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HIGHLY ORGANIZED CATALYTIC SYSTEMS

Mechanical Mixtures of Me (Ni, Pd) Ce Oxides and Silica-Supported Heteropolyacids: Role and Optimal Concentration of Each Active Species in *n*-Hexane Isomerization¶

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Abstract—Catalytic properties of silica-supported heteropolyacids (HPA) in a mechanical mixture with reduced Me–Ce oxides (Me = Ni, Pd) in *n*-hexane isomerization are studied. The role of each component of the mixed oxides (Ce and, typically, Ni and Pd) and their optimum content has been illuminated: cerium is not only beneficial for eliminating or preventing coke deposition but is also effective for maintaining the Keggin structure of the highly-organized HPA during the reaction and probably allows a better dispersion of the second metal species. Nickel and palladium, present as Ni^0 and Pd^0, reinforce the activation of the alkane, which is difficult to obtain by means of a direct attack by an acid, and, thus, enhance noticeably the activity of the catalyst. The best mechanical mixtures are obtained with 30–70 wt % NiCeO–HPW/SiO_2 and 50–50 wt % $Pd_{0.1}$CeO–HPW/SiO_2. These mixtures have the highest efficiency for a Ni/(Ni + W) atomic ratio of 0.66 and a Pd/(Pd + W) ratio of 0.40, respectively. Finally, the conversion of *n*-hexane is in the order HPW > HSiW > HBW, which seems to be consistent with the order of their acid strength as per the literature, but the isomerization selectivity appears to be slightly higher on HSiW.

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INTRODUCTION

It is well known that the isomerization of light *n*-alkanes, which leads to branched alkanes, is easier on a bifunctional catalyst [1] with the help of a synergetic effect. Indeed, such a catalyst has a hydrogenating/dehydrogenating function as well as one other—an acidic function. These two functions work simultaneously, as it is claimed that alkanes are dehydrogenated on metallic sites to the corresponding alkenes, which are isomerized by acidic sites into branched alkenes; the latter are then hydrogenated into the branched alkanes again on the metallic sites. The mechanism can be different in the mechanical mixtures that are sometimes called hybrid catalysts. For example, Zhang *et al.* [2] propose, in a physical mixture of Pt/SiO_2 and HZSM-5 powder, a mechanism based on a spillover phenomenon, the hydrogen gas being dissociated on the noble metal before it spills over onto the zeolite. Evidence was later provided for the spillover phenomenon by infra-red spectroscopy [3]. Spillover of the reactive species between metal-promoted oxide systems and acid sites has also been proposed by Vasina *et al.* [4]. Generally, the metallic species most often used is platinum. Concerning the solid acids, many catalysts, in addition to chlorinated alumina, have been tested (e.g., zeolites [5], sulfated zirconia [6], tungsten/molybdenum oxides [7], and heteropolyacids [8]). In some cases, a third component has been added to improve the role of the metallic species [9–12]. Due to their strong acidity and its amenability to “molecular tuning” (through their salts), the heteropolyanions (HPA), which are highly organized systems, are very good candidates for the cocatalyzation of *n*-alkane isomerization. Unfortunately, the Keggin structure can easily be destroyed when HPA are not protected. Ono appears to have been the first to incorporate palladium as metallic species to prevent such destruction [1]; on the other hand, we previously showed that cerium is capable of preventing the poisoning that occurs during some hydrogen treatments [13]. Moreover, very few works have addressed the role and influence of the content of each component in a mixture of metallic oxide and HPA. Thus, this work describes the results obtained for various mixed oxides and different HPA in a mechanical mixture and focuses on the specific role of each component for the *n*-hexane isomerization.

¶ The text was submitted by the authors in English.

EXPERIMENTAL

Heterophosphotungstic (HPW), heterosilicotungstic (HSiW), and heteroborotungstic (HBW) acids were prepared in the classical manner [14]. Silica-supported heteropolyacids were prepared by the wet impregnation method. Ce–Ni oxides were prepared by the reverse homogeneous coprecipitation method as described in the literature [15]. Cerium nitrate $Ce(NO_3)_2 \cdot 6H_2O$ (Prolabo Co.) solution (0.5 mol l^{-1}) and nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (Prolabo Co.) solution (0.5 mol l^{-1}) were prepared separately and then mixed. The mixed solutions were added dropwise to an excess of potassium hydroxide KOH (Prolabo Co.) solution (0.5 mol l^{-1}) under strong stirring. After filtration, the precipitates formed were washed with hot water (335 K) to eliminate K^+ until the pH value of the washing solution decreased from approximately 11 to 7. The compounds were dried in an oven at 373 K for 12 h and ground and calcined in air for 4 h at 673 K with a heating rate of 2 K min^{-1}. The Ce–Pd oxides were prepared in the same manner from $Pd(NO_3)_2 \cdot 6H_2O$ (Prolabo Co.) solution (0.5 mol l^{-1}). The samples placed into a flow reactor (U-type glass) were first reduced, at 498 and 553 K for Ni–Ce–O and Pd–Ce–O, respectively, for 4 h in hydrogen with a flowing rate of 21.8 ml min^{-1} under atmospheric pressure, and then their catalytic properties were evaluated under the same conditions, but hydrogen was saturated with *n*-hexane (WWH = 0.36 h^{-1}). The products were analyzed by gas chromatography [16].

RESULTS AND DISCUSSION

Owing to their very low surface area, pure heteropolyacids have a very poor activity. Thus, supported HPA, more specifically, on silica, are used [17]. The conversion increases remarkably with the HPA loading, though it remains low (Table 1). Unfortunately, the isomerization simultaneously undergoes a selective decrease; the yield of C_6 isomers, however, and the ratio of the dimethyl butanes (DMB) with respect to the total amount of branched alkanes (dimethyl butanes -DMB- plus methyl pentanes -MP-) increase by a small margin.

The main drawback of the silica-supported HPA alone is the rapid poisoning of the solid over time. For example, after 22 min of reaction time, the conversion is already divided by a factor of 4 (Table 2).

Table 1. Isomerization of *n*-hexane over *x* wt % HPW/SiO_2 after 5 min on stream at 498 K

x, wt %	Conversion, %	Isomerization, %	$\frac{DMB}{DMB + MP'}$, %	C_6 isomers yield, %
10	3.7	78.0	15.9	2.9
20	5.6	76.7	15.6	4.3
30	16.6	68.0	17.0	11.3
40	17.3	63.3	18.0	11.0
50	28.0	55.9	9.0	15.6

Table 2. Isomerization of *n*-hexane over 40 wt % HPW/SiO_2 on stream at 498 K

Time, min	Conversion, %	Isomerization, %	$\frac{DMB}{DMB + MP'}$, %	C_6 isomers yield, %
5	17.3	63.3	18.0	11.0
22	4.4	78.2	16.0	3.5
57	2.6	78.9	14.0	2.0

This deactivation on HPA and their salts was previously observed by Guisnet *et al.* [18], who assumed it to be related to coke formation; however, these authors worked in the absence of hydrogen, which is known to preserve a small amount of this formation. Nevertheless, the presence of hydrogen alone is clearly not sufficient to avoid poisoning in our case. One alternative to correct these drawbacks is to add a cocatalyst that is capable of avoiding the poisoning while protecting the highly organized catalytic system (viz.: HPA). On the other hand, it is well known that the isomerization reaction is easier in the presence of a bifunctional catalyst [1] with one acidic function and one hydrogenating/dehydrogenating function: if HPA, which exhibit a strong acidity, are good candidates for the former function, a metallic species must be an excellent candidate for the second one. It has also been proven that the presence of cerium is favorable for the prevention of sulfur poisoning in the course of hydro treating reactions [13]. Ono and coworkers appear to have been the first to incorporate palladium as a cation for the isomerization of *n*-alkanes [19], and it was previously reported that the reduced Ce–Ni mixed oxides could be used as promoters for the hydrogenation reactions [20]. Thus, we undertook the study of each component of a complex mixture in order to gain an understanding as to the specific role of each active species, as well as the value of their optimal content. Table 3 displays the results obtained with mechanical mixtures of HPA/SiO_2 and Ni_xCe oxide or Pd_yCe oxide, where *x* and *y* are the atomic ratio Me/Ce. No deactivation was observed, even after 4 h on stream. As expected, the presence of cerium alone does not play an important role for the activity but does prevent the poisoning of the HPA as, in absence of Ce, the activity decreases on time. Thus, the cerium probably acts as an electronic promoter due to the Ce^{4+}/Ce^{3+} redox system, which improves the rate of reducibility of the nickel and palladium ions during the reaction. We must recall that, when the metallic species used is platinum, we no longer observe poisoning, even in the absence of cerium [8]. Liu *et al.* [21] observed the same absence of deactivation on a

Table 3. Effect of the ratio Me/Ce on the catalytic properties of the mechanical mixtures of Me–Ce–O and HPW/SiO_2

Me/Ce, mol/mol	Conversion, %	Isomerization, %	$\frac{DMB}{DMB + MP}$, %	C_6 isomers yield, %
Ni/Ce ratio*				
1	27.7	91.2	17.9	25.3
2	26.2	96.0	15.1	25.1
Pd/Ce ratio**				
0	13.3***	93.2	14.0	12.4
0.05	26.4	99.2	9.5	26.2
0.10	56.2	98.2	14.4	55.2
0.15	49.8	98.6	11.1	49.1
0.20	39.0	98.9	8.9	36.6

* Mixture of 20% Ni_xCeO–80% (50 wt % HPW/SiO_2).

** Mixture of 50% Pd_yCeO–50% (20 wt % HPW/SiO_2).

*** Conversion after a few minutes.

Table 4. (a) Effect of the wt % of Ni–Ce–O mixed oxide on the catalytic properties of the mechanical mixture of Ni–Ce–O and (20 wt % HPW/SiO_2). (b) Effect of the wt % of Pd–CeO mixed oxide on the catalytic properties of the mechanical mixture of Pd–Ce–O and (20 wt % HPW/SiO_2)

MeCeO, wt %	Conversion, %	Isomerization, %	$\frac{DMB}{DMB + MP}$, %	C_6 isomers yield, %
NiCeO wt %				
10	14.5	86.6	17.0	12.6
20	19.1	87.3	15.0	16.7
30	21.8	80.4	11.0	17.5
40	20.5	76.5	11.0	15.7
50	16.9	50.4	9.0	8.5
60	14.0	41.6	4.0	5.8
$Pd_{0.1}$CeO wt %				
25	20.8	98.9	6.8	20.6
40	47.8	98.5	13.3	47.1
50	56.2	98.2	14.4	55.2
60	48.7	98.5	13.5	48.0
75	5.7	93.7	4.3	5.3

Note: DMB—dimethyl butanes, MP—methyl pentanes.

mechanical mixture of Pt/SiO_2—HPW cesium salt or sulfated zirconia or zeolite β as soon as the hydrogen pressure reached 0.2 atm. Concerning the ratio Ni/Ce, it is surprising to note that doubling this ratio (Table 3) appears to have little influence on the level of conversion; but we observe an effect on the amount of DMB obtained, and the value of 1 for the Ni/Ce atomic ratio appears to be the right value. The activity is more sensible to the ratio Pd/Ce, since it can be doubled by varying this ratio, and the best ratio seems to be 0.1. The XRD patterns of fresh and reduced solids are very interesting. For fresh Ni–Ce oxides, we observe the XRD patterns of both NiO and CeO_2 compounds, but the sample reduced at 498 K shows new peaks that can be assigned to Ni^0; at the same time, the peaks of the NiO crystal disappear, suggesting that most of the nickel oxide has been reduced in metallic species [12]. An identical result is observed with the mixed Pd–Ce oxide, namely, the simultaneous presence of PdO and CeO_2 on the fresh oxide and of Pd^0 after reduction at 553 K [11]. Thus, Ni^0 and Pd^0 species are the active hydrogenating species for the *n*-hexane isomerization, and the lower efficiency of nickel for such a reaction, partly due to the lower reaction temperature, can probably also be explained by the different behavior of the Me/Ce ratio. Thus, the ratios of 1 and 0.1 for Ni/Ce and Pd/Ce, respectively, were chosen to pursue these studies.

The respective amounts of the mixed oxide and of HPA also influence the activity of the *n*-hexane reaction. For mechanical mixtures with the nickel-based oxide, the optimal amount of NiCe is 30% (Table 4), which does not correspond exactly to the higher value of DMB obtained; for the mixture with the Pd-based oxide, the best mixture is constituted of 50% $Pd_{0.1}$CeO (Table 4), which corresponds to the larger DMB percentage.

Figure 1 displays the *n*-hexane conversion versus the Ni/(Ni + W) (Fig. 1a) and Pd/(Pd + W) (Fig. 1b) atomic ratio. This ratio is in reality representative of the relative amounts of metallic sites/acidic sites, and consequently of the magnitude of the synergy phenomenon.

For NiCeO–HPW mechanical mixtures, the higher conversion is reached for about 66% of moles of Ni with respect to the total (Ni + W), i.e., 2 moles of Ni per mole of W. For the $Pd_{0.1}$CeO–HPW mechanical mixtures, the best conversion is obtained with 40% of moles of Pd with respect to the total (Pd + W), i.e., 0.66 moles of Pd per mole of W. Moreover, these values can be linked to the number of easily accessible metal centers to or from the acid sites in terms of proximity; they are, in addition, comparable with those previously obtained by Alvarez *et al.* on PtHY catalysts [22] and confirm the superior hydrogenating nature of Pd. At this point, it seems interesting to study the influence of the central atom in the well-organized heteropolyacids. Table 5 shows the results obtained with HPW, HSiW, and HBW, respectively, for the two kinds of mechanical mixtures.

Though the results for the borotungstic acid are certainly far less interesting (we did not attempt it over $Pd_{0.1}$CeO), the conversion proceeds in the order

$$HPW > HSiW > HBW,$$

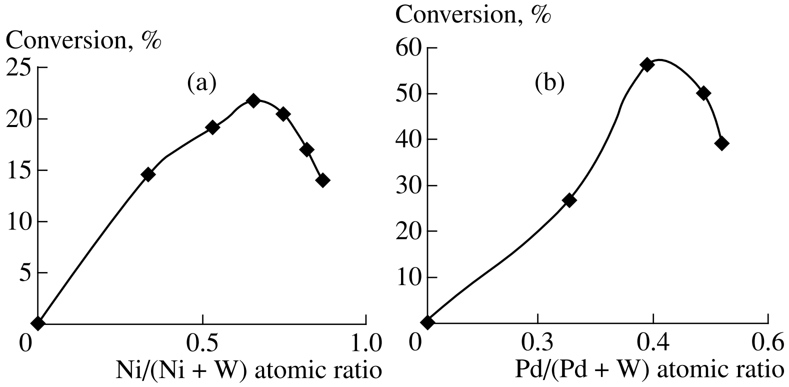

Fig. 1. *n*-Hexane isomerization conversion versus the tungsten content in the mechanical mixtures of MeCeO–HPW/SiO_2. (a) NiCeO–20 wt % HPW/SiO_2; (b) $Pd_{0.1}$CeO–20 wt % HPW.

which is consistent with the order of their acid strength as per the literature [23]. However, this is not entirely true for the isomerization selectivity, which is slightly better on HSiW, probably because $SiW_{12}O_{40}^{4-}$ is a softer base than the $PW_{12}O_{40}^{3-}$ complexing organic cation for the purpose of forming a stable intermediate.

In summary, we can now specify the role of each metallic species present in the catalyst. The cerium component has mainly a protective function, guarding against poisoning by others elements. This protection probably has its origins in the Ce^{4+}/Ce^{3+} Red-Ox system, which reinforces the protection of species as nickel, as proposed by Sauvion *et al.* [24]. Under our reaction conditions, the main reaction products are methyl pentanes (MP) and dimethyl butanes (DMB). Guisnet *et al.* [18] assume that, on pure HPA cesium salt, 2,3-DMB and MP are primary products formed by an intramolecular isomerization of a classical carbenium ion coming from a monomolecular mechanism. In the presence of a metallic species, the classical bifunctional mechanism is well acknowledged and explained in [21], justifying the necessary close proximity of the metal centers and of the acid sites for allowing the spillover of either the hydrogen species or one of the intermediates. In this latter case, nickel and palladium, both in the metallic state, constitute the hydrogenating/dehydrogenating function, providing an important synergetic effect to HPA for the global transformation. The only requirement for this kind of synergy is a sufficient amount of the Me^0 species and a good dispersion of the various active species on the support. For the former condition, the amounts of 2 Ni^0 atoms and 0.66 Pd^0 atoms, respectively, per tungsten atom appear to be optimal for the two different mixed oxides (i.e., NiCeO and $Pd_{0.1}$CeO), and for the second condition, we can reasonably assume that the 30–70 and 50–50 mixtures are homogeneous. Moreover, the attempts that have been made with co-impregnated Pd_xCeO–HPA/SiO_2 have given rise to the same range of order of conversion [25]. The last result is for the type of central atom of the HPA; we observe a higher activity with HPW than with HSiW or HBW. This is simply related to the acidic strength.

CONCLUSIONS

Mechanical mixtures of mixed Me–Ce oxides (Me = Ni, Pd) and silica-supported heteropolyacids

Table 5. Effect of the central atom in heteropolyacid for mechanical mixtures

	HPW		HSiW		HBW	
	NiCeO[a]	$Pd_{0.1}$CeO[b]	NiCeO[a]	$Pd_{0.1}$CeO[b]	NiCeO[a]	$Pd_{0.1}$CeO[b]
Conversion, %	27.7	56.2	23.3	47	2.1	–
Isomerization, %	91.2	98.2	94.2	99.3	67	–
$\frac{\text{DMB}}{\text{DMB + MP}}$, %	17.9	14.4	13.1	11.6	8	–
C_6 isomers yield, %	25.3	55.2	22	46.7	1.4	–

Note: [a] Mixture of 20% NiCeO–80% (50 wt % HPA/SiO_2).
[b] Mixture of 50% $Pd_{0.1}$CeO–50% (20 wt % HPA/SiO_2).

(HPA = HPW, HSiW, HBW) have a beneficial effect on the *n*-hexane isomerization to branched alkanes. The primary beneficial effect, in terms of synergism on the activity, can be explained by the more or less close proximity of the two important functions (i.e., hydrogenating/dehydrogenating function on the metallic species coming from the reduced mixed oxides and the acidic properties of the silica-supported heteropolyacid). The secondary beneficial effect is also important, particularly for the Ni-based system: firstly, the Keggin structure, which is a highly organized structure, is maintained; second, the susceptibility to coke deposition, and consequently to the decrease of activity by poisoning, is totally inhibited. Thus, a study on the best of the different types metallic species and their optimal content, taken in its entirety, has shown that the best mixture is the following: 50 wt % of $Pd_{0.1}CeO$ oxide and 50 wt % of (20 wt % HPW/SiO_2).

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