Synthesis, characterization and catalytic performance of modified clay materials

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Abstract

A solid, stable, porous catalyst (high surface area), with a well dispersed active phase for the activation of oxidant near the organic compound, make it possible to increase the reaction speed appreciably is the objective of this work. Various solids can meet this aim. Pillared clays constitute one of the families most largely studied among the new groups of microporous materials developed by molecular technology. This type of material is obtained by modification of Bentonite (valorization of Bentonite-type clay from Maghnia (Algeria) by oxides and impregnated by a metal of transition, in order to improve the reactivity and the selectivity of the oxidation reactions. A series of vanadia supported on Chromia pillared clay (Cr-PILC) with two different content of chromia (5 mmol and 10 mmol of Cr/ g of clay) were prepared and characterized by UV-vis DR and FT-IR. The catalysts prepared were studied for epoxidation of cyclohexene using TBHP as oxidant. The catalyst found good selectivity (74.6 %) for cyclohexene epoxide with 10V/Cr-PILC5.

Keywords: Vanadia, Chromia, Bentonite, Cyclohexene, Epoxidation.

I. Introduction

Due to their molecular sieve properties, high surface area and physical/chemical adsorption sites, pillared clays (PILCs) found many applications as adsorbents, catalysts and catalyst supports [1-3]. Generally, smectites are used due to their swelling properties and high cation exchange capacity [4, 5]. Although attention is usually focused on pillaring with monometallic pillars, there are some advantages of PILCs composed of mixed polycations. First, the thermal, hydrothermal and catalytic properties of the PILCs can be increased by the use of mixed metal pillaring agents. While one of the pillars' components provides structural and thermal stability with the desired pore structure, the catalytic/ adsorbing sites result from the correct choice of a second pillaring source. Chromium is interesting for catalytic applications because of the different oxidation states [6].

Much attention has been paid over recent years to the catalytic epoxidation of alkenes by various oxidants as epoxides are flexible intermediates [7, 8] and precursors to many useful chemical products [9] such as drugs, agrochemicals, food additives [10], perfume materials and sweeteners [11].

Epoxidation of cyclohexene has been investigated widely using both homogeneous [12, 13] and heterogeneous catalysts [14, 15]. The oxidants for the epoxidation of alkenes include peracids, organic peroxides, hydrogen peroxide, and molecular oxygen. Compared with homogeneous catalysts, heterogeneous catalysts have many advantages such as easy separation and facile recovery of the solid catalyst from the reaction mixture for recycling without tedious workup.

In this study, in order to combine the advantages of clays intercalated with metals of transitions and the properties oxidizing from vanadium and chromium. Vanadium was deposited on bentonite intercalated with chromium with various percentages of metal by impregnation method. The catalytic activity of prepared materials was studied by the epoxidation of the cyclohexene.

II.   Experimental

II.1. Material

Bentonite from Maghnia (West Algeria), was used as the starting material for the PILC synthesis.Bentonite is obtained by washing and purification of the clay of the crystalline phases, (quartz, the feldspar, and calcite). The bentonite fraction is obtained by usual sedimentation then saturated with NaCl (1.5 M). Then the clay (Na^+-bentonite) was centrifuged and washed with distilled water repeatedly until free of Cl^- . The sample was dried at 80 °C during three days. Their chemical composition is: SiO_2, 61%;Al_2O_3, 16.1 %; Fe_2O_3;2.8 %; Na_2O, 1.5 %; MgO, 3.53 %; TiO_2, 0.22 %;K_2O, 1.6 %; CAD, 3.15%; MnO, 0.04 %; H_2O, 10.16 %. The cation capacity of exchange is of 94 meq/100g of clay and it is consisted particles of average diameter lower than 50 μm.

II.2. Preparation of Catalyst

The pillaring reaction of the clay was performed following a procedure proposed by Tzou [16]. Hydroxyl-chromium solution containing chromium pillaring species formed a 0.1 M of chromium nitrate solution by the addition of 0.1 M Na_2CO_3 (OH/Cr=2). The addition was done slowly with continuous stirring and left at 65°C for 2 h. The Na^+-bentonite were dispersed in distilled water (1g/50 mL) and hydroxyl-chromium solution was slowly added with stirring. After 24 h of contact with continuous stirring the solid was washed several times with distilled water in order to remove the electrolyte excess. The amounts of chromium added were 5 and 10 mmol Cr^{3+}/meq clay, leading to Cr-PILC5 and Cr-PILC10, respectively. The resulting material was dried at 80°C and calcined at 300°C. The heating rate was 3°C/min for 4 h.

The materials containing 5 and 10 % of vanadium were prepared by impregnation method at room temperature. The samples were dried at 80 °C for 20 h then calcined at 500 °C with heating rate 10 °C/min for 5 h under flow of air.

II.3. Catalyst Characterization

The various prepared materials are followed by

UV-Visible DR. The apparatus was a spectrophotometer Perkin-Elmer Lambda 800 and was used in reflexion mode diffuses covered the spectral zone 200-800 nm. The analyses infra-red with transform of Fourier (FTIR) were carried out using a Perkin-Elmer spectrometer. The absorption spectra were carried out in the field of the average infra-red, corresponding to numbers of wave ($v = 1/\lambda$) ranging between 400 cm^{-1} and 4000 cm^{-1}).

II.4. Catalytic Application

For the extraction of water, 20 mL of solvent were mixed with 5.5 ml (38.4 mmol) of TBHP during 24 h. The mixture was then decanted to separate the aqueous phase from the organic phase. A mass of 0.1 g of catalyst was introduced into a mono col flask equipped with a cooling agent with the organic phase of (TBHP + solvent) and 3 mL (29 mmol) of the cyclohexene. The mixture was put under magnetic agitation in a Marie bath.

Products were analyzed by an FID gas chromatograph (SCHIMADZU GC 14-B, equipped with a capillary tube "Carbowax solgel" with a stationary polyethylene glycol phase) with increasing temperature (353-393 K). Before the GC analysis the remaining TBHP was decomposed by triphenylphosphine. The amount of TBHP remaining after the reaction was determined by the conventional iodometry.

III.   Results and Discussion

III.1. UV-visible Studies

The spectra of analysis by UV-visible of chromium intercalated in Bentonite with the Cr/Clay (Cr^{3+}/meq clay = 5 and 10 mmol/g) and of chromium nitrate are represented on Fig. 1.
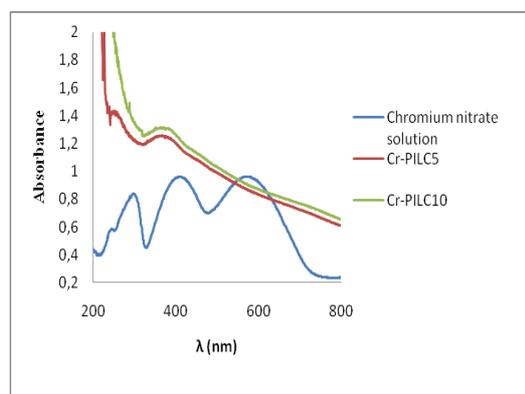

Figure. 1. UV-visible DR spectra of: nitrate of chromium, Cr-PILC5 and Cr-PILC10

For nitrate solution (Cr (NO_3).9H_2O), two broad absorption bands are observed around ~410 nm and ~568 nm (Figure 2), those which are the characteristic value of Cr^{3+} ions in an octahedral symmetry as reported in chromium acetates [16,17].

These peaks are assigned as $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions.

The spectra of Cr-PILC5 and Cr-PILC10 (Figure 2) are characterized by the presence of two intense bands around 260 and 364 nm. These bands are usually attributed to the transfer of charge O-Cr (VI) of the chromate species indicating that the majority of chromium is in the form of Cr (VI) in the tetrahedral state of coordination [18, 19]. The band around 627 nm is the characteristic value of transitions d-d from the species of Cr^{3+} [20].

Figure 2 shows the relative DRS for the catalysts 10V/ Cr-PILC5, 10V/Cr-PILC10, 5V/ Cr-PILC5 and 5V/Cr-PILC10. The spectra are dominated by bands of transfer of charge (TC) of V^{+5}: below 300 nm and the other around 350 - 400 nm. It was announced that, for oxoanions of V^{+5} ($3d^0$), a very strong absorption due to the transition from TC between the ligand and the central atom of V is generally observed in area UV-vis. The band observed below 300 nm can be assigned to the reduced energy of the transitions from transfer of load ligand-with-metal (O^{2-} in V^{5+}) "LMCT" related to the tetrahedral monomeric species of insulation and bandages. It was around 350 - 400 nm with the polymeric vanadium chains. These polymeric species were formed by tetrahedral vanadium species with the formation of the bridges of V-O-V. Moreover, the absorption band around 480 nm indicated presence of the crystalline vanadium species. The absence of the absorption bands around 600-800 nm corresponding to the transitions d-d due to the ions VO^{2+}, indicated, the complete oxidation of the V^{4+} species to V^{5+} [21].
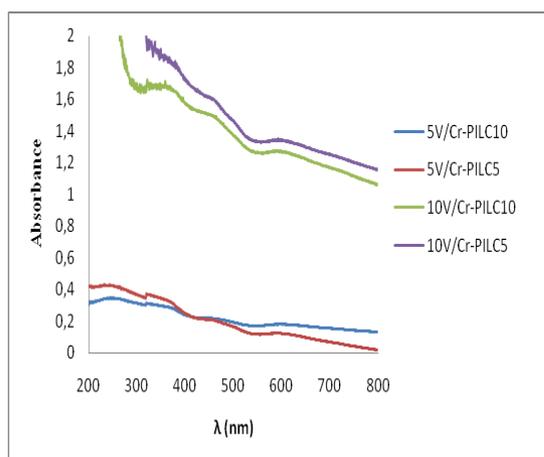

Figure 2. UV-visible DR spectra of catalyst

IR spectroscopy is a useful technique for characterizing Cr species incorporated in the framework of porous materials. The spectra of FTIR of the samples are illustrated in Figure 3. The band of 3628 cm^{-1} is attributed to the structural hydroxyl groups in the mineral layer of clay and the water molecules in spaces of the intercalated layer [21, 22]. The place and the intensity of the band were preserved during the impregnation. With the increase in the ratio Cr/clay and the percentage of vanadium, these bands widened because of the introduction of the groups additional OH$^-$; this was interpreted like an effect of bridging [21].

The band around 1600 cm^{-1} is assigned with the vibrations of the connections of water, and that to approximately 1060 cm^{-1} correspondent with the asymmetrical vibrations of tetrahedral SiO$_2$ [23, 24]. The band of the bond Al-O in the octahedral structure appears to approximately 604 cm^{-1} [25], whereas the band of the bond Al-O in bridge V-O-Al moves around 520 cm^{-1} [25]. As that to 450 cm^{-1} can be assigned to the vibrations of the connections of Si-O-Si in all the samples. A new band at 820 cm^{-1} is assigned with the vibrations of the V=O [26] resulting from the formation of the crystalline vanadium species.
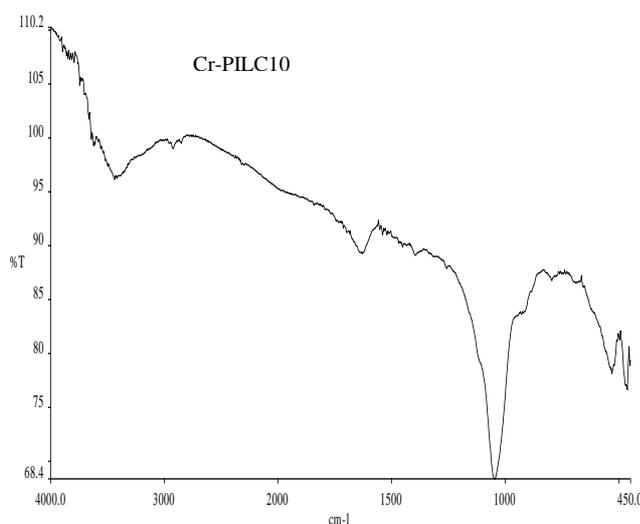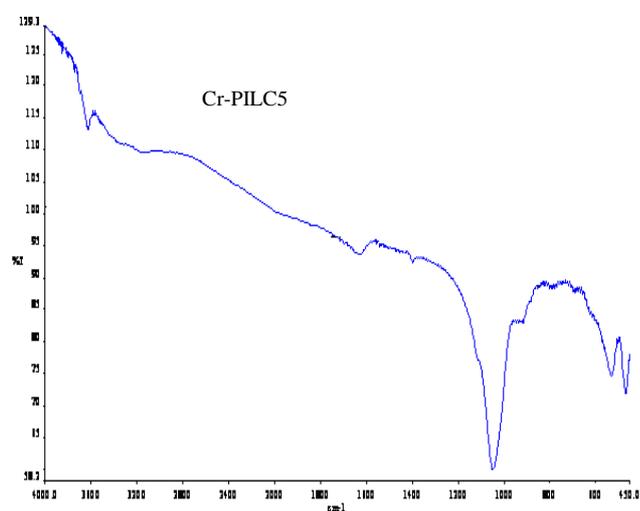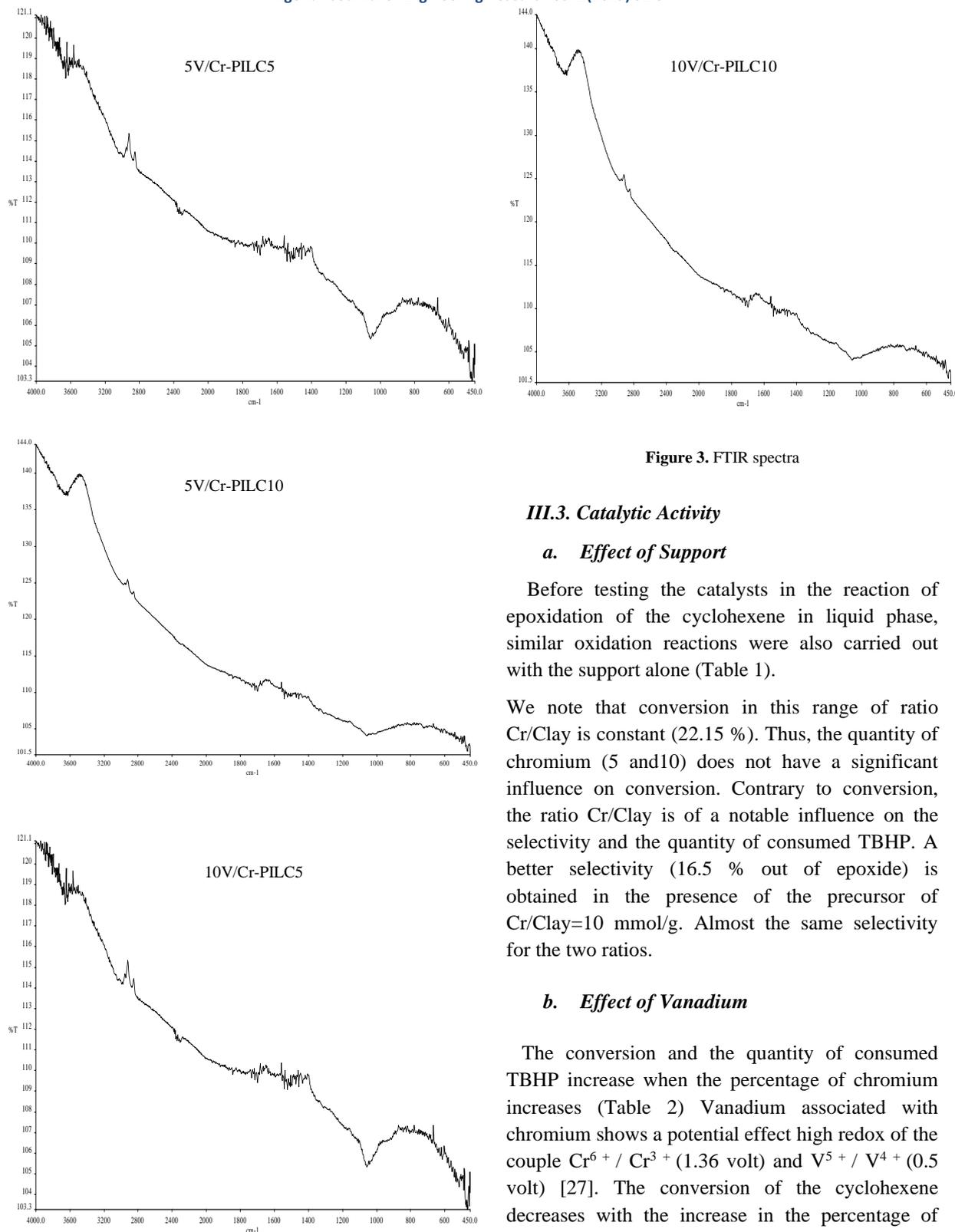
Figure 3. FTIR spectra

III.3. Catalytic Activity

a. Effect of Support

Before testing the catalysts in the reaction of epoxidation of the cyclohexene in liquid phase, similar oxidation reactions were also carried out with the support alone (Table 1).

We note that conversion in this range of ratio Cr/Clay is constant (22.15 %). Thus, the quantity of chromium (5 and10) does not have a significant influence on conversion. Contrary to conversion, the ratio Cr/Clay is of a notable influence on the selectivity and the quantity of consumed TBHP. A better selectivity (16.5 % out of epoxide) is obtained in the presence of the precursor of Cr/Clay=10 mmol/g. Almost the same selectivity for the two ratios.

b. Effect of Vanadium

The conversion and the quantity of consumed TBHP increase when the percentage of chromium increases (Table 2) Vanadium associated with chromium shows a potential effect high redox of the couple Cr^{6+} / Cr^{3+} (1.36 volt) and V^{5+} / V^{4+} (0.5 volt) [27]. The conversion of the cyclohexene decreases with the increase in the percentage of vanadium because of the high polymerization of the vanadium oxide species [28].

Table 1: Effect of support on activity of chromium

Catalyst	Conversion (%)	Selectivity (%)					TBHP Conv (%)
		Epoxide	One	Enol	Enon	Diol	
Cr-PILC5	22.6	2.7	32 .1	5.6	59.6	/	52.4
Cr-PILC10	21.7	16.5	24.7	/	58.7	/	44.9

Reaction conditions: reaction time: 6 hours, temperature; 65-70°C (reflux), solvent n-heptane (20 mL), TBHP/Cyclohexene=1.32, catalyst =0.1g.l

Table 2: Effect of vanadium

Catalyst	Conversion (%)	Selectivity (%)					TBHP Conversion (%)
		Epoxide	One	Enol	Enon	Diol	
10V/Cr-PILC5	26.0	74.6	12.5	5.5	2.4	5.0	45.1
10V/Cr-PILC10	33.5	60.9	22.5	8.6	2.9	4.2	64.3
5V/Cr-PILC5	37.0	51.7	2.7	7.9	37.6	/	37.1
5V/Cr-PILC10	38.0	51.9	21.8	26.3	/	/	46.1

Reaction conditions: reaction time 6 hours, temperature: 65-70°C (reflux), solvent n-heptane (20 mL), TBHP/Cyclohexene=1.32, catalyst = 0.1g

Table 3: Effect of solvent

Catalyst	Conversion (%)	Selectivity (%)					TBHP Conv (%)
		Epoxide	One	Enol	Enone	Diol	
10V/Cr-PILC10[a]	33.5	60.9	22.5	2.9	8.6	4.2	64.3
10V/Cr-PILC5[a]	26.0	74.6	12.5	2.4	5.5	5.0	45.1
10V/Cr-PILC10[b]	17.3	26.4	51.9	/	21.7	/	56.1
10V/Cr-PILC5[b]	29.0	51.7	63.3	/	17.7	/	54.2
10V/Cr-PILC10[c]	19.2	12.6	64.0	/	23.4	/	50.2
10V/Cr-PILC5[c]	37.9	/	86.6	/	13.4	/	70.4

Reaction conditions: reaction time: 6 hours, temperature: 65-70°C (reflux), TBHP/Cyclohexene=1.32, catalyst = 0.1g

(a) solvent : 20 mL n-heptane
(b) solvent : 18 mL n-heptane+2 mL acetic acid
(c) solvent : 10 mL n-heptane+10 mL acetic acid

c. Effect of Solvent

n-Heptane and acetic acid were studied as models to study the solvent effect on the epoxide selectivity (Table 3).

The epoxidation of the cyclohexene gave better epoxide selectivity in non-polar solvent (n-heptane). In the mixture of solvents (polar + non-polar), it lead to the formation of cycloexanone as the main product when the consumed quantity of oxidant increased. This can be explained by the redox potential of V^{5+}/V^{4+} which increased with the acidity of the reactional medium [29] with the high quantity of the acetic acid playing a role of co-catalyst by the formation of peracid [30].

With n-heptane a high selectivity was observed towards the formation of the epoxy which could be due to the effect aprotic of solvent. This quantity increased with the reduction in the percentage of vanadium due to the increase in the number of the intermediate complexes formed between oxidant and oxide of vanadium as shown by Khedher and coll. [30] and also with the increase in the active centers for oxidation which were shown by Gao and coll. [25].

In the case of mixture (c) with low content of chromia, high oxidant consumption was observed without the formation of epoxide. So it can be said that the vanadia favored epoxide formation and chromia favored

mixture (one + enone) formation.

IV. Conclusion

The bentonite intercalated with chromium with the two ratios of 5 and 10 clay mmol/g showed a similar catalytic activity by supporting the oxidation of the cyclohexene rather than the formation of epoxide.

The impregnation of vanadium on bentonite intercalated with chromium improved the catalytic activity and supported the formation of epoxide as a major product in the presence of n-heptane as solvent, justifying the study of the effect of solvent by using catalysts containing 10 % of vanadium.

The use of a mixture of solvent (n-heptane and acetic acid) showed that the increase in acetic quantity of acid supported the formation of the oxidation products compared to the formation of epoxide, as well as an increasing of its consumption without any epoxy formation in the case of 10V/Cr-PILC5.

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