

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 oxidizing properties from vanadium and chromium, the former 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 of Algeria), was used as the starting material for the PILC synthesis. Bentonite was 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: SiO₂, 61%; Al₂O₃, 16.1 %; Fe₂O₃; 2.8 %; Na₂O, 1.5 %; MgO, 3.53 %; TiO₂, 0.22 %; K₂O, 1.6 %; CaO, 3.15%; MnO, 0.04 %; H₂O, 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 form a 0.1 M of chromium nitrate solution by the addition of 0.1 M Na₂CO₃ (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 amount of chromium added was 5 and 10 mmol Cr³⁺/meq clay. The resulting material was dried at 80 °C and calcined at 300 °C. The heating rate was 3 °C/min for 4 h (referred to as Cr-PILC5 and Cr-PILC10).

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 used is a spectrophotometer Perkin-Elmer Lambda 800 used in reflexion mode diffuses covered the spectral zone 200-800 nm. The analyses infra-red with

transform of Fourier (FTIR) are 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 ($\nu = 1/\lambda$) ranging between 400 cm⁻¹ and 4000 cm⁻¹).

II.4. Catalytic Application

For the extraction of water, we mix 20 mL of solvent with 5.5 ml (38.4 mmol) of TBHP during 24 h. The mixture is then decanted to separate the aqueous phase from the organic phase. Into a mono col flask equipped with a cooling agent we introduce 0.1 g of catalyst, the organic phase of (TBHP + solvent) and 3 mL (29 mmol) of the cyclohexene. The mixture was put under magnetic agitation and thermobabbited by 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 and its amount 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 (Cr³⁺/meq clay = 5 and 10 mmol/g) and of chromium nitrate are represented on Fig. 1.

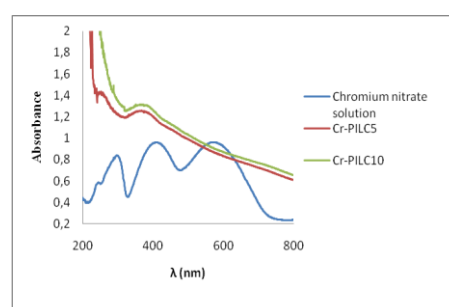


Figure. 1. UV-visible DR spectra of: nitrate of chromium, Cr-PILC5 and Cr-PILC10

For nitrate solution (Cr (NO₃)₃·9H₂O), two broad absorption bands were observed around ~410 nm and ~568 nm (Figure 2) and were characteristic values of Cr³⁺ ions in an octahedral symmetry as in chromium acetates [16,17]. These peaks were assigned as ⁴A_{2g} → ⁴T_{1g} and ⁴A_{2g} → ⁴T_{2g} transitions. The spectra of Cr-PILC5 and Cr-PILC10 (Figure 2) were characterized by the presence of two intense bands around 260 and 364 nm. These bands were usually attributed to the transfer of charge O-Cr

(VI) of the chromate species indicating that the majority of chromium was 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 with 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 around 350 - 400 nm with the polymeric vanadium chains. These polymeric species are formed by tetrahedral vanadium species with the formation of the bridges of V-O-V. Moreover, the absorption band around 480 nm indicates 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+} , indicate the complete oxidation of the V^{4+} species to V^{5+} [21].

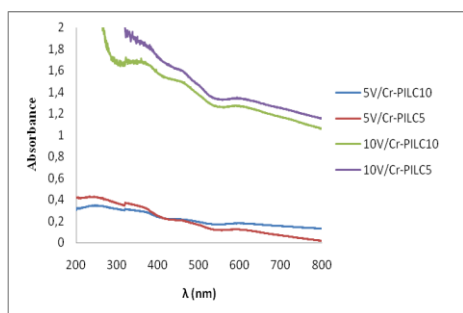


Figure 2. UV-visible DR spectra of catalyst

III.2. FTIR Studies

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 hydroxy 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 widen because of the introduction of the groups additional OH; this is 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 allotted 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 $\text{V}=\text{O}$ [26] resulting from the formation of the crystalline vanadium species.

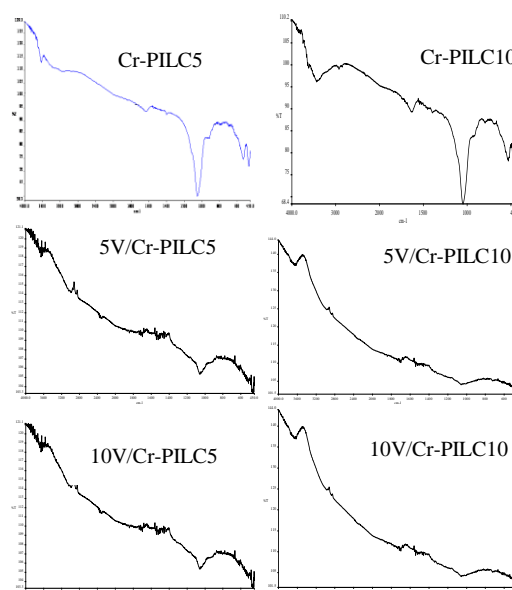


Figure 3. FTIR spectra

III.3. Catalytic Activity

a. Effect of Support

Before testing our 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 and 10) 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 $\text{Cr}^{6+} / \text{Cr}^{3+}$ (1.36 volt) and $\text{V}^{5+} / \text{V}^{4+}$ (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, catalyseur=0.1g.l

Table 2: Effect of vanadium

Catalyst	Conversion (%)		Selectivity (%)				TBHP Conv (%)
	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, catalyseur=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, catalyseur=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 are studied as models to study the solvent effect on the epoxide selectivity (Table 3).

The epoxidation of the cyclohexene gives better epoxide selectivity in non-polar solvent (n-heptane). In the mixture of solvents (polar + non-polar); it leads to the formation of cyclohexanone as

produces principal as the quantity of oxidant consumed increases. This can be explained by the potential redox of $\text{V}^{5+} / \text{V}^{4+}$ which increases with the acidity of the reactional medium [29] and the high quantity of the acetic acid plays a role of co-catalyst by the formation of peracid [30].

With n-heptane we observed a high selectivity towards the formation of the epoxy which can be due to the effect aprotic of solvent, this quantity increases with reduction in the percentage of

vanadium, that can be explained by the increase in the number of the intermediate complex formed between oxidant and oxide of vanadium, shown by Khedher and coll. [30], also with the increase in the active centers for oxidation which are shown by Gao and coll. [25].

In the case of mixture (c) with low content of chromia, we observe high oxidant consumption without formation of epoxide, so we can say that the vanadia favors epoxide formation and chromia favors mixture (one + enone) formation.

IV. Conclusion

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

The impregnation of vanadium on bentonite intercalated with chromium improves the catalytic activity and supports the formation of epoxide like majority product, this in the presence of heptane as solvent. For that we have studied the effect of solvent, by using catalysts containing 10 % of vanadium.

The use of a mixture of solvent (heptane, acetic acid) shows that the increase in acetic quantity of acid supports the formation of the products of oxidation compared to the formation of epoxide. As well as a consumption raised while oxidizing without there being epoxy formation in the case 10V/Cr-PILC5.

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