

Acid or bifunctional mechanism in paraffin isomerization reaction on Pt/SO₄²⁻-ZrO₂ and Pt/WO₃-ZrO₂ catalysts

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At low temperature (300°C) the isomerization of n-C₄H₁₀ on Pt/SZ occurs only by a monofunctional acid mechanism. It is necessary to increase the temperature to produce the amount of olefins required for the bifunctional mechanism because of thermodynamic limitations and the decrease of metallic function activity of Pt due to support interactions. Pt is less affected on Pt/WZ, presenting high hydrogenolysis activity.

The isomerization of n-C₇H₁₆ can proceed at low temperatures by a bifunctional mechanism because due to the easy dehydrogenation to n-C₇H₁₄ a very small fraction of metallic function is enough.

INTRODUCTION

Light paraffin isomerization is a very important reaction for reformulated gasolines. Classical catalysts are Pt supported on chlorided alumina and zeolitic catalysts. Few years ago the system oxoanion-promoted zirconia, mainly sulfate (SZ) and tungstate (WZ) was proposed as an alternative (1,2) and it was reported that this type of catalysts are used commercially (3-5). When the reaction is carried out in the presence of hydrogen, the addition of a metallic phase to an acid solid will theoretically enable: a) the reaction to take place via a bifunctional mechanism, with less stringent acid strength requirements, and b) activated hydrogen production over the metal, which inhibits the formation of coke precursors. The isomerizing activity for n-C₅ and n-C₆ of SZ is greatly increased by the addition of Pt (6,7). On the contrary, when the reactant is n-C₄, the effect of Pt on Pt/SZ does not produce an increase in the activity of SZ (8).

The objective of this paper is to study when it is possible to obtain a bifunctional mechanism in n-C₄ and n-C₇ isomerization reactions using Pt/WZ and Pt/SZ as catalysts.

EXPERIMENTAL

Zr(OH)₄ was prepared according to the usual technique and was promoted with sulfate (H₂SO₄2N) or tungsten (ammonium metatungstate) and calcined at 620°C or 800°C, respectively. Platinum was introduced by the incipient wetness method. The catalytic tests were carried out using a fixed bed quartz reactor under isothermal conditions at 1 atm and on-line chromatographic analysis.

RESULTS AND DISCUSSIONS

Table 1 shows total n-C₄ conversion and selectivities for WZ and SZ catalysts with and without Pt. The addition of Pt to SZ does not substantially modify the conversion level, being the selectivity slightly improved. The catalyst without Pt gradually loses its activity, while the Pt-loaded catalyst maintains it along the run. The effect of Pt addition is more pronounced for WZ, being observed a 70% increase in initial conversion, but a decrease in selectivity. The yield of i-C₄ (the product of conversion times selectivity to i-C₄) shows the superiority of Pt/SZ.

Table 1

n-Butane total conversion and selectivity to products of samples for two times on stream. Reaction temperature=300°C, H₂/n-C₄=6, WHSV=1.0

Catalyst	Time (min)	Conv. (%)	Selectivity (%)			Yield to i-C ₄
			C ₁ -C ₃	i-C ₄	C ₅	
SZ	5	29.3	15.7	75.8	8.5	22.2
	60	22.4	11.2	80.3	8.5	20.0
1% Pt	5	31.0	12.9	84.5	2.6	26.2
SZ	60	30.9	11.3	85.7	3.0	26.5
WZ	5	8.4	6.0	88.0	6.0	7.4
	60	3.4	8.8	85.0	6.2	2.9
1%Pt	5	14.1	48.3	51.0	0.7	7.2
WZ	60	10.1	33.7	65.3	1.0	6.6

Figure 1 show values of total n-C₄ conversion and selectivity to i-C₄ at 350°C as a function of time on stream for WZ and SZ catalysts respectively. For both catalyst types a considerable increase in both activity and selectivity is observed as a consequence of Pt addition. This increase is more pronounced for WZ catalysts, being observed a nearly threefold increase in activity and an increase of selectivity from 75% to 95%. In the case of SZ catalyst the conversion increase due to Pt addition is not so important, but yet significant, being also observed an important improvement in selectivity from 75% (SZ) to 95% (1%Pt/SZ). It must be pointed out that the higher temperature level in this runs produces an activity loss for 1%Pt/SZ which was not observed at 300°C.

The conversion increase due to higher temperature levels is expected, but it should not occur the same for selectivity if the operating mechanism is and acid monofunctional one. It was observed on the contrary that the selectivity to i-C₄ is practically doubled for 1%Pt/WZ due to the 50°C increase in temperature level. On the other hand, there is only a little increase in selectivity for 1%Pt/SZ catalyst. Current knowledge about acidic catalysis indicates that higher temperature levels favor disproportionation and cracking reactions which usually have higher activation energies than isomerization reactions, and this would be reflected negatively on the i-C₄ selectivities. This behavior was in fact observed when comparing the values of i-C₄ selectivities in Table 1 (at 300°C) with those shown in Fig. 1 (at 350°C) for WZ and SZ catalysts (without Pt), where a decrease in selectivity at higher temperatures is evident. It can be concluded that both for WZ and SZ catalysts the presence of Pt modifies the selectivity

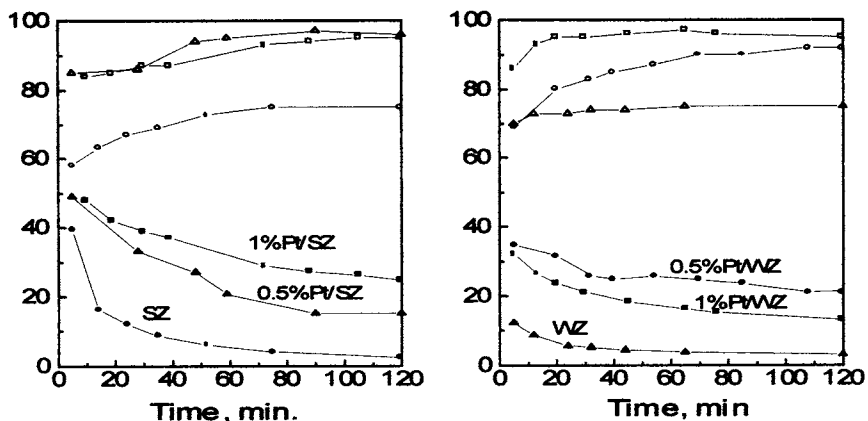


Figure 1: Conversion of $n\text{-C}_4$ and selectivity to $i\text{-C}_4$ as a function of time on stream. Solid symbols correspond to conversion values and hollow symbols correspond to selectivity values

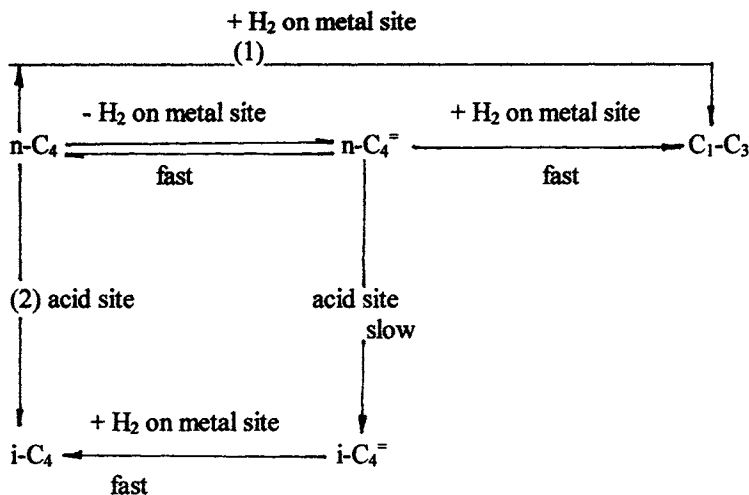
favoring $n\text{-C}_4$ to $i\text{-C}_4$ isomerization. In this case it seems that a combined metal/acid mechanism is operating, where the metallic phase could act as initiator of isomerization reaction.

A classic bifunctional isomerization mechanism (9) as shown in Scheme (1) has a first $n\text{-C}_4$ dehydrogenation step on the metallic function. This dehydrogenation step is fast and sustains an alkene concentration corresponding to thermodynamic equilibrium despite its consumption on the acid sites. The n -alkene is isomerized on acid sites and the i -alkenes are finally hydrogenated leading to the corresponding isoalkane. This mechanism proceeds in presence of hydrogen, and because of the thermodynamic limitation in the first step and the rapidity of the third one, alkenes are practically not detectable. If there is a considerable amount of metallic function in the catalysts, $\text{C}_1\text{-C}_3$ are produced by hydrogenolysis. So, both Pt and H_2 must be present only in the amount necessary for the bifunctional mechanism to proceed and to hydrogenate coke precursors which cause catalyst deactivation and not in an excess that would favor hydrogenolysis.

The existence of a combined metal/acid mechanism depends on the presence of sufficient amounts of C_4 olefins. The formation of such olefins is seriously restricted due to thermodynamic limitations. As opposed to hydrogenation, dehydrogenation is favored at high temperatures and low pressures, being C_4 alkene only measurable over 300°C and below 1 atm.

It can be observed that an increase of 50°C in reaction temperature, from 300°C to 350°C , leads to a tenfold increase in the value of the equilibrium constant ($K_{300^\circ\text{C}}=1.56 \times 10^{-5}$ and $K_{350^\circ\text{C}}=1.31 \times 10^{-4}$) so favoring the possibility of the bifunctional mechanism to occur due to the presence of higher concentration of olefins.

Hydrogen chemisorption results and conversions for cyclohexane dehydrogenation are shown in Table 2. It can be observed that SZ catalysts with Pt does not chemisorb hydrogen and have not activity for cyclohexane dehydrogenation. On the other hand, Pt-added WZ samples chemisorb hydrogen and dehydrogenate cyclohexane.



Scheme 1

Table 2

Hydrogen chemisorption at room temperature and Cyclohexane conversion values at 270°C, WHSV=10 and molar ratio H₂/CH=30.

Catalysts	Hydrogen Chemisorption (ml/g)	Cyclohexane Conversion (%)
SZ	0	0
0.5%Pt/SZ	0	0
1.0%Pt/SZ	0	0
WZ	0	0
0.5%Pt/WZ	0.027	5.0
1.0%Pt/WZ	0.380	8.1

Taking into account this results and those found for n-C₄ isomerization it may be concluded that at 300°C olefins are not produced enough to make possible a combined reaction mechanism. Only the hydrogenolysis of n-C₄ to C₁-C₃ on the metallic function (Scheme 1, path 1) or its isomerization on the acid sites (Scheme 1, path 2) could be possible. The hydrogenolysis is possible only if Pt retain, at least partially, its metallic properties, as in the case of Pt-WZ. For Pt/SZ catalysts, the deposited Pt does not exhibit metallic properties, losing therefore its hydrogenolytic capacity. In this case it could only occur the monofunctional acid isomerization (path 2).

The *n*-heptane, *n*-C₇, reaction on the same catalysts was studied at 250°C and 300°C. Figure 2-A shows the *n*-C₇ conversion as a function of Pt content. At both temperatures a small addition of Pt produces a great increase in the activity of SZ and WZ and the activity.

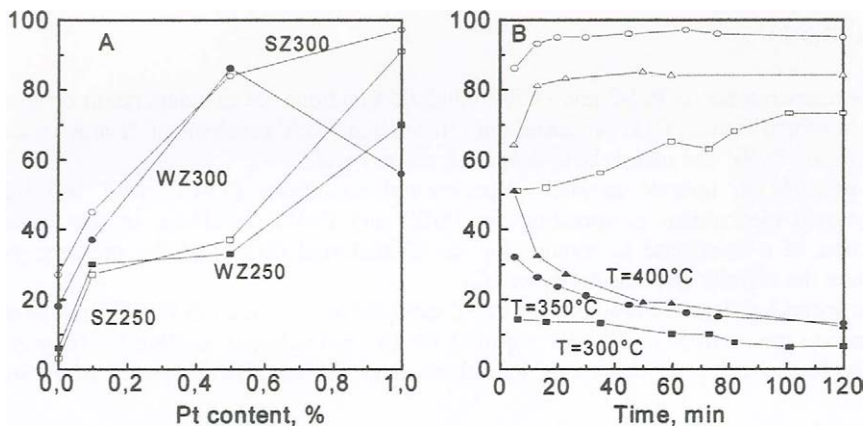


Figure 2:

A: Conversi3n of *n*-C₇ as a function of Pt content.

B: Conversion of *n*-C₄ and selectivity to *i*-C₄ as a function of time-on stream. Hollow symbols correspond to conversion values and empty symbols correspond to selectivity.

increases with the increase in Pt content. Without H₂ there is not the beneficial effect of Pt on catalytic activity. These results indicate that in these conditions is operating the bifunctional mechanism. This is possible because of the high dehydrogenation equilibrium constant of *n*-C₇, which allow a convenient formation of *n*-C₇ alkene. Historically the experiments on bifunctional mechanism were performed at high temperature (500°C, naphtha reforming) and as reactants C₆-C₈ alkane where thermodynamic equilibrium of dehydrogenation allows enough alkenes as to sustain the bifunctional mechanism of reaction. Equilibrium conversion values at a fixed temperature increase with the hydrocarbon chain length (10). This fact may explain the apparently contradictory results on the effect of Pt.

In order to verify the proposed reaction scheme an additional isomerization run was done using the catalyst 1%Pt/WZ at 400°C. A similar experience with Pt/SZ catalyst was not done due to SO₄²⁻ reduction at high temperature (11). In Fig. 2-B values are shown for *n*-C₄ conversion and selectivity to *i*-C₄ as a function of time on stream for the three temperatures tested. At 400°C it can be observed both a higher conversion level and deactivation rate as compared to the results obtained at lower reaction temperature. This behavior is due to the higher amount of olefins produced which are converted to coke.

It can be observed that *i*-C₄ selectivities are higher at 350°C than those obtained at 300°C or 400°C. This can be explained according to the proposed bifunctional reaction mechanism (Scheme 1). At 300°C olefins are not produced enough so the paths 1 and 2 are favored and the corresponding active sites act independently. At 350°C, the rate of olefin formation on the metallic sites is higher and such olefins are slowly isomerized on the acid sites following the bifunctional mechanism. At 400°C, the olefins produced in excess will then be cracked on metallic sites to C₁-C₃ hydrocarbons producing a decrease in *i*-C₄

selectivity. In other words it can be stated that at 350°C there exists an optimum balance between acid and metallic functions for 1%Pt/WZ

CONCLUSIONS

- At low temperatures on Pt/SZ and Pt/WZ catalytic functions act as independent centers for n-C₄ transformations, i-C₄ is produced only through an acid mechanism. It only produces stabilization on Pt/SZ and mainly dehydrogenolysis on Pt/WZ.
- It is possible to operate in such experimental conditions (350°C with H₂) that a bifunctional mechanism is operating for Pt/SZ and Pt/WZ catalysts. In this case the formation of n-C₄ alkene is enough for the bifunctional route and the presence of Pt improves the activity and selectivity to i-C₄.
- Higher metal loadings are required for Pt/SZ catalysts as compared to Pt/WZ ones in order to generate the amount of alkenes required for the bifunctional mechanism to proceed. This is due to a higher degree of modification in the metallic character of Pt in SZ catalyst.
- Longer chain paraffins, as n-C₇, are more easily dehydrogenated and allow the bifunctional mechanism already at 250°C.
- A perfect balance between acid and metal functions is required, if enough alkenes are not formed on the metallic function (because of insufficient metal load, thermodynamic limitation or deactivated metallic function), the global rate is adversely affected. On the contrary, if there exists an excess of metallic phase, alkenes are generated in excess and can be cracked and polymerized to coke which is responsible for catalyst deactivation.

REFERENCES

1. K. Arata, *Adv. Catal.* 37 (1990) 165.
2. E. Iglesia, D.G. Barton, S.L. Soled, S. Miseo, J.E. Baumgartner and W.E. Gates, *Proc. 14th North Amer. Meet. Catal. Soc.*, 1995.
3. U.S. Patent N° 5763713 (1998).
4. C. Gosling, R. Rosin and P. Bullen, *Petrol. Technol.-Quarterly*, Winter 1997/98, p. 55.
5. *Chemical Engineering*, March 1999, p. 19.
6. T. Hosoi, T. Shimidzu, S. Itoh, S. Baba, H. Takaoka, T. Imai and N. Yokoyama, in "Proceedings, American Chemical Society, Los Angeles, 1988", p. 562.
7. K. Ebitani, J. Konishi, A. Horie, H. Hattori and K. Tanabe, in "Acid-Base Catalysis" (K. Tanabe, H. Hattori, T. Yamaguchi and T. Tanaka, eds.), Kodansha, Tokyo, 1989, p. 491.
8. J.C. Yori, M.A. D'Amato, G. Costa and J.M. Parera, *J. Catal.* 153 (1995) 218.
9. P.B. Weisz and E.W. Swegler, *Science*, 126 (1957) 31.
10. G.E. Germain, *Catalytic Conversion of Hydrocarbons*, Academic Press, New York, 1969, Chap. 3.