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Nickel- and Rhenium-Containing Sulfated Zirconia Catalyst for Simultaneous Benzene Alkylation and Alkanes Isomerization

**Maxim O. Kazakov^a, Alexander V. Lavrenov^b,
Aleksey B. Arbuzov^b, Vladimir A. Likholobov^b,
Evgeniy A. Buluchevskiy^b and Tatyana R. Karpova^{b*}**

^a*Boriskov Institute of Catalysis SB RAS*

5 Pr. Lavrentieva, Novosibirsk, 630090, Russia

^b*Institute of Hydrocarbons Processing SB RAS*

54 Neftezhavodskaya Str., Omsk, 644040, Russia

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Nickel and rhenium promoted sulfated zirconia (SZ) was investigated as a catalyst for conversion of benzene–n-hexane mixture. This reaction may be used for benzene content decreasing through transformation of the latter to C₇–C₉ arenes by alkylation with the products of alkanes cracking. It has been shown that simultaneous benzene alkylation and n-hexane isomerization proceeds on sulfated zirconia and it is characterized with drastic deactivation due to accumulation of polycyclic aromatic compounds. Promotion of SZ with Ni and Re increases the activity in conversion of benzene and n-hexane mixture. The main pathways for benzene transformation are alkylation and hydrogenation and the main reaction for n-hexane is isomerization. Promoting effect of Ni and Re is associated with the stabilization of the activity of sulfated zirconia. The role of nickel in this case is activation of hydrogen and hydrogenation of coke precursors and the role of rhenium is hydrogenolysis of coke precursors.

Keywords: sulfated zirconia, nickel, rhenium, benzene alkylation, isomerization.

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* Corresponding author E-mail address: ktr@ihcp.ru

Никель- и ренийсодержащие катализаторы на основе сульфатированного диоксида циркония для совместного алкилирования бензола и изомеризации алканов

**М.О. Казаков^а, А.В. Лавренов^б, А.Б. Арбузов^б,
В.А. Лихолобов^б, Е.А. Булучевский^б, Т.Р. Карпова^б**

^а*Институт катализа им. Г.К. Борескова СО РАН
Россия, 630090, Новосибирск, пр. Академика Лаврентьева, 5*

^б*Институт проблем переработки углеводородов СО РАН
Россия, 644040, Омск, ул. Нефтезаводская, 54*

Проведено исследование сульфатированного диоксида циркония (SZ) с нанесенными никелем и рением как катализатора превращения смеси бензола и н-гексана. Данная реакция может быть использована для снижения содержания бензола путем превращения последнего в арены C₇-C₉ в результате его алкилирования продуктами крекинга алканов. Показано, что процесс может осуществляться на цирконосульфатном носителе, однако характеризуется быстрой дезактивацией, вызванной накоплением полициклических ароматических углеводородов на поверхности катализатора. Основными направлениями превращения бензола являются алкилирование и гидрирование, а основной реакцией для н-гексана – изомеризация. Введение в катализатор никеля и рения существенно повышает его активность и стабильность в целевом процессе за счет увеличения скорости реакций гидрирования, катализируемых никелем. Роль рения сводится к осуществлению реакций гидрогенолиза.

Ключевые слова: сульфатированный диоксид циркония, никель, рений, алкилирование бензола, изомеризация.

Introduction

Production of cleaner fuels implies significant restrictions of benzene content. In a typical refinery the main source of arenes including benzene is a catalytic reforming process. There are several options for reducing benzene level in reformat. These options are based on removing of benzene precursors from the feed of catalytic reforming or suppose separation of benzene-containing fraction from the process products with subsequent elimination of benzene by hydration, hydroisomerization, alkylation with alkenes, transalkylation with higher aromatics or extraction.

Sulfated zirconia (SZ) is an effective catalyst for different acid-catalyzed reactions of hydrocarbons including such practically important processes as alkanes skeletal isomerization and alkylation of isobutane with butenes [1, 2]. In order to provide stable performance SZ catalyst should be promoted with noble metals for the hydrogenation of coke precursors and the prevention of deactivation [3, 4]. One of the catalytic applications of SZ-based systems for cleaner fuels production is hydroisomerization of benzene-containing feed. This process provides benzene removal by hydrogenation with subsequent

isomerization of resulting cyclohexane to methylcyclopentane and it was thoroughly studied with the use of Pt-promoted sulfated zirconia [5, 6].

It is known that nickel and rhenium also improves the stability of SZ isomerization catalyst [7]. Studies on Ni- and Re-promoted SZ isomerization catalysts are devoted to alkanes conversion [7-11]. There is no information about conversion of benzene-containing feed on Ni- and Re-promoted SZ.

In this work we report the data concerning the conversion of binary mixture consisting from benzene and n-hexane on sulfated zirconia promoted with Ni and Re. In comparison with Pt nickel and rhenium have lower hydrogenation capacity resulting to benzene conversion on Ni- and Re-containing sulfated zirconia through another pathway. In this case benzene transforms to C₇-C₉ arenes by alkylation with the products of alkanes cracking. Such reaction could be a way for reducing benzene content in gasoline fractions with enhancing the octane characteristics.

Experimental

Catalysts preparation

Hydrous zirconium oxide was obtained by precipitation from an aqueous solution of 1 M ZrO(NO₃)₂ with a molar excess of NH₄OH to produce final pH of approximately 10. After washing in distilled water, the precipitate was then treated with 2 M sulfuric acid solution in the amount providing ZrO₂ : H₂SO₄ weight ratio 9 : 1. Thus prepared sulfated material was dried at 120 °C overnight and calcined at 650 °C for 4 h in a muffle furnace. The resulting acidic support was denoted as SZ. The sulfur concentration in SZ measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on VARIAN 710-ES spectrometer corresponds to 5.9 wt. % sulfate. X-ray diffraction analysis showed only tetragonal ZrO₂ in the phase composition of SZ sample.

Nickel and rhenium were added by incipient wetness technique to the calcined SZ support using the appropriate amount of an aqueous solutions of Ni(NO₃)₂ and HReO₄ respectively. The obtained solids were then dried for 12 h, calcined in a muffle furnace at 500 °C for 3 h and if required reduced at 300 °C for 4 h in a hydrogen stream. Calcined samples were denoted as xNi/SZ or xNi-xRe/SZ where x is the modifier concentration. Reduced samples were denoted as xNi/SZ-Red or xNi-xRe/SZ-Red. Ni content in Ni/SZ samples ranged from 0.5 to 4 wt. %. Ni-Re/SZ samples contained 2 wt. % Ni and from 0.2 to 2 wt. % Re.

Catalysts characterization

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 C instrument using an Ar stream containing 20 vol% O₂ at a heating rate of 10 °C/min.

Diffuse reflectance UV-Vis spectra (UV-Vis DRS) of the catalysts were recorded using a UV-2501 PC Shimadzu spectrometer with ISR-240A diffusion reflection attachment in the 190-900 nm range. Barium sulfate was used as a reference sample. Measurements were performed at room temperature. The UV-Vis spectra were transformed into the Kubelka-Munk function (F(R)) calculated as $F(R) = (1 - R)^2/2R$, where R is the experimentally measured reflectance of the samples [12].

Catalytic testing

Benzene–n-hexane (22.7 wt. % – 77.3 wt. %) binary mixture was used as a feed for catalytic testing. Experiments were carried out in a fixed bed flow reactor at 250 °C, under 1.5 MPa total

pressure, with weight hourly space velocity 1.3 h^{-1} and H_2 /feed molar ratio 3. Reaction products were analyzed with on line gas chromatography using capillary column and flame ionization detector. Prior to each experiment catalysts were reduced at 300°C for 4 h in a hydrogen stream. After the reaction catalysts were purged with He and collected for the further characterization. These samples were denoted as xNi/SZ-Deact or xNi-xRe/SZ-Deact. To characterize the activity decline deactivation parameter is used [13]. It was calculated as $D = (X_0 - X_f)/X_0 \cdot 100$; where X_0 and X_f are the initial (after 1 hour of reaction) and final (after 5 hours of reaction) conversion. It was calculated both for benzene and n-hexane.

Results and discussion

Catalysts characterization

Activation of Ni-promoted SZ catalysts is carried out in N_2 flow at 450°C [8], in air flow at 500 – 620°C [9–11] or in H_2 flow at 300°C [7]. It should be noted that in the works [7–11] Ni/SZ catalysts were prepared by impregnation of hydrous zirconium oxide with $\text{Ni}(\text{NO}_3)_2$ and H_2SO_4 solutions or by adding $\text{Ni}(\text{NO}_3)_2$ solution to sulfated hydrous zirconium oxide, followed by drying and calcination steps.

In our work we added Ni and Re precursors to the precalcined sulfated zirconia in order to prevent or minimize possible interaction between promoter and support during the calcination. Before catalytic tests treatment was carried out in a hydrogen stream in order to obtain Ni in the state that is capable of H_2 activation.

Thermogravimetric analysis of the dried at 120°C Ni- and Re-loaded samples showed that metal precursors completely decomposed below the temperature of 500°C . Thus, calcination of the promoted catalysts at 500°C should lead to the formation of Ni and Re on the surface of sulfated zirconia in oxide forms.

UV-Vis DRS was used to study the coordination of nickel species supported on SZ. Ni/SZ catalysts with different Ni loading after oxidation at 500°C are characterized by a.b. at 430 and 790 nm (Fig. 1(a)). These bands are typical for Ni^{2+} ions in octahedral or pseudo-octahedral symmetry [14, 15]. These bands grow in intensity with increasing Ni content in the sample.

Spectra of Ni-Re/SZ samples display a.b. at 430 nm and broad a.b. in the range of 650–900 nm (Fig. 1(b)). These bands can be attributed, respectively, to Ni^{2+} ions in octahedral surroundings and to Ni^{2+} species located in both octahedral and tetrahedral symmetry [16].

Spectra of reduced samples are shown in Fig. 2. After reduction at 300°C bands assigned Ni^{2+} species vanished. Changes of the absorption background in the visible range for reduced Ni- and Re-promoted samples can be related to strong structureless absorption due to the presence of large nickel metal particles.

Catalytic evaluation

The catalytic properties of sulfated zirconia in the conversion of benzene–n-hexane mixture are presented in Fig. 3. According to obtained results SZ demonstrates noticeable activity in the initial period of reaction but it drops rapidly and after 1 hour conversion of the feed components does not exceed 4%. The main pathway for benzene transformation is alkylation with the products of alkanes cracking. The composition of obtained arenes C_{7+} after 10 and 30 minutes of reaction is presented mostly with toluene and ethylbenzene with concentration about 83 wt. %.

Fig. 1. UV-Vis DR spectra of SZ, Ni/SZ (a) and Ni-Re/SZ (b) samples after oxidation in air at 500 °C

Fig. 2. UV-Vis DR spectra of Ni/SZ (a) and Ni-Re/SZ (b) samples after reduction in H₂ stream at 300 °C

Promotion of $\text{SO}_4^{2-}\text{-ZrO}_2$ with Ni increases the activity and stability of the catalyst in benzene–n-hexane conversion (Table 1). After 1 hour of reaction the highest benzene conversion corresponds to 4Ni/SZ sample. Along with alkylation reaction benzene hydrogenation is observed. Thus, Ni supported on sulfated zirconia is capable of hydrogen activation but nevertheless it has poor hydrogenation activity. This activity grows with increasing Ni content. At the same time, yield of alkylbenzenes goes through the maximum, which corresponds to 2Ni/SZ. Isomerization activity of the catalysts grows with increasing Ni loading. During the reaction deactivation of the Ni/SZ samples occurs. Decrease in activity is more pronounced for the catalysts with lower Ni loading.

The main products of benzene alkylation on Ni/SZ are toluene and ethylbenzene (Table 2). In all cases content of these components in arenes C_{7+} is between 89–93 wt. %. There is a difference in

Fig. 3. Benzene and n-hexane conversion (a) and products yield (b) with time on stream in the reaction of benzene–n-hexane mixture on SZ

Table 1. Catalytic properties of Ni/SZ samples after 1 and 5 hours of reaction

Sample	After 1 h					After 5 h				
	X ^a , %		Yield ^b , wt. %			X ^a , %		Yield ^b , wt. %		
	C ₆ H ₆	n-C ₆ H ₁₄	ArC ₇₊	Nph	iso-C ₆	C ₆ H ₆	n-C ₆ H ₁₄	ArC ₇₊	Nph	iso-C ₆
0.5Ni/SZ	11.1	56.2	2.8	0.4	37.7	3.3	28.0	0.8	0.4	20.1
1Ni/SZ	13.8	66.5	3.1	0.6	44.3	5.2	40.3	1.0	0.6	28.7
2Ni/SZ	18.8	74.6	3.4	1.1	48.5	8.3	53.8	1.3	1.0	37.7
4Ni/SZ	21.3	76.0	2.8	2.0	49.4	11.1	59.7	1.4	1.4	41.6

^a Conversion.

^b ArC₇₊: arenes C₇₊; Nph: naphthenes; iso-C₆: isohexanes.

Table 2. Alkylbenzenes composition for Ni/SZ samples after 1 and 5 hours of reaction

Sample	Arenes C ₇₊ composition, wt. %							
	After 1 h				After 5 h			
	Toluene	EB ^a	Xylenes	C ₉₊	Toluene	EB ^a	Xylenes	C ₉₊
0.5Ni/SZ	35.0	56.2	2.0	6.8	27.8	61.0	3.2	8.1
1Ni/SZ	37.4	54.0	2.2	6.4	32.9	57.1	3.0	6.9
2Ni/SZ	42.9	48.3	2.5	6.3	39.3	51.7	2.8	6.1
4Ni/SZ	46.4	45.4	2.9	5.3	42.1	49.4	2.9	5.7

^a Ethylbenzene.

toluene/ethylbenzene ratio which grows with increasing Ni content in Ni/SZ. At the same time, this ratio decreases as the catalyst deactivate.

Addition of Ni and Re to sulfated zirconia increases the activity in conversion of benzene and n-hexane with respect to Ni/SZ samples (Table 3). The promoting effect of Re is more remarkable with

Table 3. Catalytic properties of Ni-Re/SZ samples after 1 and 5 hours of reaction

Sample	After 1 h					After 5 h				
	X ^a , %		Yield ^b , wt. %			X ^a , %		Yield ^b , wt. %		
	C ₆ H ₆	n-C ₆ H ₁₄	ArC ₇₊	Nph	iso-C ₆	C ₆ H ₆	n-C ₆ H ₁₄	ArC ₇₊	Nph	iso-C ₆
2Ni-0.2Re/SZ	27.4	83.8	4.0	1.6	49.3	17.8	77.3	2.5	1.3	50.8
2Ni-0.5Re/SZ	27.1	83.2	3.1	1.7	50.2	18.4	77.6	2.2	1.5	50.9
2Ni-1Re/SZ	22.6	81.5	2.6	1.8	50.6	17.4	76.5	1.9	1.5	50.5
2Ni-2Re/SZ	18.3	78.1	1.8	1.8	52.0	14.6	73.0	1.3	1.6	50.1

^a Conversion.^b ArC₇₊: arenes C₇₊; Nph: naphthenes; iso-C₆: isohexanes.

Table 4. Alkylbenzenes composition for Ni-Re/SZ samples after 1 and 5 hours of reaction

Sample	Arenes C ₇₊ composition, wt. %							
	After 1 h				After 5 h			
	Toluene	EB ^a	Xylenes	C ₉₊	Toluene	EB ^a	Xylenes	C ₉₊
2Ni-0.2Re/SZ	46.4	45.3	2.5	5.7	44.4	48.2	2.2	5.2
2Ni-0.5Re/SZ	48.9	43.8	2.5	4.8	46.9	46.5	2.2	4.4
2Ni-1Re/SZ	48.6	44.9	2.1	4.3	46.9	47.1	2.2	3.8
2Ni-2Re/SZ	46.3	47.5	2.3	3.9	45.5	47.8	2.2	4.6

^a Ethylbenzene.

content up to 0.5 wt. %. At the same time, 2Ni-2Re/SZ sample has similar initial activity (after 1 hour) as 2Ni/SZ, but Re-promoted catalyst demonstrates higher stability. Observed decline in activity with increasing Re content is associated with acidity decrease which occurs due to interaction between ReO₄⁻ and acid sites of sulfated zirconia during the catalysts preparation.

The distribution of alkylbenzenes in the products for Ni-Re/SZ samples is rather close to that for 2Ni/SZ. Ni-Re-containing samples slightly differ in toluene/ethylbenzene ratio and C₉₊ arenes content.

Obtained results demonstrate that benzene alkylation is controlled by acidic function of the catalyst. Ni and Re in this case act as promoters which stabilize the activity of SO₄²⁻-ZrO₂. For all catalysts the main products of benzene alkylation are toluene and ethylbenzene. Probably, alkylbenzenes having side chains with three and more carbon atoms are readily dealkylated due to the high acidity of sulfated zirconia. After formation of toluene or ethylbenzene alkylation of the resulting arenes should occur with much higher rate than benzene alkylation. But in our case yield of xylenes and other dialkylbenzenes is negligible. As maximal conversion does not exceed 27.4%, concentration of benzene in reaction medium is much higher than alkylbenzenes. Thus, benzene alkylation is more preferable.

Deactivated catalysts characterization

Deactivated catalysts were investigated with UV-Vis DRS and TGA techniques in order to characterize unsaturated surface deposits formed during reaction.

After reaction of benzene–n-hexane mixture at 250 °C for 5 h new a.b. at 415 nm with a broad shoulder in the range of 450–650 nm is identified in the UV-Vis DR spectrum of SZ (Fig. 4(a)). Band at 415 nm can be assigned to polycyclic aromatic compounds [17] or trienic allylic cations [18]. Taking into account the fact that we used benzene as one of the components of the feed mixture formation of polycyclic aromatic compounds on the surface of $\text{SO}_4^{2-}\text{-ZrO}_2$ is more likely. This consideration is supported by the absence of the bands in the range of 292–330 nm and in the range of 370–390 nm assigned to monoenic and dienic allylic cations respectively [18, 19]. The asymmetric shape of the band suggests that possibly several species contribute, which could be polycyclic aromatics with different conjugation degree. It should be noted that after 10 and 30 min of reaction the same a.b. in the UV-Vis DR spectra of SZ were observed (spectra not shown).

The intensity of the band at 415 nm attributed to polyaromatic compounds decreases with increasing nickel content in Ni-promoted samples. For Ni/SZ with 2 and 4 wt. % Ni and for Ni-Re/SZ samples this band is overlapped by a broad band in the visible range related to strong structureless absorption due to the presence of large nickel metal particles.

According to TGA data after 5 hours of reaction SZ sample accumulates 2.0 wt. % of unsaturated surface deposits (Fig. 5(a)). Most part of these species deposit on SZ surface in the initial period of reaction: after 10 min concentration of coke precursors is 1.1 wt. % and after 30 min it amounts to 1.4 wt. %. Promotion of SZ with Ni and Ni-Re decreases surface deposits accumulation by a factor of 2–3 and 5–10 respectively. Benzene and n-hexane conversion decline expressed as deactivation parameter is shown in Fig. 5(b). According to obtained results Ni-Re/SZ catalysts along with the highest initial activity exhibit the lowest deactivation value. These results clearly show the main effect of promoting SZ with Ni and Re. The role of nickel in this case is activation of hydrogen and hydrogenation of coke precursors. Rhenium enhances the stability through the selective hydrogenolysis of coke precursors [20].

Fig. 4. UV-Vis DR spectra of SZ, Ni/SZ (a) and Ni-Re/SZ (b) samples after reaction of benzene–n-hexane mixture at 250 °C for 5 h

Fig. 5. Unsaturated surface deposits after reaction of benzene–n-hexane mixture at 250 °C for 5 h (a) and deactivation parameter (b) for SZ, Ni/SZ and Ni-Re/SZ samples

Conclusions

It has been shown that simultaneous benzene alkylation and n-hexane isomerization proceeds on sulfated zirconia but it is characterized with very high deactivation rate. According to UV-Vis DRS unsaturated deposits on the surface of SZ are presented by polycyclic aromatic compounds. Promotion of SZ with Ni and Re increases the activity in conversion of benzene and n-hexane mixture. The main pathways for benzene transformation are alkylation and hydrogenation and the main reaction for n-hexane is isomerization. Promoting effect of Ni and Re is associated with the stabilization of the activity of sulfated zirconia. The role of nickel in this case is activation of hydrogen and hydrogenation of coke precursors and the role of rhenium is hydrogenolysis of coke precursors.

ICP-AES, TGA and UV-Vis DRS were carried out at the Omsk Collaborative Center SB RAS (Omsk).

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