



Effect of tungsten amount on catalytic behavior of mixed WTi-pillared clay

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Abstract

Mixed Tungsten-Titanium pillared clays are prepared with various amounts of tungsten then characterized following different techniques. The n-hexane isomerisation is carried out in the gas phase in order to test the catalytic activity of the samples. The structural, textural, acidic and catalytic properties are largely influenced by the tungsten amounts added to the clay during the mixed intercalation process. Enhanced acidity and porosity by mixed pillaring resulted in a selective catalysis allowing the formation of mono-branched isomers as major products. The best mixed WTi-pillared clay can be used in the future as a support for metal transition or as a catalyst of other chemical reaction requiring surface acidity.

Keywords: Tungsten, titanium, mixed pillared clay, acidity, catalytic behavior.

1. Introduction

Recently, a new class of microporous and mesoporous solids are produced by intercalating clay with different macrocations. The intercalation process consists on a conversion of the layered clay into highly porous-structured material obtained by exchanging the initial compensating cations (Na^+) with large variety of inorganic polycations. The process requires a thermal treatment in order to transform the polycations inserted between the clay layers into rigid pillars, linking permanently the silicates sheets. The pillared clays have a wide range of potential applications in catalytic process [1, 2]. The number of chemical reactions for which the employ of pillared clays, as catalysts or as catalyst supports, is permanently in increase.

The use of TiO_2 as a catalyst support is limited not only by its specific low surface area, but also by its low porosity and low resistance to sintering. Unlike TiO_2 , Titanium pillared clay (Ti-PILC) offers a better alternative in term of surface area, porosity, thermal stability and acidity. Thus, considerable efforts have been made to investigate the substitution of conventional TiO_2 by Ti-PILC support in order to design a brand of a newly high - efficient catalyst. The Ti-pillared clays are explored in various applications, namely those requiring acid sites such as: the selective catalytic reduction of nitrogen oxide (SCR-NO) by ammonia [3]. Recently, the use of transition metals, as vanadium, supported on Ti-pillared clay, has drawn the attention of a large number of researchers. Its catalytic activity was studied through several reactions such as: selective catalytic reduction of NO by ammonia [4-7], epoxidation of allylic alcohol [8, 9], selective catalytic oxidation of H_2S [10], oxidative dehydrogenation of propane [11], etc. In our previous work, we reported that the simultaneous addition of Tungsten (9%wt.) and vanadium (3%) by incipient wetness impregnation to sulfated Ti-intercalated clay increases the Bronsted acidity as well as the SCR-NO activity [12].

The intercalation of clays with solutions containing two cations, was previously described. A summary of the catalytic applications of these mixed systems was presented in the first table of the review [1]. The isomerization reaction of light paraffins (C5, C6, C7) is an industrial process used to produce gasoline of high octane number. In laboratory, the product distribution of the catalytic n-hexane isomerisation is widely used to evaluate the surface acidity of heterogeneous catalysts. Generally, the isomerisation of linear alkane is successfully carried out in the presence of hydrogen gas and a bifunctional catalyst, typically Pt (from $\text{Pt}/\text{Al}_2\text{O}_3$) supported on an acid carrier [13-15] In this context, platinum chlorinated alumina catalyst can be used at low temperatures, i.e. 120-180°C, while zeolites require high temperature, typically 220-300°C [16]. In the industrial use of the catalyst,

the catalytic active phase is deposited on TiO₂ in order to increase the surface area. Noticing is that TiO₂ has a lower surface area and sinters more easily than Ti-pillared clay.

Usually the first cation is Al or Zr, whereas the addition of small molar fractions of a second cation (Ce, Si, Ga, La, Cr...) helps the improvement of the catalytic properties of the final pillared clays. Recently, mixed pillared clays such as: FeCr-pillared clay [17], FeMn-pillared clay [18], AlCu-pillared clay with AlFe-pillared clay [19], ZrTi-pillared clay [20], Pd and/or Cr supported on mixed ZrTi-pillared clay [21] and FeTi-pillared clay [22], have been prepared, and their catalytic activities have been evaluated in different reactions. So far, there is no published work describing the preparation method and the catalytic activity of mixed WTi-pillared clay. In fact no studies were reported concerning the effect of tungsten amounts on the physico-chemical properties of any pillared clay. Moreover to our knowledge no scientific work deals with the isomerisation of n-hexane on mixed tungsten-titanium-pillared clay prepared with different tungsten amount or assessing the effect of tungsten loadings on the physico-chemical properties of the pillared clays (PILC). In our recent paper, the catalytic activity in the n-hexane isomerisation of sulfated titanium pillared clay and tungsten titanium pillared clay is compared [23]. Consequently, in this work we illustrate the effect of different tungsten amounts on the physico-chemical and catalytic properties of mixed tungsten-titanium-pillared clay.

2. Experimental

2.1. Synthesis of mixed WTi-pillared clay catalysts

2.1.1. Starting clay

The clay used in this work is an industrial treated montmorillonite Clarsol, referenced KC2, provided by CECA (France). Before using it, the clay is purified by sedimentation removing the fraction less than 2 μm. Then, it is exchanged three times with Na⁺ ions by stirring in NaCl solution (1 M) for 24 h [8]. Carrying dialysis, the suspension obtained is washed several times with distilled water until it becomes free from Cl⁻ ions (as indicated in the test with silver nitrate solution). The solid is separated by centrifugation and dried at room temperature. The chemical analysis is subject to an exchange capacity of 80 meq./100 g. This initial material is referenced as In-clay.

2.1.2. Synthesis of the catalysts

The W-solution is prepared by dissolving ammonium metatungstate (NH₄)₆H₂W₁₂O₄₀ in water (10⁻² M). The Ti-solution is obtained by a slow addition of TiCl₄ into HCl solution (6 M) under vigorous stirring. Final concentrations of 0.82 M in titanium and 0.2 M in acid are reached by adding water. H⁺/Ti value of 0.24 is thus achieved. The W-solution and the Ti-solution are simultaneously added, a drop per 500 cm³ of a suspension containing 2 g of the initial clay under vigorous stirring at room temperature, so that the percentage of tungsten (0, 5, 10 and 15 %) added to the clay suspension with a final Ti/clay ratio of 10 mmol/g is obtained. After 24 h of stirring, the solid fraction is separated by centrifugation and filtration. Then, it was washed several times with distilled water and dried at room temperature. All samples were calcined at 400 °C at a heating rate of 2 °C min⁻¹ for 3 h under air flow. The sample prepared free of tungsten is referred to as Titanium pillared clay (Ti-PILC) where as the mixed tungsten titanium pillared clays are referenced to W_xTi-PILC, in which x is equal to 1, 2 and 3, indicating a percentage of 5, 10 and 15 % of tungsten added to the clay suspension.

2.2. Characterization of the samples

The Chemical analysis is carried out in the National Institute for Research and Physico-Chemical Analysis (INRAP) of Tunisia.

The X-ray diffraction patterns are obtained using a SIEMENS D 500 instrument equipped with a monochromatized CuKα radiation at λ = 1.541 Å.

The specific surface area, pore and micropore volume of the samples are determined by nitrogen physisorption using a Micromeritics ASAP 2020 instrument. The samples are out gassed in vacuum during 5 h at 200 °C before to nitrogen physisorption.

Total acidity measurement is evaluated by ammonia temperature programmed desorption (NH₃-TPD) using an AUTOCHEM 2910 (Micromeritics). Before NH₃ adsorption, samples are pre-treated under air flow (30 mL/min) at 450 °C (10 °C/min) for 30 min. Ammonia adsorption is carried out at 100 °C by exposing to 5 vol% NH₃ in He (30 mL/min) for 45 min and then by flushing with He (30 mL/min) during 2 h to remove the residues of the adsorbate in the gas phase and physisorbed on the catalyst surface. Finally, ammonia was desorbed in helium flow (30 mL/min) from 100 to 450 °C using a heating rate of 10 °C/min.

2.3. Catalytic test

The n-hexane isomerisation is performed in a continuous micro flow system using a tubular reactor and operated at an atmospheric pressure. Before each reaction, the pillared clay catalyst is mechanically mixed with a similar quantity of the standard Pt/Al₂O₃ (0.35% Pt in weight). Worth mentioning is that Pt/Al₂O₃ alone is inactive at a reaction temperature below 220 °C.

Each sample is pretreated in a fixed bed reactor, first under Helium flow at 400 °C for 2 h and then under H₂ flow for 30 min. Hydrogen saturated with n-hexane is passed over the catalyst during 5 min at the desired temperature reaction (150-220°C). In this work, molar flow rates of n-hexane and H₂ were independently controlled to provide the preferred WHSV (2 h⁻¹) to maintain low n-hexane conversions. All reaction products are analyzed on-line using FID gas chromatography.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Chemical analysis

The results of the elemental analysis of the initial sodium between the clay sheets and titanium with tungsten retained by the clay are illustrated in Table 1. The decrease of sodium content in the initial clay upon intercalation is observed. The exchangeable cations (Na⁺) are replaced by mixed WTi-polycations. Accordingly, the intercalation process has a threshold of 4.4 % in terms of tungsten amount that can be incorporated into the clay.

Table 1: Chemical analysis of initial sodium and titanium with tungsten retained by the clay

Samples	W _{added} (%)	Na _{initial} (%)	Ti _{retained} (%)	W _{retained} (%)
In-clay	-	0.36	0.14	0
Ti-PILC	0	0.09	25.05	0
W ₁ Ti-PILC	5	n.d	n.d	1.97
W ₂ Ti-PILC	10	0.08	27.11	4.46
W ₃ Ti-PILC	15	0.08	26.90	4.08

3.1.2. X-ray diffraction

The X-ray diffraction patterns of the investigated samples are shown in Fig. 1. Noticing is that the basal 001 peak around $2\theta = 7^\circ$ (characteristic of starting hydrated clay) is turned to below 2θ value after intercalation, which indicates an enlargement of the basal spacing of the clay as a consequence of the intercalation process. The basal spacing of the initial clay (12.26 Å) represents the distance between both clay layers including the thickness of the layer which is equal to 9.6 Å. Remarkably, the simultaneous addition of tungsten with titanium does not show an impact on the basic-interlayer distance except for the sample W₃Ti-PILC, prepared with 15 % of tungsten. Usually, a more intense (001) peak indicates a more homogeneous pillar distribution.

After intercalation with titanium and a few amount of tungsten (W₁Ti-PILC), the d_{001} is increased to about 20.86Å pointing to an improvement of the basal spacing of the clay layers by WTi-polycations. By contrast, for W₂Ti-PILC prepared with 10 % of tungsten, two diffraction lines are observed. The first peak (23.28 Å) is less intense than the second one. It is associated with the layers intercalated by mixed WTi-polycations with high degree of polymerization, while the second one appearing at $2\theta = 8^\circ$ is associated either with unexchanged layers, containing sodium, or with the layer intercalated by WTi-cations with a low degree of polymerization (smaller in size); a situation that leads to a lower opening of the clay layers. In the sample W₃Ti-PILC, the X-ray pattern reveals a high peak of $d_{001} = 21.36$ Å related to the layers intercalated by homogeneous distributed WTi-polycations with an average size of about 11 Å. A second peak about 14 Å is also perceived, either associated with the layers which remained unexchanged, containing water and probably a small amount of Na⁺ or with the ones exchanged by cations with a low degree of polymerization.

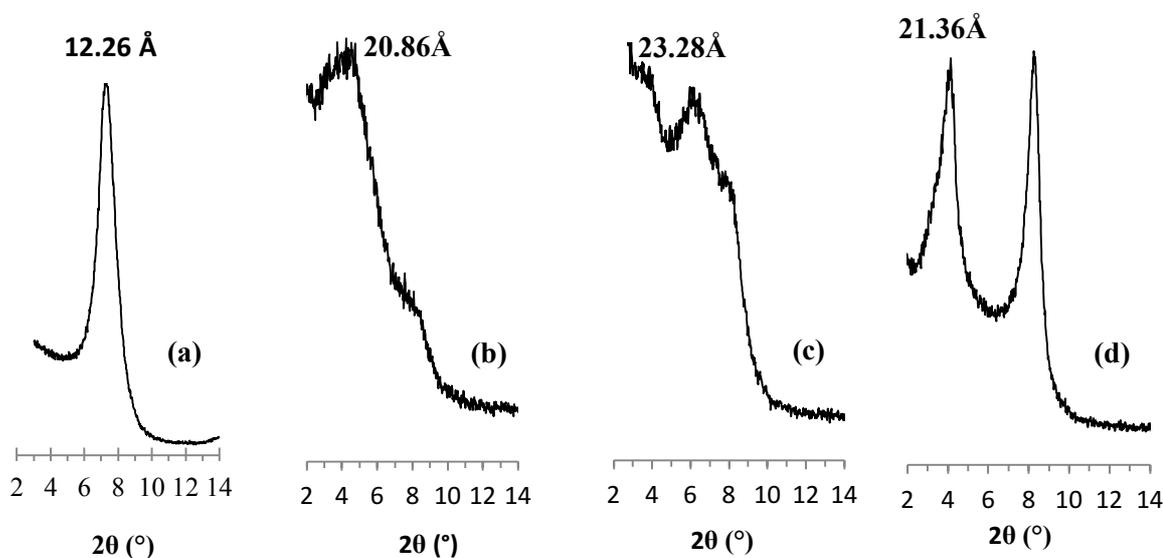


Figure 1: X-Ray diffractograms of : (a) Initial clay, (b) W_1 Ti-PILC, (c) W_2 Ti-PILC, (d) W_3 Ti-PILC.

3.1.3. Nitrogen physisorption

The BET surface area of the initial clay is $25 \text{ m}^2/\text{g}$; therefore, the higher surface area of the Ti-PILC support results in the intercalation process (Table 2). For the mixed catalyst, the surface area decreased as the tungsten content, in the intercalated solution, is increased.

Table 2: Structural and textural properties of the samples before calcination.

Samples	d_{001} (Å)	S_{BET} (m^2/g)	V_{PT} (cm^3/g)	V_{HP} (cm^3/g)
In-Clay	12.26	25	0.094	0.005
Ti-PILC	15.81	324	0.225	0,001
W_1 Ti-PILC	20.86	145	0.090	0.027
W_2 Ti-PILC	23.28	32	0.031	0.006
W_3 Ti-PILC	21.36	16	0.044	0.004

A significant decrease in the surface area is noticed in the catalyst containing an excess of tungsten (W_3 Ti-PILC). This can be caused by the blocking of some pores due to the building-up of large WTi-polycations. In this work, we also analyzed 20% and 25% of tungsten however; the results (d_{001} , S_{BET} , microporosity and also catalytic test) are insignificant. For the samples prepared with 20 and 25%, the intensity of the first peak (d_{001}) and the specific surface areas are strongly reduced compared to the sample prepared with 15% of tungsten and after calcinations the surface areas remain lower than the sample prepared with 15% of tungsten. Therefore, this paper presents the most acceptable characterization results of samples synthesized with 5, 10 and 15% of tungsten. The amounts of 20 and 25% of tungsten are not recommended for mixed WTi-pillared clay.

Upon calcinations at high temperature, the hydrated polycations dehydrate and dehydroxylate, then react to form rigid metal-oxide pillars. The BET surface areas and pore volumes of the investigated samples are summarized in Table 3. For Ti-PILC, the surface area decreases with the increase of the thermal treatment, due to the removal of water from polycations, as the surface areas of mixed WTi-pillared clay increase. The improvement of surface area and micro porosity after thermal treatment can be explained by structural changes occurring and by water removal from the mixed WTi-pillars during thermal treatments, as observed by thermogravimetric analysis [23]. The microporous structure of pillared clay is commonly characterized by the distance between the clay layers and the one between the pillars. Both interlayer and inter pillar spacing can be modified during the calcination step when dehydration or sintering of the pillars occurs. In all cases, the observed surface area (above $120 \text{ m}^2/\text{g}$) at 400°C , confirms the thermal stability of the mixed WTi-pillared clay.

Table 3: Textural properties of the samples calcined at 400°C.

Samples	S_{BET} (m ² /g)	V_{PT} (cm ³ /g)	$V_{\mu\text{p}}$ (cm ³ /g)
Ti-PILC	281	0.2149	0.0001
W ₁ Ti-PILC	130	0.1030	0.0108
W ₂ Ti-PILC	197	0.1272	0.0302
W ₃ Ti-PILC	124	0.1123	0.0281

The N₂ adsorption-desorption isotherms of the pillared materials are presented in Fig. 2. The adsorption isotherms of all samples are according to the IUPAC classification of type IV characterizing mesoporous materials. Hysteresis loops due to capillary condensation in the mesopores, generally associated with their filling and emptying, are of type H3 also characterizing mesoporous materials. In all isotherms, desorption branch shows an obvious inflection at about P/P^0 of 0.4-0.5. This result is also observed for many different types of layered materials when nitrogen is used as adsorbent [24].

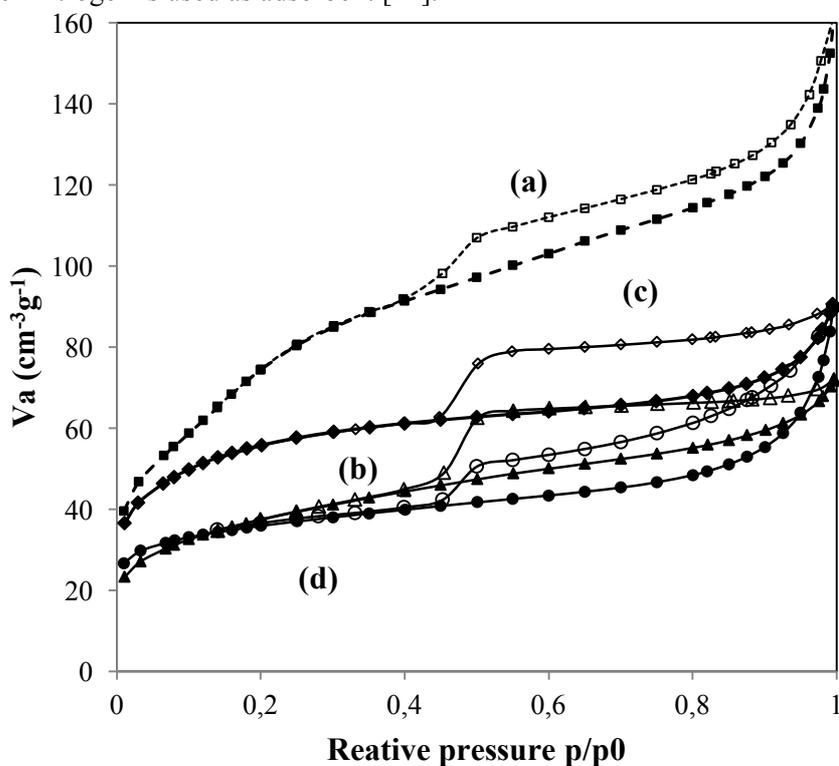


Figure 2: N₂ isotherms adsorption-desorption of : (a) Ti-PILC, (b) W₁Ti-PILC, (c) W₂Ti-PILC, (d) W₃Ti-PILC.

According to the IUPAC classification of pores, those with diameters ranging between 20 and 50 Å are described as mesopores while those with diameters less than 20 Å are referred to as micropores. Pores with diameters larger than 50 Å are classified as macropores. For all the mixed WTi-PILC catalysts, the analysis of the BJH pore size distribution (Fig. 3) shows a narrow distribution of mesopores with diameter ranging between 27 and 50 Å and a maximum diameter about 38 Å. The micropore size distribution of Ti-PILC is significantly decreased after the tungsten addition.

3.1.4. NH₃-TPD

The surface acidity is evaluated by ammonia temperature programmed desorption. The NH₃-TPD patterns of the samples are shown in Fig. 4. The shape of desorption patterns obtained for the mixed WTi-PILCs is very different from that recorded for the sample without tungsten. However, the NH₃-TPD profile of Ti-PILC (used as a reference) contains at least two maxima. The first peak is centred at about 230°C, while the second one, much

broader, appeared at about 350°C. The low temperature peak can be related to the desorption of ammonia either physisorbed or linked to weak Bronsted acid sites, while the second peak at high temperature can be attributed to ammonia desorbed from stronger Lewis acid sites [12]. The intensities of the two characteristics peaks of Bronsted and Lewis acid sites are affected significantly by the additive tungsten amount.

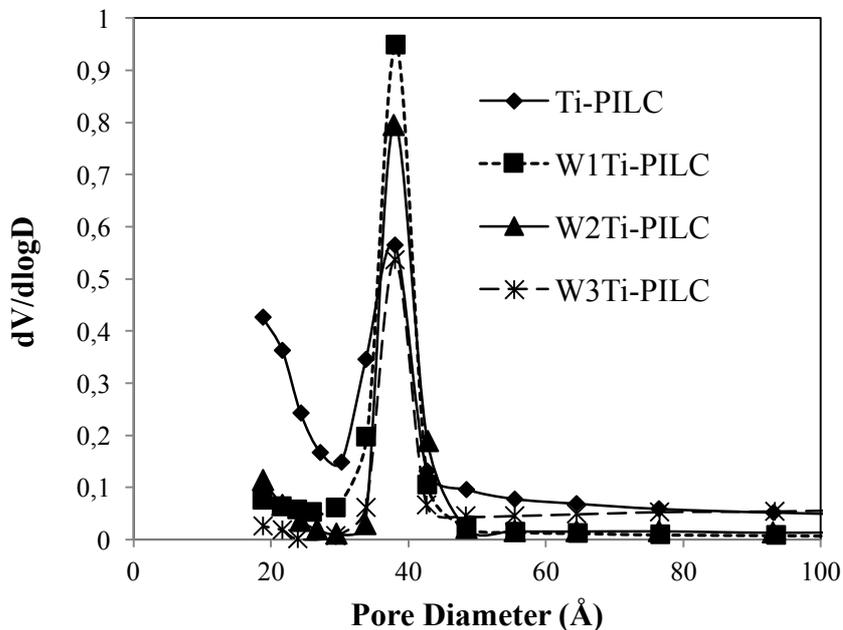


Figure 3: Pore size distribution of the samples calcined at 400°C.

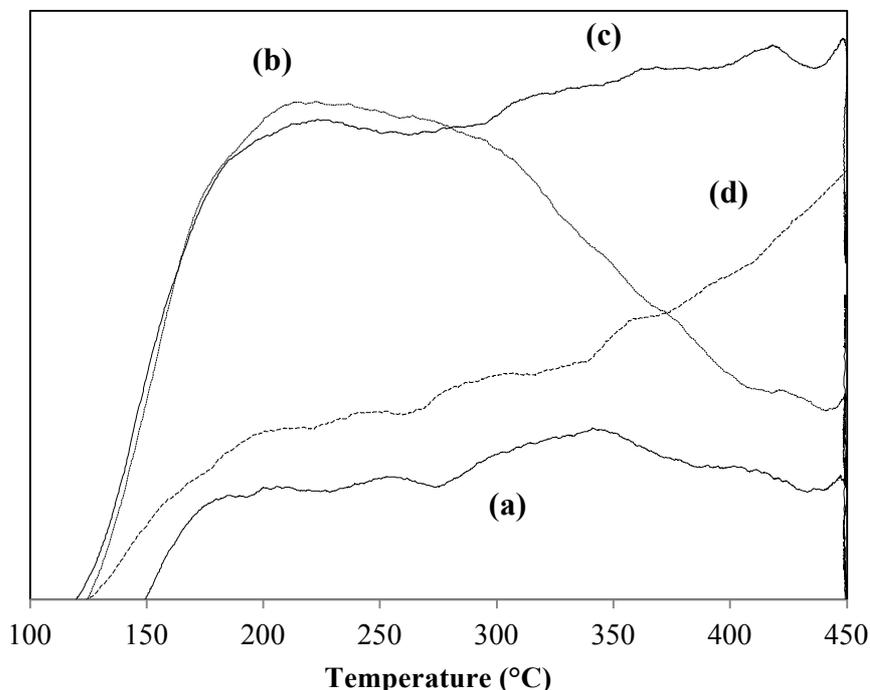


Figure 4: NH₃-TPD profiles of: a) Ti-PILC, b) W₁Ti-PILC, c) W₂Ti-PILC, d) W₃Ti-PILC.

The change in the NH₃-TPD profiles can be explained by the progressive transformation of the surface acidity after addition of different amounts of tungsten. This suggests that the incorporation of tungsten in pillared clay produces more acid sites. The existence of both Lewis and Bronsted acid sites on the Ti-PILC surface is demonstrated in our previous work [3]. The addition of a little amount of tungsten (5%) into pillared clay (W₁Ti-

PILC) increases the intensity of the first peak associated to the adsorbed ammonia by Bronsted acid sites. In the case of W₂Ti-PILC, surprisingly the acidity increases. This fact can be explained by the incorporation of higher amount of tungsten in this sample. In contrast, the shape of desorption patterns of W₃Ti-PILC is largely moved to higher temperature indicating the ammonia desorption from strong acid sites and demonstrating the existence of strong Lewis acidity on the catalyst surface.

In general, it is difficult to correlate the acidity to only tungsten content in the samples W₂Ti-PILC and W₃Ti-PILC. The XRD results indicate that the distance between two adjacent pillars and the pillar height are different among these two catalysts. It seems that the good distribution of WTi-pillars between the clay sheets, as observed by the intense line $d_{001} = 21.36 \text{ \AA}$, can affect the acidity of W₃Ti-PILC and some of the strong Lewis acid sites in the interlayer region are not covered by the pillaring species. Therefore the combination of good dispersion of the pillars, between the clay layers in W₃Ti-PILC and the well porous structure favors multiple contacts of adsorbed ammonia on the strong acid sites.

3.2. Catalytic activity measurement

The catalytic behavior of the mixed WTi-pillared clay for n-hexane isomerisation is investigated. The products is divided in two groups: (a) skeletal isomerisation products including di-branched isomers (2,2-dimethyl butane and 2,3-dimethyl butane) and mono-branched isomers (2-methylpentane and 3-methylpentane); and (b) cracking products (C1 - C5). These products (isomerisation and cracking ones) are simultaneously formed over an acid catalyst [25-28].

The conversion is approximately analogous at 190°C and 200°C then it increases with temperature increase. From Fig. 5, it is observed that the conversion of n-hexane depends of tungsten amount added to the clay. The C6 branched isomers formed at low conversion are predominantly 2-methylpentane, 3-methylpentane and 2, 3-dimethyl butane [27]. By contrast, the 2, 2-dimethyl butane containing quaternary carbons are formed in a significant amount only at high conversion [27]. This is similar to the observation made by J. Walendziewski et al. [28] who used sulfated zirconia-alumina based platinum catalyst for n-cetane isomerisation. Relatively high isomerisation selectivity ($\approx 71\%$) was determined only for very low conversion level (below 10%). At the low total conversion, the main products of isomerisation are mono-branched hydrocarbons but at the higher process temperature the share of poly-branched isomers significantly increases [28].

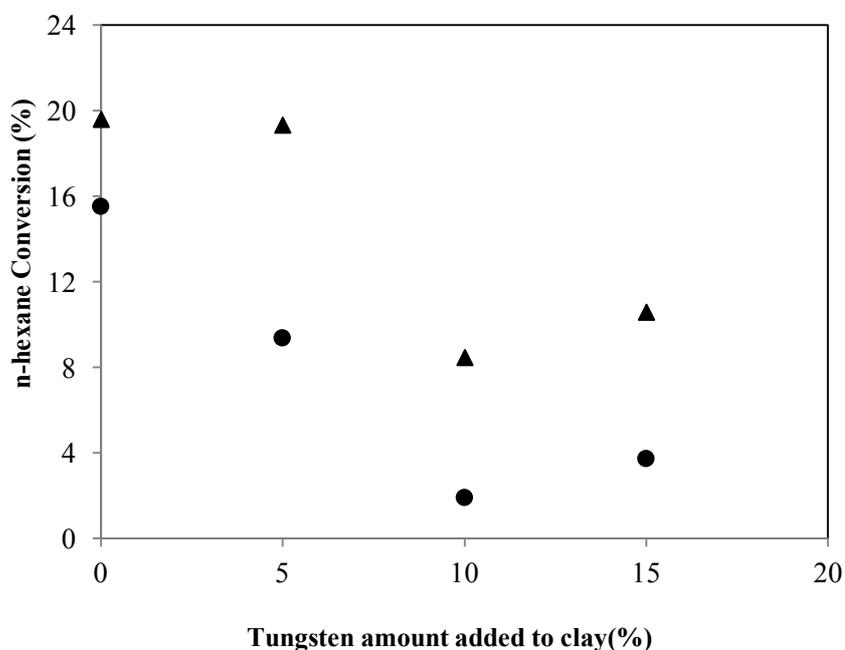


Figure 5: Effect of tungsten amount on the n-hexane conversion at 220°C (▲) and 200°C (●).

In this work, the Ti-PILC and W₁Ti-PILC catalysts exhibit superior conversions as compared with W₂Ti-PILC and W₃Ti-PILC (Fig. 5). This result is mainly attributed to the sufficient acid sites (Bronsted and Lewis) on the surface. In the case of W₁Ti-PILC, the addition of a little amount of tungsten leads to a higher Bronsted acid sites. Further increase in tungsten loading causes a decrease in the conversion. For the catalyst prepared

with higher tungsten amount (10 %), it is reasonable to think that the decrease of conversion is partly due to the partial pore blocking due to the accumulation of tungsten species on the surface, which restricts the available active acid sites for the catalytic reaction. However, the explanation of the increase of conversion over W₃Ti-PILC, prepared with 15% of tungsten, is the combination of the good microporous structure and the well dispersion of mixed WTi-pillars (as observed by XRD results) which favors the contacts of reactant with active acid sites. Recall that microporous structure of pillared clays is usually characterized by the distance between the pillars and between the clay sheets. Diffusion of n-hexane inside the pores of W₂Ti-PILC may be slow, in comparison to W₃Ti-PILC, due to the difference in the size of the micropores. Moreover, we have characterized and examined WTi-PILCs prepared with 20% and 25% of tungsten however; the results (surface area, microporosity and mainly catalytic test) are strongly reduced and insignificant compared to the sample prepared with 15% of tungsten. This may be due to the steric factor of the pores in the catalyst which prohibits the good progress of the reaction.

The activity of all samples begins from 170°C and increases with reaction temperature (Fig. 6). The activity is not related only to the quantities of tungsten retained by the clay but also to different strength of acid sites exposed on the surface. Above 170°C, the activity of Ti-PILC is better for its higher specific surface area and its moderate total acidity (Bronsted and Lewis). Pillaring process enhances surface area and both Bronsted as well as Lewis sites that cause increased activity in acid catalyzed reactions [3, 29, 30]. The high activity of W₁Ti-PILC, between 200 and 220°C, can be explained by the existence of active acid sites, arising by the few amount of tungsten, well dispersed on the high surface area. By contrast, in the case W₂Ti-PILC, the activity between 190 and 220°C is lower compared to others PILCs, despite its better surface area. In this case, the low activity can be related to less exposed acid sites on the surface due to a partial pore blocking and to the accumulation of higher tungsten species on the surface, which restrict the available active acid sites that become non accessible for reaction. Diffusion and adsorption of ammonia (to characterize acidity by NH₃-TPD) inside the pores may be fast in comparison to reactant n-hexane due to the difference in their molecule size. By contrast for W₃Ti-PILC, the accessibility of the active acid sites is superior compared to W₂Ti-PILC, due to a better microporous structure and good dispersion of WTi-pillars between the clay sheets.

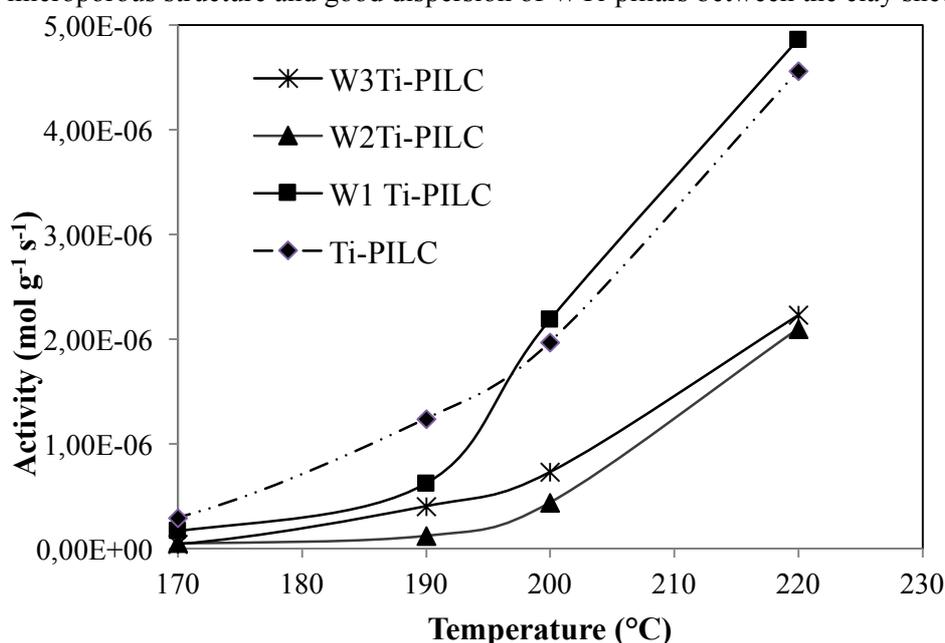


Figure 6: Evolution of activity at different temperature reaction.

The selectivity to isomers products is totally different (Fig.7). It may be explained by the strength of the surface acid sites which are more active in n-hexane isomerisation or in cracking process. Above 190°C, the activity of W₁Ti-PILC, prepared with few amount of tungsten (5%), increases rapidly but its selectivity to isomers products is lower; therefore, a higher selectivity to cracked products is perceived. Noticing is that the surface acidity of the catalysts plays a vital role in determining the catalytic efficiency of the solids for n-alkane isomerisation reaction. It seems that the Bronsted acid sites on W₁Ti-PILC surface play a minor role in

the selectivity towards isomers, which are mainly mono-branched isomers (2-methylpentane and 3-methylpentane). In contrast, the addition of high tungsten amounts (10% and 15%) during mixed intercalation results in samples (W_2Ti -PILC and W_3Ti -PILC) having more strong Lewis acidity and higher selectivity towards isomers. An increase in concentration of acid sites results in an enhanced isomerisation selectivity [13]. A further increase of temperature decreases the selectivity towards isomers; indicating that high temperatures enhance cracking process (Fig. 7).

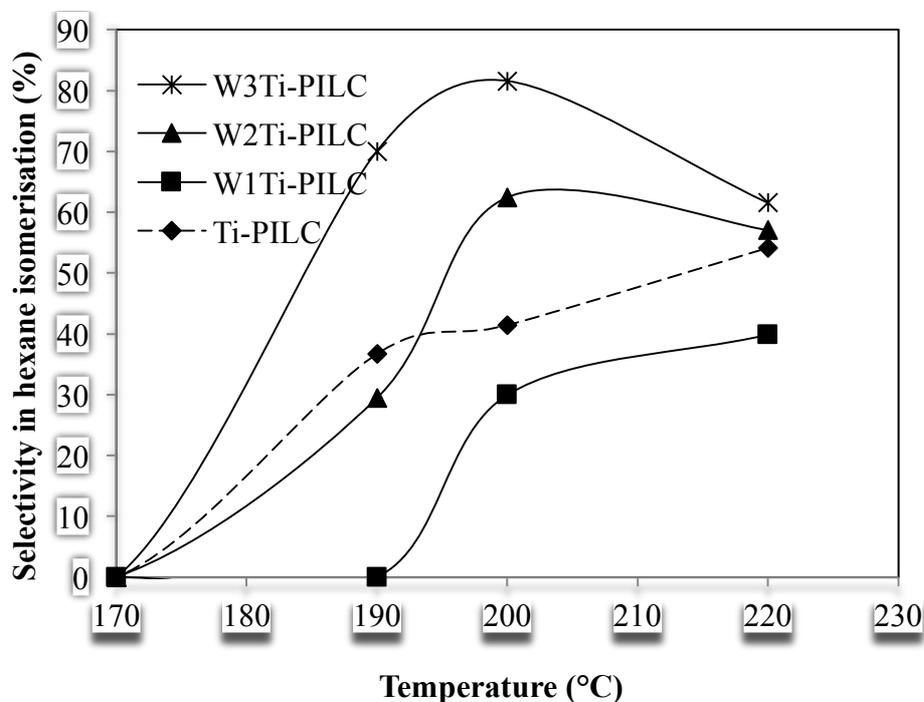


Figure 7: Evolution of selectivity towards isomers products.

As a result, the catalyst W_3Ti -PILC prepared with 15% of tungsten presents the highest isomerisation selectivity due to the presence of strong acid sites well exposed on the surface together with a good distribution of WTi-pillars between the clay sheets and to the high porous structure, as observed by X-Ray diffraction (intense line at 21.36 Å). The strong acidity in W_3Ti -PILC is powerful enough to catalyze the isomerisation towards isomer products despite its small surface area. In addition to the presence of homogeneous (uniform) distribution of pillars, some of the acid sites in the interlayer region are not probably blocked by the pillaring species. In all cases, product distributions reveal that mono-branched isomers form the major proportion of products while di-branched ones are the minor products. This result may be due to the difficult and highly limited formation of di-branched isomers as a consequence of the pore sizes as well as the easy diffusion out of the channels of the mono-branched ones. In addition, the high selectivity of isomers products over W_3Ti -PILC, prepared with 15% of tungsten, may be due to the fast contacts of n-hexane with active acid sites on the surface and the fast diffusion of the products. The increased interlayer distance of PILC allows insertion of more and more reactants within the layers where shape selective constraints leads to a high quantity of mono-branched isomers as the only products.

It is concluded that the good dispersion of WTi-pillars, the well pore structure, the surface acidity on WTi-PILC, prepared with 15% of tungsten, play an important role in the n-hexane isomerisation. This WTi-PILC system needs further investigation using others techniques of characterization and others catalytic tests not available in our research laboratory.

Conclusions

This work is the first report about mixed WTi-pillared clay prepared by simultaneous addition of tungsten and titanium to the clay. The structural, textural, acidic and catalytic properties are largely influenced by the tungsten amounts added to the clay suspension during the mixed intercalation process. The intercalation process is a threshold of 4.4% in terms of tungsten amount that can be incorporated into the clay. The catalytic results, in the

n-hexane isomerisation, show that mono-branched isomers are the products appearing in major proportion over all solids while di-branched isomers are the minor products. The highest efficiency of the best mixed WTi-pillared clay is directly related to its strong acid sites, a great content of tungsten retained by the clay, a good porosity, a high length of pillar and a homogenous pillar distribution between the clay sheets. The results of this first study demonstrate that the physicochemical and catalytic properties of the best mixed WTi-pillared clay make this material very attractive as catalyst or as catalyst support.

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