



Physicochemical properties of vanadium impregnated Al-PILCs: Effect of vanadium source



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SUMMARY

Clay from the Middle Anatolian previously pillared by Al_{13} -Keggin ions and then calcined at $300^\circ C$ (Al-PILC) was impregnated with aqueous solutions of vanadium precursors by impregnation from solution (I), wet impregnation (WI) and washing after wet impregnation (WWI) methods. The crystal and textural properties were evaluated by X-ray powder diffraction (XRD), nitrogen sorption and transmission electron microscopy (TEM) images. Vanadium incorporation into the Al-PILC resulted decreases in the basal spacing from 1.75 nm to 1.35 nm with the preserved typical layered structure. The use of sodium metavanadate ($NaVO_3$) as the source and the impregnation from solution as the incorporation method resulted in less structural deformation in the final solid. Loading of the vanadyl sulfate hydrate ($VOSO_4 \cdot H_2O$) resulted in a higher V/Si ratio in the solid since both settling and ion exchange mechanism occurred. The vanadium was usually bonded in the +5 oxide form, and the particles were settled between these layers and onto the outer surface of the clay particles. The existence of V–O structural bonds and Bronsted and Lewis acid sites were observed in the Fourier transform infrared spectroscopy (FTIR) results. Up to $300^\circ C$ dehydration with high mass loss was observed, followed by the decreases in mass loss, and finally, at around $900^\circ C$, hydroxylation reactions were observed in the TGA/DTA analyses.

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1. Introduction

Intercalated/interlayered materials are prepared by propping apart the lamellae with nano-size pillars, creating a 2-dimensional network of pore. Pillared intercalated layered clays (PILCs) are known examples of this type of material with mesoporous structure [1–9]. Most clay structures pillared by metal precursors are thermally stable, and they exhibit attractive properties as catalysts and catalyst supports because of considerable amount of micropores and broad and still largely pore size distributions in that range [4,5,7,10–12]. They have found a wide range of potential applications as environmental catalysts for air pollution control [13–15]. They are also candidate selective catalysts for the conversion of hydrocarbon-aromatics and enrichment of syngas [16–19] due to their surface acidity in addition to their controlled textural properties. The Al-polyoxocation, i.e., Keggin ion- Al_{13} , has a well-defined chemical composition, structure and charge, and it yields thermally stable PILCs [1,3,6,20]. Second metal incorporation by post-synthesis, such as impregnation from solution, incipient wetness, ion exchange or isomorphous replacement of the aluminum

in the Keggin ions was suggested by several authors to improve the catalytic properties [6,15,16,18,20–25]. Vanadium metal is a common active species used to enhance the activities of pillared clays largely in desulfurization [26–31], NO_x abatement [32–35] and organics conversions, such as selective oxidation, dehydration, dehydrogenation, and alkylation [36–40].

In this study, sodium metavanadate ($NaVO_3$) or vanadyl sulfate hydrate ($VOSO_4 \cdot H_2O$) were loaded as active compounds to the previously synthesized Al-PILC by wet impregnation (WI), washing after wet impregnation (WWI) and impregnation from solution (I) methods. Effect of ionic forms and acid or base character of vanadium sources were investigated by performing several characterization techniques.

2. Experimental

2.1. Starting material and synthesis of Al-PILC as a support

The physicochemical and mineralogical properties of the starting bentonite from the Hancili region (small town in Middle Anatolia), named as Hancili White (HW) bentonite were previously reported by Turgut Başoğlu and Balci (2010) [25]. Synthesis of the Al-PILC support was conducted by following the recipe used by them [25] by keeping all of the parameters the same except for the

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pH of the pillar solution. The pillar solution was synthesized under little acidic conditions, which were adjusted to 3.8 with HCl solution. Air dried (5 days) intercalated samples were calcined at 300 °C for 3 h under air atmosphere.

2.2. Vanadium incorporation to Al-PILC structure

Vanadium incorporated Al-PILCs syntheses were performed by taking advantages of the procedures reported in the literature [36,41–43]. The active compound was loaded to the pre-synthesized Al-PILC support by use of lab-grade sodium metavanadate (NaVO_3) or vanadyl sulfate hydrate ($\text{VOSO}_4 \cdot \text{H}_2\text{O}$) as the second metal source with wet impregnation (WI), washing after wet impregnation (WWI) or impregnation from aqueous solution (I) as the incorporation methods. The quantity of the vanadium in the treatment solution was set as 1 mmol or 2 mmol per gram of Al-PILC. The metal impregnated and dried samples were then calcined at either 300 °C or 500 °C for 3 h under air atmosphere.

Wet Impregnation (WI) method: Five milliliters of vanadium solution containing the desired vanadium content was prepared using of either of the metal sources. The solution was added dropwise onto 1 g of Al-PILC until wetness of the entire solid was achieved; the solid was then dried at 100 °C for 1 h. These wetting and drying steps were repeated 3 times using all of the metal solution. After a final drying at 100 °C for 30 min, the samples were calcined.

Washing after Wet Impregnation (WWI) method: The incorporation of vanadium into the pillared structure was achieved following the steps described in the WI method with the same parameters. The impregnated samples were washed with deionized water to get rid of excess sodium or sulfate ions as confirmed by silver nitrate or barium chloride tests. Four day air dried samples were calcined.

Impregnation (I) from solution method: One gram of Al-PILC powder was added to 100 ml of vanadium solution with the desired loading quantities, and the resultant suspension was stirred for 24 h at 50 °C. The vanadium incorporated solids were separated by centrifugation and then washed, dried at room temperature for four days and then calcined.

2.3. Characterizations

2.3.1. X-ray diffraction patterns

The crystal structure of the bentonite and PILC samples (previously calcined at 300 °C) and the vanadium phases in the structure were evaluated by X-ray powder diffraction (XRD) patterns collected with a Philips PW 3040 diffractometer using a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15406 \text{ nm}$) in the 2θ range of 2–70° with a scan speed of 0.025 s^{-1} and a step size of 0.02.

2.3.2. Nitrogen adsorption/desorption

The textural characteristics of all samples were determined from nitrogen adsorption/desorption isotherms performed on a Quantachrome Autosorb 1C at 77 K. Prior to the physisorption, the samples were degassed at 300 °C for 3 h under high vacuum then, the isotherms were obtained within P/P_0 values of 10^{-7} –0.999. To obtain an adequate characterization of the micropore region, sufficient data points at low pressures were taken. The total pore volume (V_{tot}) and the micro + meso pore volume ($V_{\mu+m}$) were estimated from the desorption data at P/P_0 values of ~ 0.99 and 0.96, respectively. Single (at P/P_0 value of 0.30) and multipoint BET (within P/P_0 values of 0.05–0.30) surface areas were calculated. Mesopore surface areas ($S_{\text{m,BJH}}$), mesopore size distributions and mesopore volumes were estimated by the Barrett–Joyner–Halenda (BJH) method. Micropore size distributions were estimated by the Horvath–Kawazoe (HK) method and the Dubinin–Radushkevich (DR) method. Further t -plots were obtained using the de Boer thickness; then, total surface area ($S_{\text{tot,t}}$) and external surface area ($S_{\text{ext,t}}$)

values were estimated from the slopes of the first and second linear segments of the plots, respectively. The micropore surface area ($S_{\mu,t}$) was found from the difference between the BET and the external surface areas. Micropore volumes, $V_{\mu,t}$ were determined from the intercept of the second linear segment of the t -plots, respectively [44].

2.3.3. Transmission electron microscopy (TEM)

Transmission electron microscopy images of the Al-PILC support and the support impregnated with NaVO_3 via WI were taken on a TESLA BS 500 and Jeol JEM 1010 equipped with a Mega View III CCD camera at different magnifications. The TEM specimens were prepared by dispersing the powders in 2-propanol by 20 min ultrasonic treatment, dropping them onto holey carbon film supported on a copper grid by means of a micro pipette and then drying in air.

2.3.4. Energy dispersive X-ray spectroscopy (EDS)

The near surface compositions of the bentonite and the metal-PILCs, which were calcined at 300 °C, were obtained using energy dispersive X-ray spectroscopy (EDS) equipped in the electron microscope JSM Jeol 6060 with an accelerating voltage of 25 kV. The metal compositions were measured over the selected area and reported in their oxide and metallic forms.

2.3.5. X-ray photoelectron spectroscopy/electron spectroscopy for chemical analysis (XPS/ESCA)

XPS data were obtained by a SPECS ESCA X-ray photoelectron spectrometer equipped with an Mg/Al quadrupole anode and a EA 200 multiple channel detector. Binding energies were calibrated using the C1s peak (284.5 eV) as a reference.

2.3.6. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy spectra of the oven dried bentonite and all of the PILCs (previously calcined at 300 °C) were collected at 4 cm^{-1} resolution on a Bruker Vertex 70 equipped with a MCT detector to qualitatively identify the chemical composition and surface acidity of the materials. The samples were mixed with KBr with a mass ratio of 1/100 for the measurement. Bronsted and Lewis properties were studied by means of pyridine adsorption at room temperature and subsequent desorption at different temperatures by allowing approximately 1 h dwell time at each desorption temperature. The pyridine dosing was achieved by exposing the oven-dried samples to pyridine vapor at room temperature under a vacuum of 10^{-4} torr for a week.

2.3.7. Thermal analysis (TGA/DTA)

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of the raw bentonite, Al-bentonite, Al-PILC and some vanadium impregnated pillared samples were performed on a Setaram Simultaneous TG/DTA instrument under air flows with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ from room temperature to 1000 °C.

3. Results and discussion

In this work, supported vanadium catalysts on aluminum-pillared clays were synthesized to study the role of the vanadium source, quantity and incorporation method. Sodium metavanadate (NaVO_3) and vanadyl sulfate hydrate ($\text{VOSO}_4 \cdot \text{H}_2\text{O}$) which give respectively basic and acidic solutions, were used as the sources to see the interaction of them with Al-Keggin pillar. The Al-PILC support was calcined at relatively low temperature (300 °C) in order to bind some of the vanadium to the semi-stable Al-Keggin structure. With various characterization techniques, how the synthesis conditions affected the product properties were investigated.

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