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# Isomerization of hexane on PtAu nanoparticles supported on zeolites

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## Abstract

When lead-based anti-knock additives were withdrawn, petrol was enriched with benzene and benzene derivatives in order to maintain an excellent octane number. However, because of their toxicity, it is planned to eliminate these also and to replace them by methylated alkanes, whence the importance of *n*-alkane isomerization.

Some PtAu-zeolite catalysts tested for *n*-hexane isomerization reveal that the addition of gold to platinum generally changes the activity and/or the selectivity for methylpentane to the detriment of cracking. The influence of the zeolite structure is also important. At 275 °C, the activity and selectivity of PtAu-HZSM5 are about 75%, showing that this catalyst can be useful for such a reaction.

*Keywords:* *n*-Hexane isomerization; PtAu/zeolite catalyst

## 1. Introduction

Because of their toxicity, benzene and its derivatives must be eliminated from petrol. The only way to maintain a high octane number is to replace them by methylated hydrocarbons, whence the importance of the isomerization of *n*-alkanes, which can be currently performed in liquid superacid media. However, for various reasons, including easier engineering and catalysts which can be reused often, but also because of the local pollution and toxicity associated with liquid superacids, industry prefers heterogeneous catalysis. The isomerization of *n*-alkanes can be performed in the presence of so-called low-temperature and high-temperature solid catalysts. The main disadvantage of the first is their sensitivity even to small admixtures of water and sulfur compounds in the stocks. As an alternative, zeolites can be used as a basis for bifunctional high-temperature catalysts.

The catalytic properties of the noble metals, gold and platinum, have attracted great interest in recent years. These metals are now proposed as catalysts in various reactions [1–4]. In order to prepare an active material, small particles of noble metals, 5 nm or less in size, which are supported typically on a metal oxide support, are necessary. Bifunctional catalysts consisting of noble metal and solid acid are widely used for reforming processes including skeletal isomerization, dehydrocyclization, etc. [5]. These bifunctional catalysts provide both acid and hydrogenation–dehydrogenation functions which are required to be well-balanced to promote the desired reaction selectivity, and they are thus expected to be available for various reforming reactions of hydrocarbons.

In this connexion, our present study deals with the search for and development of new highly active and selective bifunctional heterogeneous catalysts consisting of zeolite-supported nanoparticles of noble metals (Pt, Au), which can be used as model systems for the isomerization of *n*-hydrocarbons on an industrial scale. Using *n*-hexane, we show that certain PtAu/zeolite-based catalysts can be useful for *n*-alkane isomerization.

## 2. Experimental

Samples were prepared with 1 wt.% of Pt on HY or HZSM5, to which is added the amount of gold required to give Au/Pt

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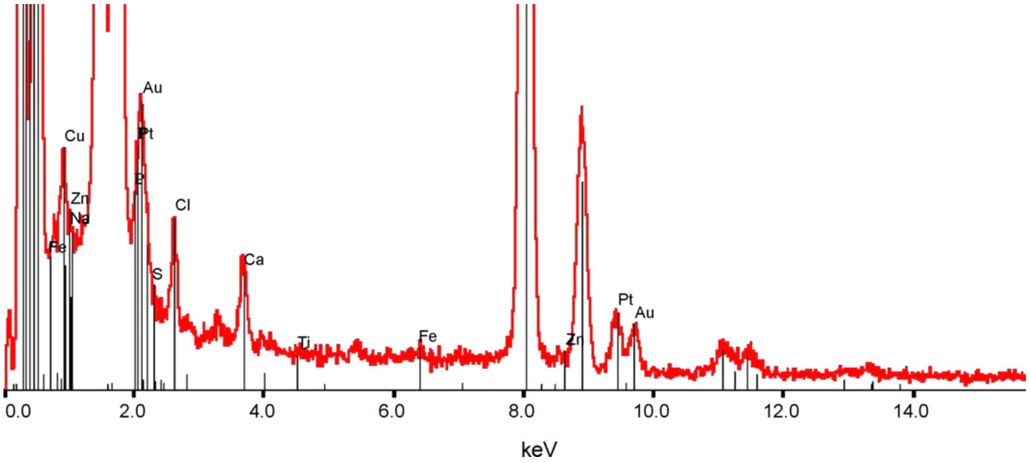

Fig. 1. EDX spectra of $Pt_{80}Au_{20}HY$ showing the signals of Pt and Au in one particle.

ratios of 20%. Our previous studies [6,7] have proved that for a molar ratio of 20% the particles of PtAu on HY are bimetallic. This bimetallic character decreases when the ratio is increased: Pt and Au start to segregate at a molar ratio $\geq$40%.

The method for preparing these catalysts consists in introducing $[Pt(en)]^{2+}$ and $[Au(en)_2]^{3+}$ (en = $H_2N–CH_2–CH_2–NH_2$) by cation exchange. The cations are autoreduced by the ligands in a stream of inert gas at 300 °C [6,7]. The catalysts obtained have been characterized by several techniques described in these references: electron microscopy using the microtomy technique, Xe-NMR of adsorbed Xe used as a probe, UV–vis spectroscopy and EDX (equipment type: Jeol JEM 2010 with 200 kV energy).

The use of acidic zeolites favours the dispersion of the metal and the thermal stability of the particles. This stability is explained by chemical anchoring of metal clusters by the Brönsted sites of the support.

The hydro-isomerization of hexane was carried out at 200–350 °C in a flow-type fixed-bed stainless steel reactor. A granular catalyst sample (4.0 $cm^3$) with a particle size of 0.5–1 mm, placed in the isothermal zone of the reactor, was mixed with silica sand (particle size, 1–2 mm) for uniform heating of the *n*-hexane. Prior to the reaction, the sample was pretreated by heating (2 °C/min) to 360 °C under hydrogen flow (30 ml/min); the catalyst was held at this temperature for 2 h. Then the reactor temperature, *T*, was decreased to 200 °C, the $H_2$ pressure within the reactor adjusted to 3 MPa, and the reactor fed with *n*-hexane (WHSV of 1 $h^{-1}$) using a liquid micropump ($H_2$/*n*-hexane = 1). Gaseous and liquid products were analysed by gas chromatography with the column (50 m, internal diameter 0.2 mm) at 50 °C and flame ionization detection at 200 °C.

## 3. Results and discussion

Electron microscopy, using the microtomy technique, and Xe-NMR of adsorbed xenon used as a probe have established that the metal particles are located in the supercages of the HY zeolite. Their average size is 2.5 nm. As is now well known, the environment of the supercages containing these particles is slightly broken. EDX spectroscopy shows that the particles of PtAu/HY are essentially bimetallic for this Au/Pt ratio of 20% (Fig. 1). This result is confirmed by UV–vis spectroscopy. There is no difference between the spectra of Pt/HY and PtAu/HY. The band at 510 nm characteristic of gold is not detected, proving that most of the gold is located inside the mixed PtAu

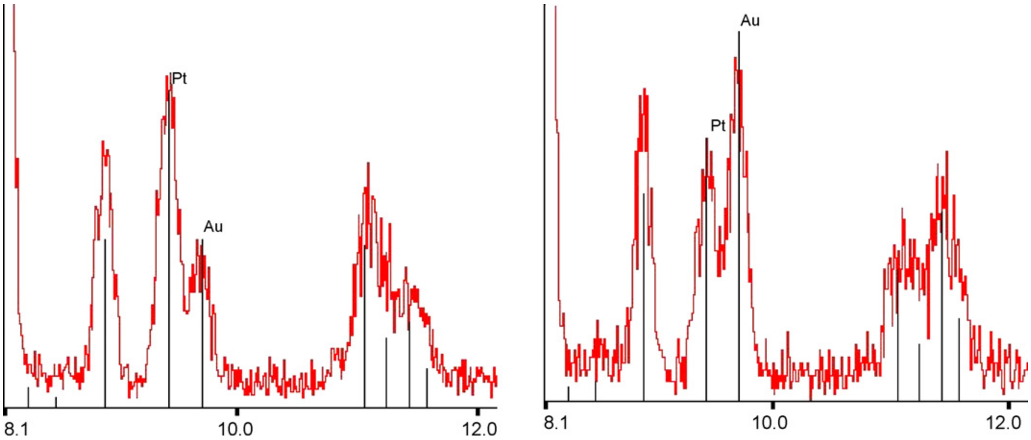

Fig. 2. EDX spectra of $Pt_{80}Au_{20}ZSM5$ showing the signals of Pt and Au in two different particles.

Table 1
Hydro-isomerization of $n$-hexane by PtAu/HZSM5 (Au/Pt = 0.20)

| $T$ (°C) | Composition of isomerizate (wt.%) | | | | | | | | | | Conversion of $n$-C6 (wt.%) | Selectivity[a] (%) | Total $i$-$C_6$ (wt.%) | 2.2-DMB[b] | 2-MP/3-MP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_2$ | $C_3$ | $i$-$C_4$ | $n$-$C_4$ | $i$-$C_5$ | $n$-$C_5$ | 2.2-DMB | 2-MP | 3-MP | $n$-$C_6$ | | | | | |
| 20 | | | | | | | | 0.20 | 0.40 | 99.40 | | | | | |
| 200 | 0 | Trace | 0 | Trace | 0 | Trace | 0 | 1.26 | 0.99 | 97.74 | 2.26 | 100 | 2.26 | 0 | 1.27 |
| 225 | 0 | 0.21 | 0 | 0.10 | 0 | Trace | 0 | 4.85 | 2.27 | 92.59 | 7.41 | 95.93 | 7.11 | 0 | 2.14 |
| 250 | 0.30 | 1.75 | 0.10 | 0.45 | 0.13 | 0.32 | Trace | 18.60 | 10.59 | 67.75 | 32.25 | 90.52 | 29.19 | 0 | 1.76 |
| 275 | 3.21 | 7.18 | 0.97 | 2.17 | 1.42 | 1.47 | 0.58 | 35.63 | 21.29 | 26.08 | 73.92 | 77.79 | 57.50 | 1.02 | 1.67 |
| 300 | 4.52 | 17.26 | 3.15 | 5.41 | 3.94 | 2.37 | 2.85 | 25.84 | 18.10 | 16.56 | 83.44 | 56.08 | 46.79 | 6.10 | 1.43 |

[a] Selectivity for total $i$-$C_6$ on converted $n$-$C_6$ (%).

[b] 2,2-DMB content of total $i$-$C_6$ (wt.%).

particles. In the case of HZSM5 the initial complex is too big to enter the channels directly. Some of the metal diffuses partially into the pores when the complexes are decomposed, so there are small particles in the channels and some larger particles on the external surfaces of the crystallites. However, both are generally bimetallic, as shown by EDX (Fig. 2), but the concentrations of Pt and Au are not the same for all particles.

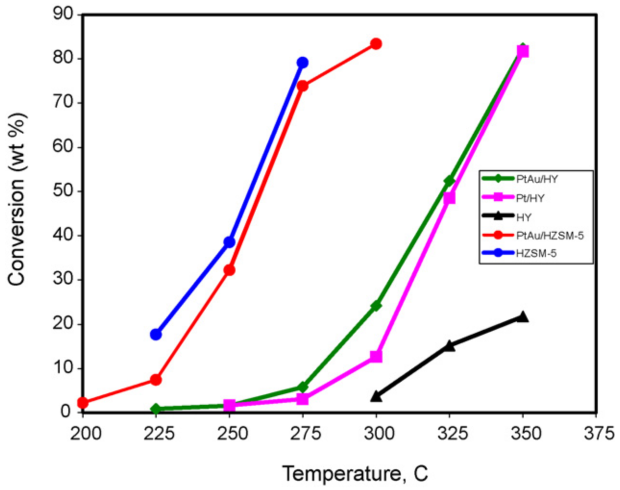

Fig. 3. Conversion of $n$-hexane vs. temperature.

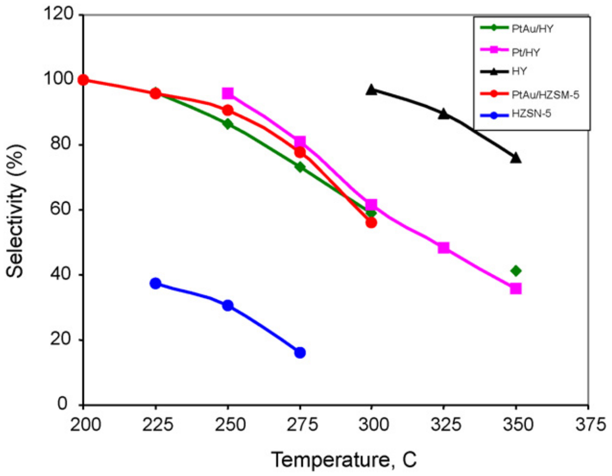

Fig. 4. Selectivity for total $i$-$C_6$ on converted $n$-$C_6$.

The results concerning $n$-hexane isomerization are summarized in Figs. 3 and 4. HY is of no interest for this reaction. The selectivity for methylpentane is close to 100% at 300 °C but the activity is negligible. This increases with T but to the detriment of the selectivity, which is 80% at 350 °C for an activity of 20%. The activity of the other catalysts is more interesting: Pt/HY and PtAu/HY have the same activity and selectivity. However, this latter is only high for $T$ close to 250–275 °C, at which temperature the degree of conversion is low. When the latter is 80% at 350 °C, the selectivity is only 38%. HZSM5 and PtAu/HZSM5 have the same activity for each temperature, relatively high as of 250 °C (40%), but the selectivity of PtAu/HZSM5 is far higher. The efficiency of this catalyst is noteworthy; it is remarkably stable over 1 week with a selectivity and an activity for methylpentane of about 75% at 275 °C. At 250 °C the selectivity is better than 90% for an activity of 32%. Cracking is relatively low; some other reaction products are $i$-$C_5$ and $i$-$C_4$ (Table 1).

## 4. Conclusion

Given the difficulty of developing solid superacid catalysts which are active in the isomerization of $n$-alkanes, but which are not rapidly poisoned, other possibilities must be explored. Many tests remain to be performed with other $n$-alkane molecules, but the first results obtained with hexane show that PtAu/HZSM5 seems to be an interesting catalyst for the isomerization of $n$-alkanes on solids.

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