LOW-TEMPERATURE CONVERSION OF OLEFIN-CONTAINING INDUSTRIAL GASES ON Me(Zn,W)/KH-4/Al_2O_3 HETEROGENEOUS SYSTEMS

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Received 03.01.2025
Accepted 24.04.2025

Abstract: *Heterogeneous composite catalytic systems of the type Me(Zn,W)/KH-4/Al_2O_3 were investigated in the conversion of the butane–butylene fraction obtained from the catalytic cracking unit of the Heydar Aliyev Refinery Plant. The initial carrier was an industrial catalytic cracking catalyst KH-4, modified with Zn and W salts. The catalysts were tested on a laboratory setup at 220ºC, t=1-6 hours, WSHV=500 h^{-1}. The analysis of feedstocks and reaction products was carried out on a Perkin Elmer AutoSystem XL chromatograph. The thermal stability of the samples was studied using JUPITER synchronous thermal analyzer TG/DTA STA-449 (Germany) V-10°/min, T=25-700°C, V_{N2}=20 ml/min, m=10 mg. The content of the compaction products was determined by burning coke, followed by gravimetric determination of the weight gain of ascarite tubes, and also by the DTA and TG methods, V=20 K·min^{-1} in the air flow. The formation of high-octane components $\Sigma(C_5-C_8)$ was established with a conversion of 66.9% on Zn/KH-4/Al_2O_3 with a selectivity for fr.ΣC_5-C_6 of 53.5%, and on the catalyst W/KH-4/Al_2O_3 of 76.3% with a selectivity of fr.ΣC_5-C_6 of 54.8%. Both fresh and spent catalysts are thermally stable up to 750ºC and exhibit stable catalytic activity for 6 hours, and the coke content up to 3.5% for Zn/KH-4/Al_2O_3 and 6.5% for W/KH-4/Al_2O_3 does not change the conversion of feedstocks.*

Keywords*: oligomerization, industrial catalyst, thermal stability, conversion, selectivity, butane-butylene fraction, hydrocarbon compounds, stability*

Introduction

The heterogeneous conversion process of light alkenes, particularly the butane-butylene fraction leaving the catalytic cracking units of oil refineries, into the components for both diesel and gasoline fractions takes place on modified zeolite catalytic systems. The oligomerization process is quite complex and involves stages of hydride transfer, accompanied by the formation of paraffins, cycloparaffins, and aromatic hydrocarbons [1-3]. Thermal stability and unique selectivity of zeolite catalyst structures have made them a popular choice for gas-phase petrochemical processing. For example, ZSM-5 zeolite is used as a catalyst in MOGD (Mobil Olefins to Gasoline and Distillate), i.e., a process for oligomerization of light alkenes C_2–C_4 to produce high-octane gasoline and middle distillates, developed by the company Mobil. After hydrogenation, the middle distillates can be used as high-quality diesel or jet fuel. The oligomerization process is conducted at 285-375°C, with a pressure up to 3 MPa, in a reactor with a fluidized bed of catalyst. The yield of the gasoline fraction ranges from 27 to 57%, depending on feedstock and process conditions. The gasoline fraction contains 94% olefins, about 2% aromatic hydrocarbons, and has an octane number of 92 according to the research method (RON) or 79 according to the montane method (MON) [4].

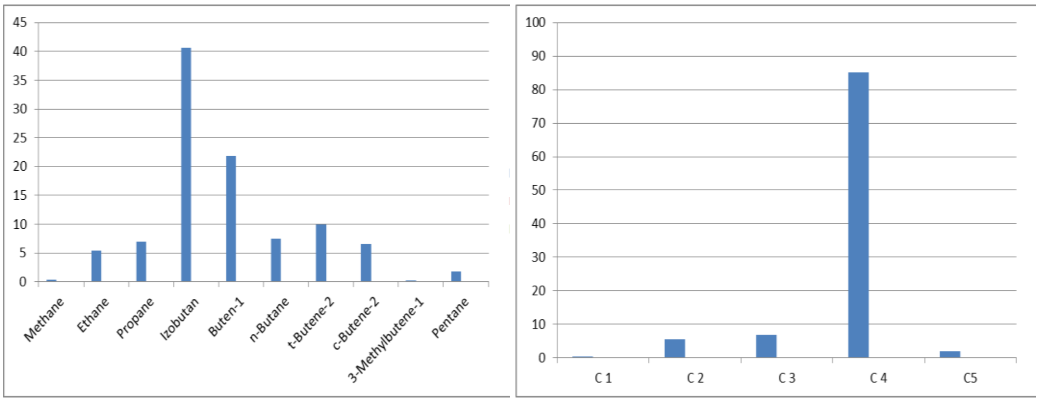
The high-temperature oligomerization process of alkene-containing C_3-C_4 catalytic cracking gases for obtaining components of high-octane gasoline with low aromatic hydrocarbon content (up to 10%) was implemented on the OB-2 zeolite-containing catalyst developed by SAPR-Neftekhim LLC [5, 6]. The catalyst was based on pentasil-type zeolite ZSM. The process was carried out at a pressure of 2.1 MPa and a temperature of up to 450°C. The resulting liquid product contained 45-50% alkenes, up to 10% aromatic hydrocarbons, had a boiling point of up to 225°C, and had an octane number of 92-96 RON. The process was implemented at an oil refinery in Lithuania. Since high-silica zeolites are potentially used in industry, the study of their thermal properties is extremely important. There’s considerable research in the literature on thermal properties of various zeolites and catalysts based on them [7-10]. The results of studies [7] prove that these catalysts thermally decompose within a few hours at temperatures above 600°C, highlighting the importance of operating conditions for the long-term operation of the catalyst.

The thermal stability and structural changes at high temperatures were also studied using synchrotron (X-ray) powder diffraction of TPA-ZSM-5 with different Si/Al ratios (15, 25, 50, and 100) and their structural modifications [8]. High-temperature treatment confirmed the high thermal stability of all ZSM-5 samples, which remained crystalline until the end of the thermal treatment (800°C). No significant changes were observed in the geometry of the framework or the shape of the channels that confirm the high flexibility of the MFI framework. The thermal stability of TPA-Na type ZSM-5 was indicated by exothermic peaks on the DTA curve, as the peak increases with the increasing amount of Al ions replacing Si ions [9]. Although the thermal stability of Na-type ZSM-5 also increased with the increase in the value of x in $Na_xAl_xSi_{1x}O_2$, it completely decomposed to cristobalite when heated to 1100°C for 3 hours. The H-type ZSM-5 had higher thermal stability than the Na-type and was resistant to heating at this temperature for 3 hours. The specific surface area of the H-type ZSM-5 was higher (360-420 m^2/g) in comparison to the Na-type ZSM-5 and retained a specific surface area above 300 m^2/g even after heating for 3 hours at 1100°C.

In light of the above, the aim of this study is to investigate the catalytic and thermal properties of the modified heterogeneous composite system Me(Zn,W)/KH-4/Al_2O_3, based on the industrial catalytic cracking catalyst KH-4 exhibiting high oligomerization activity in the conversion of olefin-containing gases from the catalytic cracking process at the Heydar Aliyev Oil Refinery at lower temperatures and atmospheric pressure [11].

Experimental part

The catalytic activity of the samples was studied on a flow laboratory setup at atmospheric pressure and a temperature of 220ºC with a volumetric flow rate of 500 h^{-1} and an experimental duration of 1-5 hours. The feedstock was the gases discharged from the catalytic cracking unit at the Heydar Aliyev Oil Refinery. The composition is shown in Fig. 1.



1. 2.

Fig. 1. Component (1) and fractional (2) composition of catalytic cracking gases at the Heydar Aliyev Oil Refinery

The analysis of the feedstock and reaction products was carried out using a chromatograph from Perkin Elmer AutoSystem. The base material for the synthesized catalytic systems was the catalytic cracking catalyst KN-4, obtained from the Novosibirsk Chemical Concentrates Plant. The synthesis was conducted by the modification of KN-4 with ion-exchange impregnation using aqueous salts of $Zn(CH_3COO)_2{\cdot}2H_2O$ and tungsten $(NH_4)4W_5O_{17}{\cdot}2.5H_2O$, followed by forming an alumina hydrogel, drying for 4 hours at 80°C and 110°C, and calcining at 350°C for 2 hours and 550°C for 4 hours. Before the experiment, the catalysts were reduced in a hydrogen stream at 380°C with a flow rate of

2 *l*/hour until complete moisture removal. All samples contained 25% Al_2O_3 as a binding component. The conversion of the olefin-containing fraction on the prepared samples was studied on a laboratory flow unit at atmospheric pressure, at a temperature of 220°C, with a volumetric flow rate of 500 h^{-1}, and experiment durations τ = 1-5 hours. Catalytic activity was evaluated by the degree of feedstock conversion, yields, and selectivity for the formation of high-octane C_5-C_6 components. The indicators of catalytic activity included the total conversion of the feedstock $K_{hydr.}$, the conversion of the butane-butylene fraction $K_{fr.\Sigma C4}$, mass selectivity $S_{hydr.}$ for the hydrocarbon fractions ΣC_5-C_6, ΣC_7, ΣC_8, and ΣC_9-C_{14} and hydrocarbon yields based on the following calculations:

$$K = \frac{n(HCs_f)-n(HCs_p)}{n(HCs)} \quad [1]$$

$$S_{HCs.} = \frac{\Sigma n(HCs_f)-(HCs_p)}{n(\Sigma HCs_f)-n(\Sigma HCs_p)} \quad [2]$$

$$y_{HCs} = k * S_{HCs} \quad [3]$$

where ($nHCs_f$) is the amount of hydrocarbons at the reactor inlet (%); ($nHCs_p$) is the amount of hydrocarbons at the reactor outlet (%); and Y is the yield of hydrocarbons in mass %.

Thermal stability of the synthesized samples was determined by a synchronous thermoanalyzer TG/DTA STA-449 JUPITER (Germany) with a temperature ramp rate of 10°C/min, in a nitrogen flow, dynamic mode, over a temperature range of 25-700°C. The inert gas flow rate (N_2) was 20 ml/min, and the sample amount for analysis was 10 mg.

Thermal treatment of zeolites before using them as catalysts was carried out before the experiments in an air stream with a flow rate of 2 *l*/hour at 550°C for removing adsorbed water from the zeolite pores. The carbon content on the catalysts was determined by burning off the coke, followed by gravimetric measurement of the weight gain of ascarite tubes installed after the reactor, as well as by differential thermal analysis (DTA) and thermogravimetry with a heating rate of 20 $K\cdot min^{-1}$ in an air atmosphere.

Results and discussion

The Table 1 presents comparative data on the catalytic activity of the synthesized samples 5%W/KH-4/Al_2O_3 and 5%Zn/KH-4/Al_2O_3 at 220°C and a volumetric flow rate of 500 h^{-1} for 1 hour of operation. Both catalysts exhibited high catalytic activity in the conversion of the butane-butylene fraction, with $K_{hydr.}$ values of 76.3% and 66.9%, respectively, for 5%W/KH-4/Al_2O_3 and 5%Zn/KH-4/Al_2O_3 samples with the conversion of all components of the initial butane-butylene fraction. The results of the studies on the synthesized samples are set into Table 1.

Table 1. Comparison of catalytic indicators of the oligomerization process in the presence of synthesized samples (t = 220°C, τ = 1 h, WSHV= 500 h^{-1})

Catalysts	Conversion, % $K_{hydr.}$	Component composition of catalyzate, mas. %								
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9-C_{14}
5%W/KH-4/Al_2O_3	76.3	0.01	0.37	1.29	2.41	9.37	2.9	7.9	5.75	0.01
5%Zn/KH-4/Al_2O_3	66.9	0.014	0.2	8.9.	9.3	6.5	8.73	5.35	4.8	0.014

As is evident from the results of the studies, both catalysts exhibit quite high oligomerization activity, producing high-octane components of gasoline fractions C_5-C_8 in the conversion of the butane-butylene fraction, with the involvement of all components of the reaction medium. The conversion of the butane-butylene fraction is 65.3%, with selectivity for the C_5-C_6 fraction at 65.3%, and the overall conversion of feedstock is 76.3% on 5%W/KH-4/Al_2O_3 catalyst.

Table 2. Catalytic parameters of 5%W/KH-4/Al_2O_3 and 5%Zn, KH-4/Al_2O_3 samples in the conversion of butane-butylene fraction (t = 220°C, τ = 1 h, WSHV = 500 h^{-1}).

Catalysts	$K_{fr.\Sigma C4}$, %	Selectivity on fr.ΣC_5-C_6, %	Selectivity on fr.ΣC_7, %	Selectivity on fr. ΣC_8, %
5%W/KH-4/Al_2O_3	65.3	65.1	36.2	12.5
5%Zn/KH-4/Al_2O_3	63.1	61.3	31.1	10.3

Thus, methane, ethane and propane underwent almost complete conversion in the transformation of the butane-butylene fraction (63-65% butane-butylene fraction), resulting in obtaining fractions C_5-C_{14} with selectivity of the fractions, as presented in Table 2, on catalysts 5%W/KH-4/Al_2O_3 and 5%Zn/KH-4/Al_2O_3.

The stability of the catalysts was studied over 1-7 hours without regeneration, and it was shown that the catalysts operated stably during 6 hours (Fig. 2). The content of coking products on both catalysts was also determined during 1-3-5-6 hours of operation.

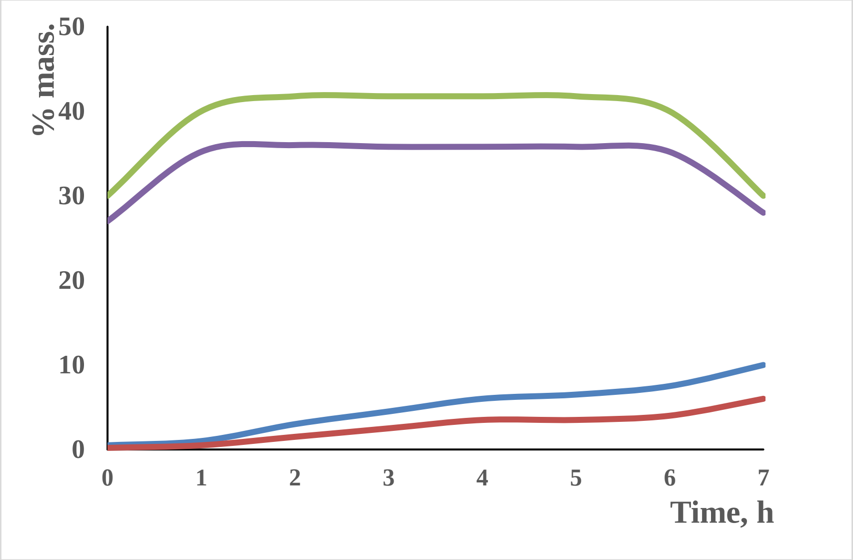


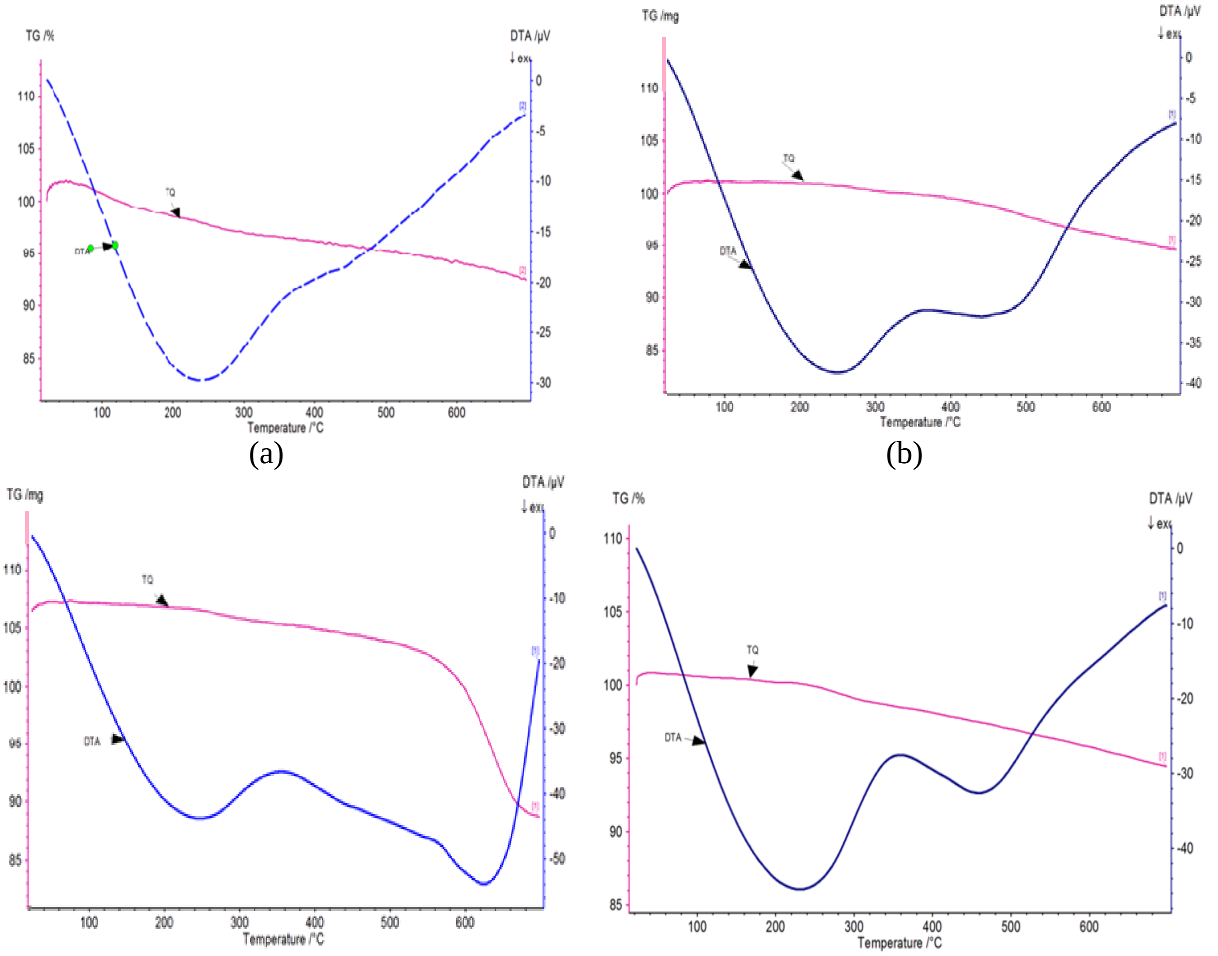
Fig. 2. Dependence of the yield of ΣC_5-C_6 fraction and the accumulation of coking products on the operating time of the catalysts 5%W/KH-4/Al_2O_3 and 5%Zn/KH-4/Al_2O_3
1 - Yield of the ΣC_5-C_6 fraction (%) on 5%W/KH-4/Al_2O_3
2 - Yield of the ΣC_5-C_6 fraction (%) on 5%Zn/KH-4/Al_2O_3
3 - Hydrocarbon deposit content (%) on 5%W/KH-4/Al_2O_3
4 - Hydrocarbon deposit content (%) on 5%Zn/KH-4/Al_2O_3

As is seen from Fig. 2, the coke content up to 6.5% does not affect the conversion change of 5%W/KH-4/Al_2O_3 with higher dehydrogenation activity in comparison to the zinc catalyst. This promotes an increase in the amount of coking products, with the content reaching 6.5% after 6 hours of operation, leading to a decrease in the catalytic activity of the sample after 6 hours of operation. The carbonaceous deposits are approximately half as much (3.5%) on 5%Zn/KH-4/Al_2O_3 catalyst. However, stable operation of the catalyst is observed for 6 hours, after which the conversion drops to 50.3%.

Deactivation occurs on both catalysts after 6 hours of operation, corresponding to the accumulation of 3.5% hydrocarbon deposits on the surface of the carrier. This pattern is presumably related to the difference in the active centers formed by tungsten and zinc, and the discrepancy in activity during the stable operation of the catalysts is likely due to the deactivation of the active centers on the carrier.

Further studies were focused on the study of the thermal stability properties of both fresh and spent samples of 5%Zn/KH-4/Al_2O_3 and 5%W/KH-4/Al_2O_3. The catalysts were subjected to preliminary thermal treatment at temperatures of 80°C and 110°C (4 hours) and calcination at 350°C (2 hours) and 550°C (4 hours).

Fig. 3 shows the thermograms of 5%Zn/KH-4/Al_2O_3 and 5%W/KH-4/Al_2O_3 catalysts.



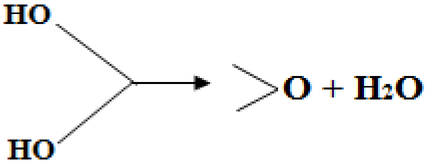
(a) (b)

(c) (d)

Fig. 3. Thermograms of TGA and DTA analysis of catalysts
(a) 5%W/KH-4/Al_2O_3 (fresh); (b) 5%W/KH-4/Al_2O_3 (spent);
(c) 5%Zn/KH-4/Al_2O_3 (fresh); (d) 5%Zn/KH-4/Al_2O_3 (spent).

As is evident from the presented thermogram spectra of the fresh, unused catalyst 5%W/KH-4/Al_2O_3, subjected to thermal treatment at temperatures of 80°C and 110°C (4 hours), and calcination at 350°C (2 hours) and 550°C (4 hours), there is a slight decrease in the mass of the catalyst in the temperature range of 250-350°C. This is likely due to the release of minor atmospheric impurities that were adsorbed. In the temperature range of 250-300°C, a more noticeable decrease in the mass of the catalyst occurs, presumably mainly related to the dehydration of both the binder (Al_2O_3) and the zeolite catalyst KH-4.

As the temperature increases above 600°C, tungsten is reduced, and the weight loss is associated with the instability of WO_3, which decomposes, transitions to a lower valence state, and is more easily reduced due to the presence of a reactant, which was apparently adsorbed during the reaction with an accompanying exothermic effect. Further increasing the temperature above 600°C leads to dehydration of the acidic centers with the decomposition of hydroxyl groups of the type:



A monotonic decrease in the catalyst weight is observed up to 600°C on the TGA curve of the 5%W/KH-4/Al_2O_3 catalyst, which was used in the butane-butylene fraction conversion at 220°C for 1 hour. Judging by the small change in the thermogravimetric curve up to 250°C, the weight loss may be related to the release of adsorbed atmospheric impurities and water. Further weight loss at temperatures between 450 and 500°C can be attributed to the release of hydrogen due to the dehydrogenation of hydrocarbon deposits formed during the experiment, converting them into carbonaceous deposits. The increase in weight loss starting from 600°C is likely related to the crystallization of the structured surface, forming graphite, which is accompanied by an exothermic effect and simultaneous intensification of hydrogen release. This is confirmed by the blurred TGA peaks and the breakdown of terminal -CH_3 groups present in the initial hydrocarbon deposits, resulting in methane. The absence of a peak on the spent sample at temperatures above 550°C, observed on the fresh sample, is likely related to the reduction of tungsten in the conditions of the catalyst's preliminary treatment before the experiment (reduction by hydrogen) at 380°C.

On the DTA curve of the fresh, unused 5%Zn/KH-4/Al_2O_3 catalyst, a blurred peak is observed above 200°C, which is similar to the one seen in the fresh tungsten-containing catalyst. Therefore, this peak can be attributed to the common feature for both catalysts - the KH-4 support. The peak in the 450°C range corresponds to the dehydration of zinc hydroxide $Zn(OH)_2$.

Dehydrogenation of hydrocarbon products occurs above 600°C on the spent 5%Zn/KH-4/Al_2O_3 catalyst, similar to the tungsten-containing sample.

Thus, high-temperature treatment confirmed the high thermal stability of both catalyst samples, which remain crystalline until the end of thermal treatment (750°C).

Conclusions

1. Catalytic, performance and thermal stability properties of modified catalytic systems Me(Zn, W)/KH-4/Al_2O_3 on the basis of the industrial catalytic cracking catalyst KH-4 were studied in the process of low-temperature conversion under atmospheric pressure of olefin-containing gases from the catalytic cracking unit at the Heydar Aliyev Oil Refinery;
2. A high oligomerization activity of the catalytic systems was established, leading to the formation of high-octane gasoline additives: the feedstock conversion on the 5%Zn/KH-4/Al_2O_3 catalyst is 66.9% with a selectivity of the ΣC_5-C_6 fraction of 53.5%, while on the 5%W/KH-4/Al_2O_3 catalyst, the conversion is 76.3% with a selectivity of the ΣC_5-C_6 fraction of 54.8%;
3. High-temperature treatment confirmed the high thermal stability of both fresh and spent catalysts, remaining crystalline until the end of thermal treatment (650-750°C) and exhibiting stable catalytic activity for 6 hours, and the coke content up to 3.5% for 5%Zn/KH-4/Al_2O_3 and 6.5% for 5%W/KH-4/Al_2O_3 does not affect the change in catalytic activity of the zinc and tungsten-containing industrial catalyst KH-4.

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