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Examination of Gold as a Metal Promoter of Sulphated Zirconia in n-Heptane Isomerisation at Low Temperature

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Isomerisation of nC₇ over a sulphated zirconia (SZ)-based bifunctional catalyst was studied at 150 °C. Au, Ir, Pd and Pt were used as promoters of SZ. The first objective was the production of C₇ isomers with high octane numbers. PtSZ is the most suitable catalyst despite low conversions and a high proportion of methylhexanes instead of dimethylpentanes. The second objective was to assess Au as a promoter of SZ. Au shows slight hydrogenation abilities, displaying behaviour similar to that of Pd, but is inactive towards alkane activation. These promising but inadequate results suggested that Au could be used as the metallic function of bifunctional catalysts if the support were judiciously chosen and the preparation method optimised.

Introduction

Faced with increasingly severe environmental legislation, the petrochemical refining industry looks for clean-burning fuels like isoparaffins with high octane numbers. Sulphated zirconia (SZ) is known to isomerise n-butane into isobutane at room temperature.¹ However, it rapidly deactivates due to production of coke on the catalyst surface from olefins formed under the reaction conditions or present in the feed.¹ To overcome such deactivation, various metals, particularly transition metals, are added as promoters. Pt, Fe and Mn improve the activity and stability of SZ.² For example, Pt supported over SZ (PtSZ) is industrially used for, e.g., n-pentane isomerisation into isopentane.³

To the best of our knowledge, gold, as a lone promoter for SZ, has not been examined in the literature, while it has been used as the second metal for Pt- or Pd-based bimetallic alloys.^{4,5} Gold has long been regarded as a poorly active catalyst because its high catalytic activity is unexpected as bulk gold is quite inert.⁶ Nevertheless, when highly nano-sized and dispersed over a well-chosen metal oxide, its catalytic behaviour changes positively. Such catalysts have shown high activity in several reactions, e.g., NO_x reduction,⁷ CO oxidation,⁸ selective hydrogenation of crotonaldehyde,⁹ methane oxidation,¹⁰ hydrogenation

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of unsaturated hydrocarbons¹¹ and borohydride oxidation.¹² The synthesis of highly dispersed nano-sized gold particles is sensitive to the preparation method⁸ and conditions.¹³

Metal supported over SZ (MSZ) is a bifunctional catalyst, on which the isomerisation reaction proceeds following either the classical bifunctional mechanism¹⁴ or the modified bifunctional mechanism,^{15–18} where, for both, the metal's role is to dehydrogenate and hydrogenate the alkane (Figure 1). According to the second mechanism, the active site is the metal-proton adduct $[(H-M_m)(H_x)^{x+}]$, which acts as a collapsed bifunctional site. At low temperature, i.e. 150 °C, M associatively adsorbs and then dehydrogenates the alkane, this being transformed by the acid function placed side by side.¹⁷

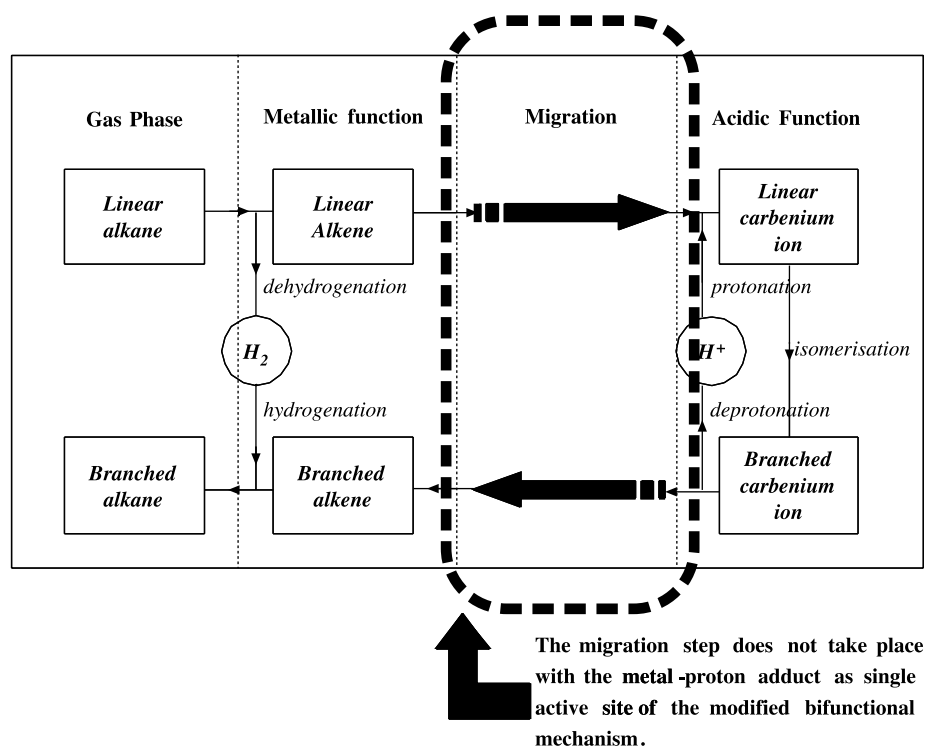


Figure 1. Classical bifunctional mechanism and modified bifunctional mechanism (for which the migration step is suppressed) for the skeletal isomerisation of alkanes over metal supported over solid acid catalysts.

The aim of the present study was to investigate the isomerisation of n-heptane over MSZ at low temperature (150 °C). Four metals were investigated: Au, Ir, Pd and Pt. The first objective was to find a bifunctional catalyst highly active for the isomerisation of linear alkanes into branched ones at temperatures as low as possible. The second objective was the examination of Au as a metal promoter of SZ.

Experimental

SZ was prepared according to a one-step sol-gel method.¹⁹ An aqueous solution of sulphuric acid was added to n-propyl alcohol solution of zirconium n-propoxide. The solid was dried at 80 °C for 1 h and calcined at 625 °C for 4 h. SZ produced in this way showed a tetragonal crystalline phase. The metal was introduced by impregnation. The desired amount of the metal (0.2 wt%) was added from an aqueous solution of the metallic salt ($H AuCl_4$, $H_2 IrCl_6$, $Pd(NH_4)_2 Cl_6$, $Pt(NH_3)_4(NO_3)_2$). The mixture was stirred for 2 h and was

dried in an oven for 12 h. The catalyst was reduced under H₂ at 350 °C for 2 h. The catalysts are denoted SZ, AuSZ, IrSZ, PdSZ and PtSZ, or MSZ (with M as metal).

Elemental analyses, i.e. sulphur and metal content assessment, were carried out by the “Service Central de Micro-Analyse du CNRS” (Vernaison, France). The specific area was determined by the Brunauer Emmett Teller (BET) method. Transmission electron microscopy (TEM) was used to assess the dispersion, size and shape of the metallic particles.

The nC₇ conversion was carried out in a pulse flow system with a fixed bed reactor (0.1 g of catalyst) working at the atmospheric total pressure and at 150 °C. The reactant (5 μL) was introduced into the gas flow of H₂ at around 6.7 mbar by using a cooled trap kept at -18 °C (benzyl alcohol melting point). The molar ratio between H₂ and nC₇ was about 150. The products were analysed by a gas chromatograph (Varian 3300) equipped with a flame ionisation detector and a capillary column (CP-Sil 5CB 50 m x 0.53 mm ID x 0.32 mm film thickness). The GC was coupled at the outlet of the catalytic reactor. From the chromatogram, the total conversion α_T , the isomerisation selectivity %S_{isom} and the products selectivities %S_i were calculated according to the calculations already described elsewhere.¹⁷

Results and Discussion

Table 1 proposes some physical characteristics of the catalysts. All of them display similar specific surface areas, i.e. between 81 and 88 m² g⁻¹, and similar sulphur contents, i.e. between 1.04 and 1.17 wt%. The target of 0.2 wt% of metal is almost achieved with Ir, Pd and Pt, while for Au the metal content is slightly superior (0.26 wt%). Unfortunately, from TEM, metallic particles were not detected and therefore it was not possible to assess the dispersion, size or shape of the particles.

Table 1. Physical characteristics of SZ, AuSZ, IrSZ, PdSZ and PtSZ.

	SZ	AuSZ	IrSZ	PdSZ	PtSZ
Specific surface area (m ² g ⁻¹)	88	83	84	81	81
Sulphur content (wt%)	1.14	1.17	1.04	1.13	1.14
Metal content (wt%)	-	0.26	0.18	0.17	0.22
Metal particles size	-	n.d.	n.d.	n.d.	n.d.

n.d.: not detected from TEM.

Table 2 shows the initial catalytic activity of the catalysts. The experimental conditions were identical, from support preparation to catalytic tests. The SZ support was taken from a 10-g sample. Hence, the differences observed in the catalytic activities can be attributed to the metal presence. SZ is highly active at 150 °C for catalysts in the conversion and the cracking of nC₇ (Table 2). More than 80% of nC₇ is exclusively cracked into propane and butanes. Small fractions of C₅ and C₆ are detected. These products likely stem from the cracking of oligomers, precursors of coke. Compared to SZ, the initial activities of the MSZs are lower (54%, 91%, 79% and 76% for AuSZ, IrSZ, PdSZ and PtSZ, respectively). Moreover, except for AuSZ, the catalyst catalytic behaviour is changed by the metal introduction since the isomerisation selectivity surges to 33.7%, 51.8% and 64.5% for PdSZ, IrSZ and PtSZ, respectively. Hence, the presence of Ir, Pd or Pt has an important negative effect on the catalytic activity and a positive one on the isomerisation selectivity. AuSZ has different behaviour. It is 2 times more active than PtSZ and, as SZ, it cracks nC₇. Furthermore, its products distribution is similar to that of SZ. About 8% of C₅ and C₆ is formed with both

AuSZ and SZ. A detailed analysis of the products distribution is given in Table 3. It proposes C₃/C₄ and 2MH/3MH molar ratios that are similar for IrSZ, PdSZ and PtSZ. Hence, one can assert that both cracking and isomerisation mechanisms are identical with these 3 catalysts. For each, one nC₇ cracks into one C₃ and one C₄, and nC₇ statistically isomerises into 2-methylhexane and 3-methylhexane. Over AuSZ, the nC₇ cracking seems to follow a different mechanism because the C₃/C₄ ratio is below 1 but above the 0.3 value of SZ. In fact, no conclusion can be drawn from these values. It is probable that AuSZ would not hinder the formation of oligomers that could crack and provide C₅, C₆, C₃ and C₄ products, unpredictably changing the C₃/C₄ ratio.

Table 2. Conversion of nC₇ over SZ, AuSZ, IrSZ, PdSZ and PtSZ at 150 °C (H₂ flow rate: 10 mL min⁻¹).

	α_T (%)	%S _{isom} (%)	Product selectivity ^a (%)							
			C ₃	iC ₄	C ₅	C ₆	MH	DMP	TMB	EP
SZ	82.4	0.1	22.6	69.9 ^b	6.8	0.6	0.1			
AuSZ	38.1	0.0	39.4	52.6 ^b	6.9	1.1				
IrSZ	7.6	51.8	24.8	23.4			40.1	10.5		1.2
PdSZ	17.0	33.7	34.2	32.0		0.1	25.2	7.5	0.1	0.9
PtSZ	19.7	64.5	18.3	17.2			50.3	12.4	0.2	1.6

^aC₃: propane; iC₄: iso-butane; C₅: pentanes; C₆: hexanes; MH: 2- and 3-methylhexane; DMP: 2,2-, 2,3- and 2,4-dimethylpentane; TMB: trimethylbutane; EP: ethylpentane.

^bIncluded nC₄ selectivity: 2.6% for SZ; 3.4% for AuSZ.

Table 3. Detailed analysis of the product distribution given in Table 2.

	α_T (%)	%S _{isom} (%)	C ₃ /C ₄ ^a	2MH/3MH ^b
SZ	82.4	0.1	0.3	
AuSZ	38.1	0.0	0.8	
IrSZ	7.6	51.8	1.2	0.9
PdSZ	17.0	33.7	1.1	1.0
PtSZ	19.7	64.5	1.1	1.0

^a Molar ratio between propane and n-butane + iso-butane.

^b Molar ratio between 2-methylhexane and 3-methylhexane.

A way to check the possible participation of Au in the dehydrogenation of the alkane is to follow the catalyst activity at the time of several pulses of reactant. Figure 2 shows the total conversion and the isomerisation selectivity for each catalyst after a first, a second and a third pulse of nC₇. As expected, SZ deactivates and loses all activity (coke deposition). All MSZ catalysts deactivate as well but less severely than SZ. At 150 °C, the different metals do not sufficiently stabilise the catalyst activity. The best metal is Pt, as expected,² for which the isomerisation selectivity increases with the decrease in the conversion.¹⁷ With Ir, the total conversion slightly decreases and the isomerisation selectivity severely drops, as reported previously.²⁰ Regarding AuSZ, the total conversion is better than that of SZ after the first pulse and is similar to that of PdSZ. Moreover, AuSZ remains a cracking catalyst even if a very small contribution of isomerisation appears. These 2 observations are important. They show that Au has a small hydrogenating power of the (hydro)carbon residues when they are SZ supported and that the Au presence does not affect the cracking ability of the acid sites.

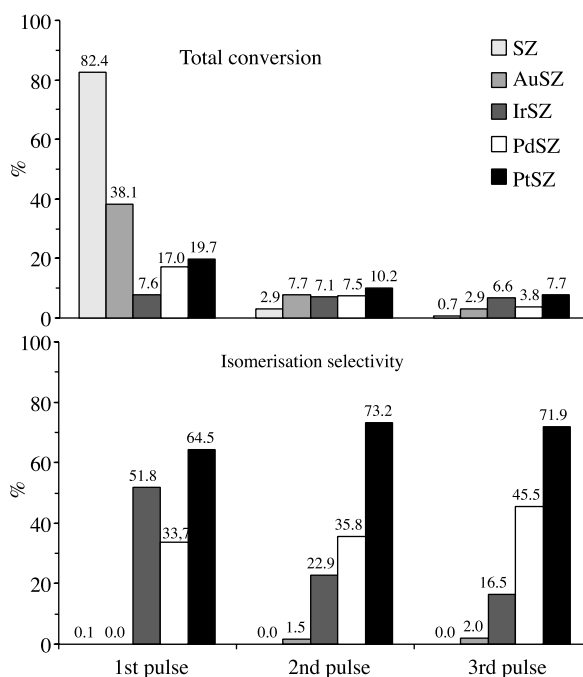


Figure 2. Total conversion and isomerisation selectivity for nC₇ conversion over SZ, AuSZ, IrSZ, PdSZ and PtSZ after 3 pulses of reactant at 150 °C (H₂ flow rate: 10 mL min⁻¹ H₂, 0.1 g of catalyst).

The first objective of this study was to investigate an isomerisation catalyst based on SZ support. According to the data provided, PtSZ is the best candidate, with more than 64% isomerisation. However, there are 2 drawbacks:

- The total conversion is initially too low and decreases with deactivation.
- The proportions of dimethylpentanes and trimethylbutane represent only 20% of the C₇ isomers.

IrSZ could be viewed as a possible candidate if the conversion were better. With IrSZ and PdSZ, the proportions of dimethylpentanes and trimethylbutane are 20% and 23%, respectively. These results are promising but the main challenges are now both stabilisation and improvement of the low-temperature catalytic activity. SZ-based bimetallic catalysts could be an investigation area.²¹

A great number of metals have been used as promoters of SZ for the nC₄ isomerisation reaction and Pt, Ir, Ni, Fe and Mn have shown the best promoting effects.^{22–24} For nC₆ isomerisation, the following classification has been proposed: Pt > Ir ~ Rh > Ru > SZ.²⁵ In the present study, it is difficult to propose a final ranking (Figure 2) but a possible trend could be Pt > Ir > Au ~ Pd. Understanding this classification is quite difficult because the metal as the metallic function of the metal-proton adduct site is supposed to have many roles:¹⁷

- The metal is in interaction with the SZ support, which modifies its electronic structure,
- The metal is a pool of hydrogen, adsorbing and dissociating the H₂ molecules,
- The metal adsorbs and activates the alkane thanks to its electron-deficient character,
- The metal participates in the dehydrogenation and hydrogenation reactions.

Hence, this multitude of roles complicates the use of any catalyst property to understand the proposed ranking. It is likely a compromise between the electronic properties of the metal, its geometry shapes and the presence of impurities and the reactant nature.^{21,24}

The second idea of this work was to assess gold as a promoter of SZ. Grzybowska-Świerkosz²⁶ reviewed catalysis by gold and reported that gold nano-particles must be low-sized, i.e. 2-5 nm, in order to lose their metallic character and become hemispherical because they are more active than spherical ones. The support may stabilise the gold dispersion, modify its electronic state and participate in reactant activation.

In the present investigation, the first function expected from gold is to provide enough hydrogen for hydrogenating the reaction intermediates and thus to prevent coke formation at the origin of the catalyst initial deactivation. It is of note here that the H₂ dissociation is commonly regarded as impossible on gold.²¹ From Table 2 and Figure 2, Au seems to carry out this expected function because the catalyst deactivation rate is slowed down if compared to SZ even if Au does not stabilise the catalyst activity. This last observation suggests that the hydrogenation ability of Au might be insufficient for preventing coke formation, which is due to impurities, such as olefins and aromatics, present in either n-heptane or gasoline fractions. Louis²⁷ briefly reviewed heterogeneous catalysis with Au and underlined that Au has a lower activity but a higher selectivity for hydrogenating unsaturated hydrocarbons than both Pt and Pd. According to our results, AuSZ and PdSZ seem to show similar behaviour in terms of their hydrogenation ability.

IrSZ, PdSZ and PtSZ are regarded as particular kinds of bifunctional catalyst, for which the active site is single, namely the metal-proton adduct site where the metal and the acid functions are united.^{15–18} This site supposes strong interaction between the metal and the SZ support.²⁸ Such interactions may occur between Au and SZ. This would suppose that H₂ adsorbs and then dissociates on Au, which would explain the hydrogenation ability of Au, but at a lower degree than Pt. However, Au does not participate in the alkane transformation and this suggests that the interaction between Au and SZ would be weak and would not sufficiently modify the Au electronic state. Such sites would not be active enough for alkane activation.¹⁷ Grzybowska-Świerkosz²⁶ has suggested that, despite the lack of data about the interactions of hydrocarbons with gold particles, the activation of a hydrocarbon should be highly difficult on Au nano-particles. Moreover, this author has concluded that catalysts containing Au dispersed on easily reducible metal oxides would be more active for the activation of hydrocarbons. This remark likely explains the insufficient activity of AuSZ in the present study. ZrO₂ of SZ is probably not easily reducible for 2 reasons: the presence of sulphur compounds that stabilise the Zr electronic state, and the noble character of gold. In summary, it seems that interactions between Au and SZ exist, providing the Au-proton adduct with hydrogenating ability. Nevertheless, these interactions are weak and therefore insufficient for hydrocarbon activation over the Au sites.

Conclusion

PtSZ is the most suitable catalyst for the isomerisation of nC₇ into isomers with higher octane numbers even if the conversion is low and the proportion of methylhexanes is higher than that of dimethylpentanes. Furthermore, Pt is the best promoter of SZ. Au as a promoter of SZ provides promising but inadequate results. The results are promising because Au participates slightly in both reactant dehydrogenation and intermediate hydrogenation. Au displays hydrogenating behaviour similar to that of Pd. The results are inadequate because the interactions between Au and SZ are insufficient to change the Au electronic state

so that Au could participate in both adsorption and activation of the alkane. Au could thus be used as the metallic function of a bifunctional catalyst if the support were judiciously chosen and the preparation method optimised.

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