n-Alkane isomerization on heteropolyacids 1. The influence of acid-base properties of alumina systems on the state of supported 12-tungstophosphoric heteropolyacid in Pt-containing catalysts and their activity in *n*-pentane isomerization

A. V. Ivanov,^a* T. V. Vasina,^a O. V. Masloboishchikova,^a E. G. Khelkovskaya-Sergeeva,^a L. M. Kustov,^a and J. I. Houzvička^b

^aN. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: aivanov@ioc.ac.ru ^bHaldor Topsoe A/S, DK-2800, Lyngby, Denmark

Acid-base properties of bulk 12-tungstophosphoric heteropolyacid (HPWA) and HPWA supported on alumina and fluorinated alumina were studied by DRIFT spectroscopy using adsorption of probe molecules. Catalytic properties of Pt-containing catalysts carried by these supports were studied in *n*-pentane isomerization. It was shown that the Pt/HPWA/Al₂O₃ system is almost inactive in isomerization as a result of the interaction of HPWA with basic sites of the alumina support. On the contrary, the presence of acidic sites in fluorinated alumina prevents HPWA destruction and favors the uniform distribution of HPWA on the support surface. As a result, enhancement of the activity and selectivity of the Pt/HPWA/Al₂O₃-F catalyst in *n*-pentane isomerization is observed.

Key words: heteropolyacids, 12-tungstophosphoric heteropolyacid, isomerization, *n*-pentane, platinum, adsorption, acidity, probe molecules, basicity, IR spectroscopy, DRIFT spectroscopy.

Among the variety of catalysts of the isomerization of light *n*-alkanes $C_4 - C_6$,¹⁻⁶ heteropolyacidic systems represent a promising class. Bulky heteropolyacids (HPA) and their salts contain strong acidic sites capable of catalyzing reactions of the carbocationic type,⁷⁻¹⁰ The use of supported HPA increases the specific surface area of the catalysts and modifies their acidic and catalytic properties. The immobilization of HPA on the basic supports is accompanied by a partial decomposition of the heteropolyanions^{7.8} or the formation of salts due to interaction with the OH groups of the support, resulting in a decrease in the concentration of HPA with the support is of importance in understanding the properties of supported HPA-based catalysts.

The purpose of this work is to study the catalytic properties of systems based on 12-tungstophosphoric heteropolyacid $H_3PW_{12}O_{40}$ (HPWA) in *n*-pentane isomerization as a function of the acidic properties of the alumina support.

Experimental

Preparation of catalysts. The catalysts were prepared from $H_3PW_{12}O_{40} \cdot xH_2O$ (Acros Chemical). The HPA sample was dried *in vacuo* for 4 h at 50 °C until the composition $H_3PW_{12}O_{40} \cdot 6H_2O$ was achieved and then used for the preparation of solutions.

The supported catalysts (HPWA/Al₂O₃ and HPWA/Al₂O₃·F) were prepared by the stepwise impregnation of γ -Al₂O₃ (A-64) (available from the Ryazan Plant, specific surface area

 $S_{sp} = 180 \text{ m}^2 \text{ g}^{-1}$) and y-Al₂O₃-F (3.5% F, industrial support for the preparation of the IP-25 catalyst) with a 7 mM aqueous solution of H₃PW₁₂O₄₀. The content of H₃PW₁₂O₄₀ in the eatalyst was 20 wt.%. Platinum was precipitated from an aqueous solution of H₂PtCl₆. The concentration of platinum in all samples was 0.5 wt.%. The catalysts were dried for 3 h at 120 °C and calcined in an air flow for 2 h at 350 °C.

For comparison, we prepared the bulky system 0.5% Pt/HPWA and the catalysts 0.5% Pt/Al₂O₃ and 0.5% Pt/Al₂O₃-F containing no HPA.

IR spectroscopy. Before measurements, the samples were placed in a quartz reactor with a CaF₂ window and activated for 2 h at 300-400 °C *in vacuo*. The spectra were recorded on a Nicolet Protégé 460 FTIR spectrometer using a diffuse-reflection attachment with a resolution of 8 cm⁻¹ at 20 °C. C_6D_6 , C_2D_4 , CO, and CD₃CN were used as probe molecules for the study of Brönsted and Lewis acidic sites (BAS and LAS). C_2H_2 was used as a probe molecule on basic sites. The substances were adsorbed from the gas and vapor phase at 20 °C and 10-30 Torr.

Study of catalytic properties. *n*-Pentane was isomerized in a flow-type installation under atmospheric pressure, at 170-440 °C, flow rate of *n*-pentane of 1 h⁻¹, and H₂: *n*-C₅H₁₂ molar ratio of 3 : 1. The load of the catalyst was 3 cm³. The reaction products were analyzed by GLC on a column packed with phenylmethylsiloxane on Celite C-22.

Results and Discussion

Isomerization of n-pentane

The results of studying the behavior of the catalysts in *n*-pentane isomerization are presented in Fig. 1 and Table 1. The Pt/Al_2O_3 system containing no HPA is

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almost inactive in this reaction (see Fig. 1, *a*). The yield of isopentane does not exceed 8% at a selectivity of ~20%. On Pt/Al₂O₃ *n*-pentane is transformed mainly into the cracking products C_1-C_3 . The yield of isopentane on Pt/Al₂O₃-F at 400 °C reaches 45% with a selectivity to isopentane of ~75%. The by-products formed in the transformation of pentane on Pt/Al₂O₃-F are represented by light hydrocarbons C_1-C_3 and disproportionation products, paraffins C_4 and C_6 and the products of their secondary transformations (isoparaffins C_4 and C_6). The data presented in Table 1 show that the Pt/Al₂O₃-F system exhibits a low selectivity to isopentane. In addition, the maximum yield of isopentane is achieved at a relatively high temperature, which is thermodynamically unfavorable for paraffin isomerization.

The HPA-based catalysts are active in *n*-pentane isomerization at lower temperatures of 200–300 °C. The bulk HPA containing no platinum shows a low activity. The yield of isopentane does not exceed 7%. The introduction of platinum considerably increases the catalyst activity (Fig. 1, *b*). For example, the yield of isopentane on Pt/HPWA reaches 50% at 210 °C and 53% at 230 °C. The selectivities to isopentane are 90 and 80%, respectively. An increase in the reaction temperature to 250 °C further increases the conversion of *n*-pentane. The yield of isopentane decreases because of side disproportionation reactions to form C₄ and C₆ products. When the reaction is performed at $T \ge 250$ °C, the catalyst is deactivated, which is probably related to the formation of carbonaceous deposits on the surface.

The yield of isopentane on the supported Pt/HPWA/Al₂O₃ system does not exceed 7%, although the selectivity to isopentane for Pt/HPWA/Al₂O₃ is higher than that for Pt/Al₂O₃. On the contrary, the yield of isopentane on the fluorinated catalyst Pt/HPWA/Al₂O₃-F at 290 °C reaches 62%, and the selectivity to isopentane over the whole studied temperature range is 94–97%.

Analysis of the obtained catalytic data raises two important questions. First, what is the reason for the increase in the activity of the platinum catalyst when HPWA is carried by fluorinated Al_2O_3 -F rather than by pure alumina? Second, what is the reason for the enhancement of the selectivity to isopentane and stability of activity of the Pt/HPWA/Al_2O_3-F system as compared to that of the bulky catalyst Pt/HPWA?



Fig. 1. The yield (1-6) and selectivity (1'-6') to isopentane as a function of the reaction temperature in the transformation of *n*-pentane on the catalysts: *a*, Pt/Al₂O₃ (1, 1'), Pt/Al₂O₃-F (2, 2'), HPWA (3, 3') and *b*, Pt/HPWA (4, 4'), Pt/HPWA/Al₂O₃ (5, 5'), Pt/HPWA/Al₂O₃-F (6, 6').

To answer the above questions, the nature of the acidic sites of the catalysts was studied by DRIFT spectroscopy using adsorbed probe molecules.

The nature of acid-basic sites by the data of IR spectroscopy

Systems Al_2O_3 and Al_2O_3 -F. The IR spectra in the region of stretching vibrations of the OH groups of Al_2O_3 and Al_2O_3 -F are presented in Fig. 2. The spectrum of Al_2O_3 (curve *I*) exhibits absorption bands (AB)

Table 1. *n*-Pentane isomerization at temperatures corresponding to the maximum yield of isopentane (flow rate 1 h⁻¹, H₂: *n*-C₅H₁₂ = $3:1 \pmod{10^{-1}}$, $V_{cat} = 3 \pmod{3}$)

| Catalyst | T | Conversion (%) | Selectivity to <i>i</i> -C ₅ H ₁₂ (%) | Yield (wt.%) | | | |
|---|-----|-------------------|--|--------------|------------------------------------|--|------------------|
| | /°C | | | $C_1 - C_3$ | i-C ₄ /n-C ₄ | <i>i</i> -C ₅ H ₁₂ | C ₆ , |
| Pt/Al ₂ O ₃ | 380 | 38.8 | 22.9 | 16.7 | 0.5/8.9 | 8.9 | 2.9 |
| Pt/Al ₂ O ₃ -F | 400 | 58.6 | 75.8 | 6.9 | 0.7/3.2 | 44.4 | 2.6 |
| HPWA | 290 | 8.3 | 77.1 | 0.6 | 0.8/0.3 | 6.4 | 0.2 |
| Pt/HPWA | 230 | 63.6 | 83.2 | 1.2 | 5.0/1.3 | 52.9 | 3.2 |
| Pt/HPWA/AbO | 300 | 12.7 | 52.0 | 3.9 | C.n./2.2 | 6.6 | |
| Pt/HPWA/Al ₂ O ₃ -F | 310 | 64.1 | 96.9 | 0.8 | 0.6/0.6 | 62.1 | |

terminal, two- and threefold bridging hydroxyls and to the OH groups that form hydrogen bonds.¹³ The fluorination of the Al_2O_3 surface (curve 2) decreases the intensity of the most basic terminal groups due to their replacement by fluorine anions, which agrees with the previous results.¹⁴ The intensity of the threefold bridging OH groups decreases simultaneously, which can be stipulated by the interaction of fluorine with the framework oxygen, resulting in the Al—O bond cleavage by the following reaction:



The strongest AB in the spectrum at 3715 cm⁻¹ characterizes the two-fold bridging OH groups. The shift of all AB to low frequencies relative to the maxima of the corresponding AB in the spectrum of Al_2O_3 can indicate the enhancement of the BAS of Al_2O_3 -F due to the induction effect of the F atoms.

Data on CO and CD₃CN adsorption on the LAS of Al_2O_3 and Al_2O_3 -F at 20 °C are shown in Table 2. The frequencies of vibrations of the CO and C=N bonds in the CO and CD₃CN molecules adsorbed on the Al^{3+} ions increase due to surface fluorination. This agrees with data on the enhancement of the LAS of Al_2O_3 when fluorine is introduced (the data were obtained from analysis of the spectra of CO adsorbed at -110 °C and benzonitrile and pyridine¹⁴).

To study the basic sites of Al_2O_3 and Al_2O_3 -F as probe molecules, we used C_2H_2 (Fig. 3). After the adsorption of C_2H_2 on Al_2O_3 , AB at 3165 and 1945 cm⁻¹ appear in the spectrum. According to the previously obtained data,¹⁵ they characterize vibrations of the CH and C=C bonds of the C_2H_2 molecule interacting with the surface sites of Al_2O_3 . The significant low-frequency



Fig. 2. IR spectra in the region of vibrations of the OH groups of Al_2O_3 (1) and Al_2O_3 -F (2).

| System | v/cm ⁻¹ | | | |
|--------------------------------|--------------------|---------------------------|--|--|
| | со | C=N in CD ₃ CN | | |
| Al ₂ O ₃ | 2200 | 2316 | | |
| AbO3-F | 2215 | 2330 | | |
| HPWA/ALO | 2205 | 2320 | | |
| HPWA/ALO | 2215 | 2320 | | |

shift of AB of C_2H_2 relative to vibrations in the gas phase (v(CH) 3287 cm⁻¹, v(CC) 2006 cm⁻¹⁻¹⁶) (Δ v(CH) 122 cm⁻¹, Δ v(CC) 51 cm⁻¹) indicates, most likely, the formation of acetylene σ -complexes with basic sites of Al₂O₃ and probably represented by bridging Al- O^{2-} -Al and terminal Al-OH groups.¹⁷



Fig. 3. Adsorption of C_2H_2 on Al_2O_3 (7) and Al_2O_3 -F (2): IR spectra in the region of vibrations of the OH and CH (a) and C=C (b) bonds after subtraction of the spectra of the initial samples.

The absorption bands at 3290 and 2000 cm⁻¹ are characterized by smaller shifts relative to the vibrations of the CH and C=C bonds in the C₂H₂ molecule in the gas phase. These bands appear due to the formation of π -complexes of C₂H₂ with Al³⁺ cations, which are the LAS of Al₂O₃.¹⁵

The band at 3565 cm⁻¹ appearing in the spectra after the adsorption of C_2H_2 on Al_2O_3 is related, most likely, to the interaction of acetylene with the threefold bridging OH groups that exhibit an AB at 3675 cm⁻¹. The low intensity of the AB of the OH groups of Al_2O_3 -F perturbed by acetylene adsorption agrees with a decrease in the concentration of the threefold bridging OH groups upon fluorination (see Fig. 2).

Only the AB at 3240 and 1955 cm⁻¹ characterizing the σ -complexes of C₂H₂ (see Fig. 3) are present in the spectra of the fluorinated samples. The high-frequency shift of the AB for the CH and C=C bonds of adsorbed C₂H₂ relative to the corresponding bands in the spectrum of the nonmodified samples (AB at 3165 and 1945 cm⁻¹) indicates a decrease in the polarization of the acetylene molecule and, hence, a weakening of the strength of the basic sites in Al₂O₃-F.

Thus, Al_2O_3 fluorination enhances the BAS formed by the twofold OH groups and LAS and decreases the strength of the O^{2-} sites and the concentration of the basic OH groups.

Systems HPWA/Al₂O₃ and HPWA/Al₂O₃-F. The IR spectrum in the region of vibrations of the OH groups of bulk HPWA (Fig. 4) represents broad absorption with a maximum at \sim 3100 cm⁻¹, which can be attributed to the OH groups participating in the formation of the secondary structure of HPWA and forming strong hydrogen

bonds.^{7.8} The bands at 2250 and 2030 cm⁻¹ correspond to the first overtones of vibrations of the W–O and P–O bonds and characterize the Keggin ions that form the secondary and tertiary structures whose individual ions interact strongly.⁷

The immobilization of HPWA results in a decrease in the intensity of the AB of the OH groups of the support (see inset in Fig. 4) with the most pronounced reduction in the HPWA/Al₂O₃ system being for the terminal OH groups with a maximum at 3760 cm⁻¹. The position and intensity of the AB corresponding to vibrations of the HPA framework change simultaneously (see Fig. 4, *b*). The spectrum of the supported systems contains only one AB at 2015–2035 cm⁻¹ corresponding to the first overtone of vibrations of the W—O bond. Disappearance of the AB at 2250 cm⁻¹ characteristic of bulk HPWA can be attributed to a change in the HPA structure upon interaction with the active sites of the surface, leading, in particular, to dispersion of HPA over the support surface.

HPWA does not adsorb CO at 20 °C and, hence, manifests only Brönsted acidity. The supported catalysts contain both BAS and LAS. For the HPWA/Al₂O₃-F system, the frequency of vibrations of adsorbed CO and, hence, the strength of LAS remains unchanged as compared to those on the starting Al₂O₃-F (see Table 2). By contrast, in the case of HPWA/Al₂O₃, the frequency of the CO vibration increases from 2200 cm⁻¹ (for Al₂O₃) to 2205 cm⁻¹ (for HPWA/Al₂O₃), which can indicate surface modification and enhancement of the LAS upon HPA immobilization.

Analysis of the spectra of adsorbed CD_3CN indicates the formation of a complex of one type, which, as those in the HPWA/Al₂O₃ and HPWA/Al₂O₃-F systems, is



Fig. 4. IR spectra in the region of vibrations of the O-H bonds (a) and first W-O and P-O overtones (b) of bulky HPWA (1), HPWA/Al₂O₃ (\mathcal{I}), and HPWA/Al₂O₃-F (3) after subtraction of the spectra of the initial supports.

characterized by an AB at 2320 cm⁻¹ (see Table 2). This can be produced if the heteropolyacid blocks the sites accessible for CD₃CN adsorption, due to which the CD₃CN molecules first interact with sites of similar nature formed with the involvement of HPWA.

When BAS are represented in the IR spectrum by broad bands in the region of vibrations of OH groups, it is impossible to determine their strength by measurement of the shift of the frequencies of vibrations of the OH groups, which occurs upon the formation of a hydrogen bond with bases.¹⁸ In this case, the strength of acidic sites can be evaluated by test reactions: lowtemperature olefin oligomerization and H--D exchange with basic deuterosubstituted molecules, such as $C_{\rm p}D_{\rm b}$.^{19,20}

The studies showed that Al_2O_3 and Al_2O_3 -F were inactive in both the H-D exchange of benzene-d₆ and the low-temperature oligomerization of ethylene-d₄. This implies that these catalytic systems do not contain strong BAS. This agrees with the low activity of the Pt/Al₂O₃ and Pt/Al₂O₃-F catalysts in *n*-pentane isomerization.

Bulky HPWA also shows a low activity in ethylened₄ oligomerization. However, after C_6D_6 adsorption, the spectrum of the acid (Fig. 5, *a*) exhibits an increase in the intensity of the AB at 2390–2030 cm⁻¹, which can indicate processes of H--D exchange that are impossible without strong BAS. The absence of the AB at 2275 cm⁻¹ characteristic of the CD vibration of the C_6D_6 molecule may indicate a low surface concentration of adsorbed benzene and inaccessibility of a part of the surface for the reaction. Thus, the low activity of HPWA in oligomerization and H--D exchange can be related to a low specific surface area of HPA.

The HPWA/Al₂O₃ system does not exhibit noticeable activity in C_2D_4 oligomerization, which is indicated by the absence of bands of the oligomers (2200-2100 cm⁻¹) (Fig. 6, inset). The spectra of adsorbed C_6D_6 (see Fig. 5, b, curve 2) also have almost no changes, indicat-



Fig. 5. IR spectra before (1) and after (2, 3) 2-h H--D exchange at 20 °C with C_6D_6 for three systems: a, HPWA and b, HPWA/Al₂O₃ (2) and HPWA/Al₂O₃-F (3). The absorption bands of C_6D_6 are marked with asterisks.



Fig. 6. IR spectra of C_2D_4 adsorbed on HPWA/Al₂O₃-F 1 (1), 10 (2), 30 (3), 60 (4), and 240 (5) min after C_2D_4 admission. The spectra of C_2D_4 adsorbed on HPWA/Al₂O₃ measured 1 (1) and 240 (2) min after admission are shown in inset.

ing a low activity of the HPWA/Al₂O₃ system in the H-D exchange.

The HPWA/Al₂O₃-F system surpasses bulk HPWA in activity in the low-temperature oligomerization of ethylene-d₄ (see Fig. 6). Immediately after C₂D₄ adsorption, the spectrum exhibits, along with AB at 2250 and 2190 cm⁻¹ belonging to the physically adsorbed olefin molecules, an increase in AB at 2210 and 2095 cm⁻¹, which can be assigned to the oligomerization products with predominantly linear structures. The AB of the CH and OD groups at 2925 and ~2500 cm⁻¹, respectively, appear simultaneously in the spectra, which indicates H—D exchange accompanying oligomerization.

The HPWA/Al₂O₃-F system exhibits similar activity in H-D exchange when interacting with C_6D_6 (see Fig. 5, b, curve 3). This is followed by an increase in the AB at 2550 cm⁻¹, whose position differs considerably from that of the bands of the OD groups of Al₂O₃-F (2690 cm⁻¹). Therefore, this AB can be assigned to vibrations of surface-localized OD groups in HPWA.

Evidently, the immobilization of HPWA on Al_2O_3 -F increases the concentration of the acidic HPA sites rather than affecting their acidity. When HPWA is supported on Al_2O_3 , the strength of the acidic sites changes, probably, due to the interaction of HPA with basic surface sites and to the partial decomposition of HPWA.

Nature of catalytic activity

n-Alkane isomerization on bifunctional catalysts can be described by a mechanism involving the steps of activation of a paraffin molecule on metal particles, migration to BAS, skeletal isomerization, and inverse migration

followed by desorption.²¹ The alternative mechanism of alkane transformation on $[Pt-H]^{+}$ sites formed by the direct interaction of a metal particle with a proton excludes the migration of intermediates.²² In both cases, the step of skeletal isomerization can occur via the mono- and bimolecular mechanism, depending on the alkane chain length. It has been shown²³ that for *n*-pentane the main pathway of transformation is monomolecular isomerization, whereas side disproportionation processes occur via the bimolecular mechanism. According to the proposed scheme, the strength and concentration of BAS are the main factors determining activity and selectivity of the catalyst.

Thus, the questions formulated in the analysis of the kinetic data can be answered from the data of IR spectroscopy.

The catalytic Pt/Al_2O_3 system manifests a low activity in *n*-pentane isomerization because of the low strength of the BAS of the support. Fluorination of the Al_2O_3 surface enhances the acidic sites and activity in isomerization. However, the strength of the acidic sites remains insufficient for efficient paraffin activation, and the Pt/Al_2O_3 -F catalyst is active only at high temperatures (380-400 °C). Under these conditions, side reactions such as cracking and disproportionation occur with high rates, thus decreasing the selectivity to isopentane.

The acidic sites of bulk HPWA are stronger than the sites of unpromoted supports and, hence, the Pt/HPWA catalyst is active at lower temperatures (210-230 °C). The acidity of the support affects the acidity of supported HPWA. Moderately basic Al₂O₃ is characterized by a strong interaction with HPWA, destroying the HPA structure and deactivating the catalyst. The immobilization of HPWA on Al₂O₃-F, in which the strong basic sites are suppressed and the acidic sites are enhanced, does not destroy the HPA structure, and the catalyst retains its high activity.

The immobilization of HPWA on Al₂O₃-F does not change the character of the process. The noticeable yield of isopentane on Pt/HPWA/Al₂O₃-F catalyst is observed at higher temperatures than on the bulk Pt/HPWA system (see Fig. 1, b). However, Pt/HPWA/Al₂O₃-F is characterized by insignificant formation of the products of *n*-pentane disproportionation (C_4 and C_6 hydrocarbons) (see Table 1), and the selectivity of the process remains high over the entire range of temperatures used. Evidently, the density of acidic sites on bulk Pt/HPWA is sufficiently high for isomerization via both the monoand bimolecular mechanisms due to the interaction of adjacent adsorbed fragments. The development of the bimolecular processes increases the rate of formation of side products resulting from disproportionation and cracking, whereas increasing temperatures lead to the formation of condensation products.

The immobilization of HPWA results in HPA dispersion over the Al_2O_3 -F surface. HPWA can simulta-

neously interact with the poorly basic OH groups, and the formation of HPA salts, whose activity, as shown previously,^{7,8} can exceed that of the bulk systems. The density of the acidic sites decreases, and the probability of the bimolecular processes decreases. As a result, the high selectivity of the process is retained in a wide interval of reaction temperatures.

Thus, the immobilization of 12-tungstophosphoric heteropolyacid on the support can considerably increase the selectivity of the system in *n*-pentane isomerization and the time-on-stream behavior of the catalyst.

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