

A comparative study of physico-chemical and catalytic characterization of M-modified SZ catalysts (M = Pt, Nb or Re) in n-hexane isomerization

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Three M-modified SZ catalysts (M = Pt, Nb or Re) are synthesized from Zr(IV)-alkoxide precursor and corresponded metal salts, and their physicochemical properties are correlated with activities in *n*-hexane isomerization reaction. Platinum performs a multifunctional role simultaneously stabilizing and promoting activity of the bare sulfated zirconia catalyst. The attempt of SZ-based catalyst modification by Nb and Re results in diminishing the catalytic efficiency. The key distinction in the resulted SZ-modification by concrete metal might be in different metal dispersion, being quite low in the case of two later catalysts. This implies the importance of metal precursor right choice, tailoring final catalyst properties.

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1. Introduction

The skeletal isomerization of light naphtha being relatively simple and cost effective is key reaction in the petroleum industry for increasing the octane number (ON) of the gasoline pool. It is well known that liquid acid catalysts as HF and H₂SO₄ were traditionally used in the industrial process of alkylation in order to obtain ON > 94 [1-3]. However, these catalysts have shown potential corrosion problems and harmful environmental impact (namely, 20 ppm HF is lethal dose). Recently EU standard has imposed new legislative restriction on level of aromatics and olefins known as high ON components in petrol [1-3]. Similarly, lead-base additives were eliminated from gasoline long before. Less hazardous components such as isoalkanes may represent a potential replacement also providing higher ON of the gasoline. The conventional technologies applied either traditional chlorided-alumina-based or zeolite-based catalysts [3]. Former are very effective, however, undergo easy poisoning by water and/or sulfur in the feed and ecologically unfriendly due to the presence of chlorine. On the contrary, zeolite-based catalysts, being resistant to impurities, are less active requiring higher reaction temperatures. Relevantly, design of new environmentally friendly isomerization catalysts has been recognized as a task; among them solid acids as popular candidates have been extensively investigated. Sulfated zirconia (SZ) has attracted considerable attention due to its acidity and activity in isomerization of short alkanes at mild conditions [4]. Unfortunately, SZ suffers from a fast

deactivation and although regeneration is possible a short operating cycle makes it impractical [5].

Possible solution is offered in transition metals (e.g. Fe, Mn and/or Ni) incorporation resulting in catalysts with higher activity than unmodified SZ for *n*-butane isomerization [6]. Addition of either Fe or Mn to sulfated zirconia increases the catalytic activity, but SZ promoted exclusively by Mn shown an order of magnitude lower activity than Fe impregnated SZ-based catalytic material [7]. Although SZ promoted with both iron and manganese (FMSZ) has been found to possess higher activity for *n*-butane isomerization, there are different points of view regarding nature and final metal impact [8]. There is an opinion that SZ promotion occurs by both increasing number of acid sites and their strength [9]. Contrary, some authors claim no significant difference in acid strength between SZ and FMSZ on the other side [10]. The main role of Mn was accepted as an increase of Fe dispersion [11]. Platinum loaded SZ significantly inhibited coke formation as well as fast deactivation thus improving stability of catalyst [12]. Investigations concerning SZ modified by noble metals have demonstrated the highest activity of Pt-modified catalyst, considerably higher than one of commercial zeolite-based catalyst [13]. The catalytic material impregnated with iridium or rhodium showed lower, but comparable activity with previous one, while ruthenium gave less stable catalyst [14]. Regardless of variety of metals impacts on SZ activity reviewed in literature, the exact role of platinum, niobium and rhenium as possible metal promoters is still unlighted. More in dept, their promoting roles, i.e. modifying or stabilizing

are not consistent, even in the case of Pt-SZ being the most extensively studied [15,16].

2. Experimental procedure

SZ catalyst was prepared from Zr(IV)-propoxide (70% solution in 1-propanol) (Aldrich Co.) by mixing two solutions: zirconium(IV)-propoxide in propanol, and propanol in de-ionized water. Ratio of water to zirconium(IV)-propoxide was 2 : 1. Solutions were mixed vigorously with a magnetic stirrer in order to obtain zirconia-sol (concentration 0.5 mol/dm³), and by adding NH₄OH (25%) such obtained sol was kept at pH = 9.5. The precipitate was aged for 6h, centrifuged, rinsed with deionized water (8 times) and finely with alcohol, filtered and then dried at 110°C for 24h. Sulfation was performed by impregnation of the dried solid with desired volume of sulfuric acid (0.5 M H₂SO₄) for nominal sulfur content of 3 mass% S per g of zirconium-hydroxide, following additional drying at 110°C for 3h. Finely, SZ precursors were calcined at 600°C for 3h in air flow of 20 ml/min [17]. Three M-SZ catalysts were synthesized by the procedure reported previously [18]. M-SZ catalysts were prepared by incipient wetness impregnation with corresponding volume of H₂PtCl₆ in order to obtain 1 mass% of Pt in Pt-SZ, or by repeated fractional addition of alcohol solutions of NbCl₅ or ReCl₅ to obtain 1 mass% of metals in Nb-SZ and Re-SZ. The M-SZ precursors were further dried at 110°C for 3h before the final calcinations at 450°C for 3h.

Physicochemical properties of catalyst samples were evaluated by means of their textural (LTNA, ASAP 2000), structural (XRD, Philips APD-1700) and morphological (SEM, JOEL JSM-6460LV) properties. In addition, TEM characterization was carried out by TEM/EDX CM20, Philips, Lab 6 at 200 keV. Catalyst crystallite size was calculated using full width at half-maximum in XRD patterns additionally applying Scherer's equation. Volume fractions of tetragonal/monoclinic phase were calculated from corresponding XRD lines. Thermal characteristics were followed in dynamic conditions, from ambient temperature to 1000°C, using temperature ramp of 10°C/min. Acid/base properties were investigated by FTIR analysis of catalyst surface pre-adsorbed with pyridine.

Activity was tested in isomerization of *n*-hexane at 200°C, atmospheric pressure, using either H₂ or He as carrier gases premixed with *n*-hexane (molar ratio, carrier gas/*n*-hexane = 15) and space velocity of 6·10⁻² mmol *n*-C₆/g_{cat}·min. Helium was co-feed to hexane in the cited reaction circumstances when the bare SZ catalyst, with no metallic promoter, was used. A fresh catalyst sample (0.5 g) was loaded into a fixed-bed quartz micro-reactor and either directly exposed to reaction condition (SZ), or previously *in situ* reduced (M-SZ) in H₂ flow of 20 ml/min at different temperatures (300, 350°C) for 2.5h. Activity and selectivity of catalyst samples were ranked by means of *n*-hexane conversion to corresponded isomers normalized by the number of C-atoms in products. Reaction progress was followed during time-on-stream (TOS) by gas chromatography (HP 5890 Series II), using 50 m long capillary PONA column for hydrocarbon separation and FI detector, and an external standard for their identification and quantification. Product composition comprised hydrocarbons from CH₄ to benzene, and selectivity was calculated as a sum of monobranched (2- and 3-methylpentanes) and dibranched (2,2- and 2,3-dimethylbutanes) C₆-isomers.

3. Results and discussion

Textural properties of catalyst samples, as well as, their volume fraction of tetragonal/monoclinic phases and crystallite size are summarized in Table 1. The specific surface areas of M-SZ catalysts present completely different values in range from 53 m²/g (Nb-SZ) to 116 m²/g in the case of platinum modified SZ-based catalyst (Pt-SZ). Accordingly, pore volumes and pore sizes show higher values in the case of Pt-SZ than Nb-SZ catalyst with the exception of these values being unexpectedly high for Re-SZ catalyst sample. Such meso-pore size in the case of Re-modified SZ was not crucial for catalytic activity, but rather for a specific kind of catalyst deactivation mechanism reported previously [19]. Namely, coverage of individual active sites with coke was found earlier when pores of larger size were involved, which resulted in longer catalytic life [19].

Table 1. Textural properties, phase composition, and crystallite size of SZ-based catalyst samples

Sample	Surface area, m ² /g	Mean pore diameter, nm	Pore volume, cm ³ /g	Volume fraction of tetragonal/monoclinic SZ phases, %	SZ crystallite size, nm	
					tetragonal	monoclinic*
SZ	92.5	5.42	0.176	88/12	12.5	13.7
Pt-SZ	116.4	4.58	0.143	94/6	8.2	16.4
Nb-SZ	53.3	3.55	0.052	69/31	10.3	13.7
Re-SZ	65.1	8.32	0.155	61/39	9.2	11.7

*calculated at 2θ = 28.25°

It has been commonly accepted that tetragonal crystalline phase of the SZ-based catalytic systems, as well as critical value of particle size are both known as important for catalytic efficiency in *n*-alkane isomerization reaction [20,21]. It is clear that the all SZ-based catalyst samples investigated here are well crystallized with prevailing tetragonal crystal phase (Table 1). Incorporation of platinum into bare SZ-based catalyst significantly changes both textural and structural properties of unmodified SZ. This finding is proved by means of specific surface area value and fraction of zirconia-tetragonal crystal phase increases, as well as, a decrease of tetragonal phase crystallite size. It seems that Pt plays a crucial role as both textural and structural promoter of SZ by stabilizing the catalytic active tetragonal crystal phase, keeping its crystallite size below critical value of 10 nm [22], and consequently delaying process of sintering.

On the other side, modification of SZ by Nb or Re has performed quite opposite situation resulting in both textural and structural features. The authors impose that attempt of SZ grafting by either niobium or rhenium has caused a dramatic effect on surface area diminishing its value to almost a half of that of the unmodified SZ catalyst, Table 1. The observed very low surface area value of Nb-SZ catalyst, as characteristic of Nb inhibition effect, is the lowest one among literature data dealing with this material [23]. At the same time, fractions of zirconia-tetragonal crystal phase substantially decrease when these metal modifiers are incorporated into SZ-based material. Besides, both Nb and Re induced reduction of tetragonal phase particle size comparing to value of unmodified SZ catalyst (Table 1). However, this fact seems not to be equally important for the catalytic activity as the fraction of tetragonal crystal phase is important in isomerization of *n*-hexane, Table 1 and Fig. 1.

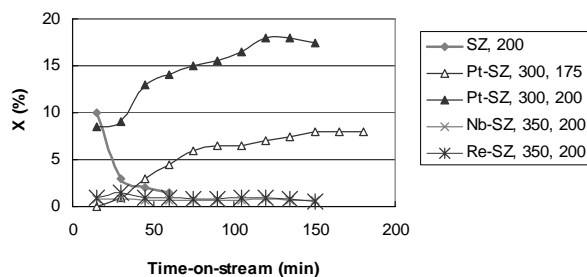
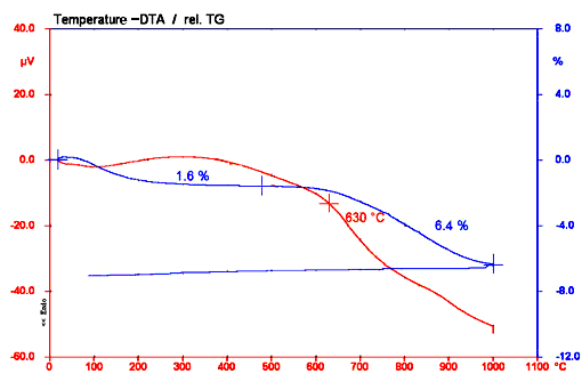


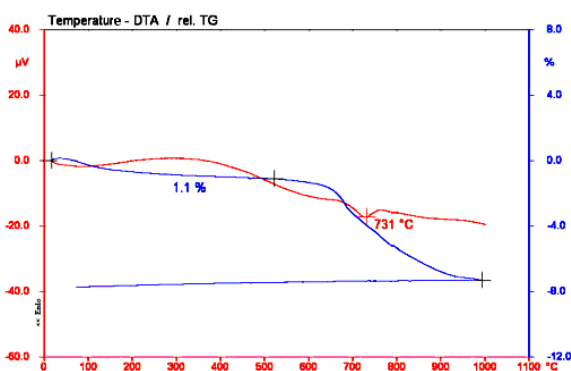
Fig. 1. Conversions of *n*-hexane (*X*) over *M*-SZ catalysts as a function of time-on-stream (First number in catalysts denotation announces reduction temperature and second one, reaction temperature applied).

TG/DTA analysis gave results concerning surface hydration degree and amount of remaining sulfates after calcinations in dependence on concrete metal modifier incorporated into SZ (Figs. 2 a-c). As seen from TG curve in Fig. 2a and taking into account previous TG results dealing with unmodified SZ catalyst [23,24], the presence of platinum in Pt-SZ catalyst causes an increase of surface

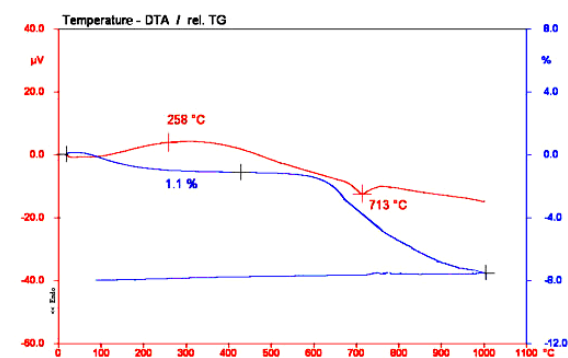
hydration degree (from 1.2 mass% (SZ, not shown) to 1.8 mass % (Pt-SZ)) and remaining sulfates content upon thermal treatment (4.8 mass% in Pt-SZ compared to 3.2 mass% in SZ (not shown)). It was published that certain water content is crucial to develop full catalytic activity of SZ [25].



a)



b)



c)

Fig. 2. TG/DTA curves of catalytic samples: a) Pt-SZ, b) Nb-SZ and c) Re-SZ.

TG curve, Fig. 2a, indicates platinum contribution to early process of sulfates elimination. Namely, removal of sulfates, followed by evolution of SO₂/SO together with

O/O₂ [26], starts at 50°C lower temperature when Pt is present in SZ comparing to the situation of unchanged SZ catalyst [23,24]. The former is related to labile sulfates decomposition, the process resulting in generation of surface acidic centers of the highest activity [27]. Different locus of TG curves indicating slower mass loss when Pt is present may be due to stabilization of remaining sulfates as the consequence of metal support interaction (MSI), Fig. 2a and results reported previously [23,24]. An endothermal broad shoulder-like effect up to 200°C, seen on DTA curve, in Fig. 2a can be explained by removal of physisorbed water. Additionally, an exothermal effect around 630°C on the same curve is result of superimposing of two effects: exothermal one due to phase transformation from amorphous to more stable monoclinic crystal phase at temperatures over 600°C, and endothermal effect at the same temperature region representing the heat needed for sulfates decomposition [28].

Contrary to Pt, it seems that Nb retards the evolution of sulfates species from Nb-SZ comparing to the bare SZ (not shown). As shown in Fig. 2b, removal of sulfates starts at almost equal temperature as in SZ [23,24], followed by higher rate of sulfate decomposition than it is the case for Pt-SZ. In details, sulfates decomposition starts at about 680°C achieving maximum at 730°C followed by corresponding endothermal effect on DTA curve, Fig. 2b. Opposite of affirmative Pt effect, neither two sulfates type nor labile sulfates presence responsible for catalytic activity [27] are evidenced in the case of Nb-SZ catalyst. As will be discussed later, this brings a dramatic effect on the Nb-SZ catalytic activity, Fig. 1. In line with the previous findings, introduction of rhenium into SZ results in reduction of surface hydration level mentioned as important characteristic for activity of SZ-based catalysts (Fig. 2c). Content of sulfates eliminated at temperatures up to 700°C is almost equal to the one of Nb-SZ catalyst, implicating on similar activity of both catalysts, as would be discussed later. High amount of catalytically inactive monoclinic crystal phase in Nb-SZ and Re-SZ catalysts together with poor textural properties (Table 1) may be related to an early sintering process additionally imposed with a lack of sulfates (Figs. 2b,c).

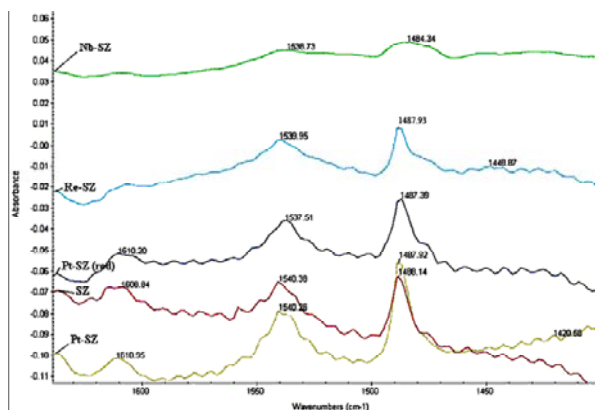


Fig. 3. FTIR spectra of pyridine preadsorbed on surfaces of SZ and M-SZ catalysts samples.

The concentration of Lewis and Brønsted acid sites (LAS and BAS) has been recently related to the level of surface hydration/dehydration degree [25]. Characterization of acid sites in M-modified SZ catalysts in this study was performed by FTIR analysis of pre-adsorbed pyridine on catalytic surface (Fig. 3). Concentration of acid sites hardly increased after platinum incorporation comparing to unmodified SZ (see bands at about 1490 cm⁻¹ representing LAS and at 1540 cm⁻¹ corresponding to BAS), shown in Fig. 3. The broad bands of smaller intensity at 1610 cm⁻¹ in principle may be attributed to adsorbed water, although it also may be correlated with the existence of strong LAS [25]. Namely, unsaturated surface-coordinated Zr⁴⁺ adsorbing pyridine in molecular form is responsible for the formation of the LAS [27].

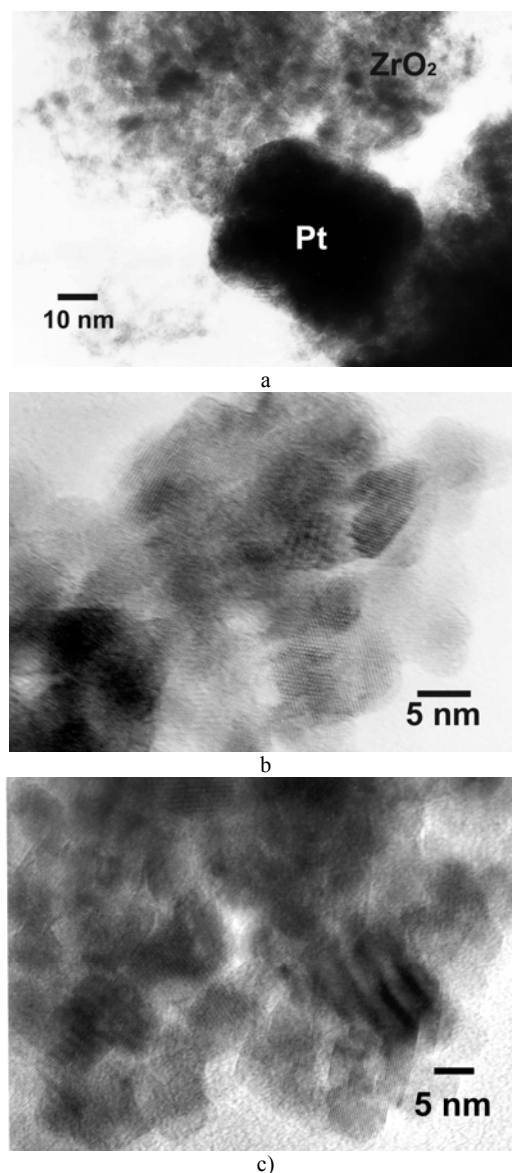


Fig. 4. TEM micrographs of catalysts samples: a) Pt-SZ, b) Re-SZ, c) Nb-SZ.

It has been proposed that BAS are related to activity of catalyst, while LAS are not directly involved in conversion of *n*-butane [27]. As far as participation of these centers in the reaction of *n*-hexane isomerization is concerned, consensus is not still established. In the present experiments using Pt-SZ catalyst, the existence of two types of LAS (bands around 1610 cm⁻¹ and 1490 cm⁻¹) may be proposed. Therefore, mutual participation of both acidic sites next to metal ones may be expected in the reaction of isomerization. On the contrary, situation is totally opposite after incorporation of niobium or rhenium to bare SZ, drastically diminishing both concentrations of BAS and LAS comparing to the same ones in unmodified SZ catalyst (Fig. 3).

In an attempt to make an insight into catalyst morphology and additional estimation of particle size, TEM analysis is carried out (Fig. 4). However, as shown in Fig. 4, only platinum can be detected in Pt-SZ catalyst, while neither Nb nor Re are visible in corresponded catalytic samples, Fig 4a-c. In Pt-modified SZ sample, platinum crystallizes in cubic form particle 30x40nm (Fig. 4a), being much larger than ZrO₂ particle of both tetragonal and monoclinic phases (Table 1). The absences of two other metal modifiers in TEM micrographs are curious and according to the magnification applied it can not be attributed to their high dispersions. In contrast, these metals are probably concentrated in isolated metal islands, which appearances are statistically quite low in TEM images.

The all discussed properties have synergistic impact on the final catalytic properties in *n*-hexane isomerization reaction. As shown in Fig. 1, in contrast to the bare SZ sample the activity profile of Pt-SZ catalyst is different undergoing to completely different reaction mechanism. On the other side both starting from similar initial activity slowly reach steady state conversion of 18%. Unmodified SZ catalyst deactivates very fast, but in case of Pt-SZ catalyst, furthermore catalyst stability is markedly improved. This may indicate a simple stabilizing effect of platinum demonstrated throughout hydrogenation of a coke precursor [12], but also a different reaction mechanism comprising both acidic and metal active sites [5]. It was claimed previously that bare SZ undergoes an oxidative dehydrogenation reaction mechanism during *n*-hexane conversion, leading to the reduction of S⁺⁶ to S⁺⁴, water and oxidized hydrocarbon species [5]. Over M-SZ catalysts, however, isomerization of *n*-hexane follows classical bifunctional mechanism, which has been proved by kinetic studies [13,14]. As seen in Fig. 1, Pt-SZ catalyst is active in *n*-hexane isomerization reaction even at as low temperature as 175°C, which is comparable to the reaction temperature of some commercial chlorided-alumina-based isomerization catalysts. Oppositely, Nb-SZ and Re-SZ catalysts show a negligible activity at reaction temperature of 200°C even after reduction at as high temperature as 350°C.

Table 2. Selectivity in *n*-hexane isomerization reaction over M-SZ catalysts.

Sample	Composition of isomers and <i>i</i> -C ₆ selectivity, %				
	3-MP	2-MP	2,3-DMB	2,2-DMB	<i>i</i> -C ₆ selectivity
SZ 200	10.1	9.4	1.2	0.7	21.4
Pt-SZ,300,175*	32.7	49.4	11.9	0.8	94.8
Pt-SZ,300,200	23.1	50.9	20.1	1.4	95.6
Nb-SZ,350,200	55.0	30.4	5.4	0.0	90.8
Re-SZ,350,200	48.6	34.1	0.0	0.4	83.1

*first number in catalyst denotation is related to reduction temperature, and second one to reaction temperature

N-hexane isomerization product distributions of reactions using M-SZ catalysts are listed in Table 2 showing hydrocarbon compositions at a steady state. However, the product distribution shows only smaller changes during time-on-stream (TOS). Isohexanes selectivity over the investigated catalysts is decreased in the following order: Pt-SZ(200) > Pt-SZ(175) > Nb-SZ(200) > Re-SZ(200). It is worth to underline that fraction of highest ON-gasoline contributor, *i.e.* 2,3-dimethyl butane (2,3-DMB) is maximal when Pt-SZ catalyst is used (Table 2). Therefore, it can be suggested that introduction of platinum to bare SZ, and catalytic run at 200°C are preferred for improvement of catalytic efficiency of unmodified SZ-based catalyst.

4. Conclusions

Catalytic efficiency of M-SZ catalyst (M = Pt, Re, Nb) in *n*-hexane isomerization depends on interplay of various factors, including surface area, the presence of SZ tetragonal crystal phase and its crystallite size, the existence of labile sulfates determining surface acidic properties, as well as dispersion of the specific metal included. Beside textural and structural promotion effect, reflected in both surface area value and SZ tetragonal phase fraction increases, platinum has additional roles in Pt-SZ catalyst. Firstly, by its small well dispersed particles it can facilitate dissociative chemisorption of hydrogen and through its spillover onto support may further hydrogenate coke precursors and hence improve catalyst stability. Secondly, by an early process of decomposition of remaining surface sulfates, Pt influences number and/or

strength of acidic sites formed on the SZ surface. Contrary, the attempt of SZ-based catalyst modification by Nb and Re diminishes catalytic activity. The reason for this fact might be in metal low dispersion caused by poor solubility of metal-precursor salts used in the procedure of catalyst preparation. Such viewpoint offers the conclusion that the right choice of metal modifier, its precursor reflected probably as prolonged precursor memory effect, as well as method of preparation, are all extremely important in controlling the activity of modified SZ.

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