h.

Conversion and isomerization selectivity were calculated using the following equations:

$$x_{iso} = \frac{\text{consumed } n - \text{hexadecane}}{\text{initial } n - \text{hexadecane content}} = \frac{\text{iso} - \text{hexadecanes}}{\text{initial } n - \text{hexadecane content}'}$$
(1)

The reaction rate constant of the hydroisomerization was determined using the following equation:

$$k_{iso} = -\frac{F}{m} \ln(1 - x_{iso}),$$
 (2)

where k_{iso} is the pseudo-first-order reaction constant for the n-hexadecane hydroisomerization (mol g⁻¹ h⁻¹); x_{iso} is the conversion (%) of n-hexadecane into the C₁₆ isomers; *F* is the reactant (n-hexadecane) flow (mol h⁻¹) and *m* is the weight of the catalyst (g).

The inhibiting effect was defined as the ratio of the reaction rate constant after reaching the steady state with poison-containing feedstock processing and the initial reaction rate constant.

$$E_{inh} = \frac{k_{iso}}{k_{iso}^0},\tag{3}$$

where k_{iso}^0 is the initial reaction rate constant during pure n-hexadecane isomerization and k_{iso} is the reaction rate constant for poison-containing feedstock processing.

The residual catalytic activity declared in the manuscript refers to the values of catalytic activity measured after the n-hexadecane conversion stopped decreasing, in the cases of sulfuror nitrogen-containing feedstock.

4. Conclusions

Transition metal sulfide (CoMoS and NiWS) and platinum-containing bifunctional catalysts were prepared by a incipient wetness impregnation technique, using a freshly synthesized Al_2O_3 -SAPO-11 composite support with favorable acidic properties. The structure of the support was confirmed by powder XRD and SEM techniques. All the solids have comparable specific surface areas, from 200 to about 270 m²/g, and the bimodal pore size distributions, with maximums at 3.8 and 8.0 nm, come from SAPO-11's and alumina's nature, respectively. The introduction of active components has no significant effect on textural properties. The well-dispersed nanosized active phase of the prepared bifunctional catalysts was characterized by the HR TEM method to calculate morphological properties. The CoMoS active phase has slightly higher dispersion in comparison with the NiWS one.

CoMoS- and NiWS-catalysts demonstrate perfect stability during the experiments with sulfur-containing feedstock. The reaction rate constants are comparable for both sulfide catalysts during these experiments, and are equal to the initial values for pure n-C₁₆ processing; $0.8-0.9 \times 10^4$ mol g⁻¹ h⁻¹. Low sulfur concentration of 10 ppm in feedstock inhibits Pt-catalysts by about 50%. Regardless, Pt-catalyst provides more intense n-C₁₆ isomerization, and the reaction rate constant is two times higher in comparison with the NiWS-catalyst. The situation reverses when 100 ppm of sulfur is introduced into the feedstock. The inhibiting effect of sulfur for Pt-catalyst is 77% in this case, which is equal to an isomerization rate constant 3.0 times lower than the NiWS-catalyst.

The catalytic behaviors of the prepared TMS- and Pt-based bifunctional catalysts are quite similar in nitrogen-containing feedstock processing. Isomerization activity is inhibited by nitrogen through a similar mechanism, which differs from the one for Pt-catalysts poisoned by sulfur. The residual catalytic activity is the result of the strong limitation of the isomerization reaction, caused by nitrogen in the feedstock. The isomerization reaction rate constants evaluated during the processing of the feedstock with 50 ppm of nitrogen increase from 0.09 to 0.21×10^4 mol g⁻¹ h⁻¹ µmol/g in the following order: Pt-, CoMoS-, NiWS-catalysts. In addition, nitrogen in the feedstock has a more intense inhibiting effect on isomerization catalytic activity. Reaching the steady state of n-hexadecane conversion takes about 20 h in the case of nitrogen poisoning, and about 38 h for sulfur-containing feedstock.

Therefore, it can be concluded that transition metal-based bifunctional catalysts have a significant advantage over Pt-catalyst in n-alkanes isomerization, when the amount of sulfur in the feedstock is equal to, or higher than, 100 ppm. Nitrogen has an intensive inhibiting effect on both TMS- and Pt-containing bifunctional catalysts, which is most probably due to support acid sites poisoning, in which case, additional improvements of the support are required.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/6/594/s1. Figure S1. XRD spectra of synthesized Al_2O_3 -SAPO-11 composite support; Figure S2. SEM image of Al_2O_3 -SAPO-11 composite support; Figure S3. Chromatogram of the feedstock n- C_{16} in hexane.

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