

CHARACTERIZATION OF ACID-BASE CENTRES OF VERMICULITE/ α -Fe₂O₃ NANOPARTICLES CATALYST APPLIED FOR DEPOLYMERIZATION OF POLYSTYRENE

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<https://doi.org/10.37904/nanocon.2019.8466>

Abstract

The acid-base centres on the catalyst surface play important role in catalysis chemistry, influencing protons activity in reaction mechanism. The work presents the characteristics of acid-base centres on the vermiculite/ α -Fe₂O₃ nanoparticles composites, when used as catalyst for the chemical recycling of polystyrene to styrene. The iron oxides are often used in chemical/petrochemical application as catalyst. The vermiculite is cheap natural clay mineral, which is commonly used as catalyst support. The vermiculite/ α -Fe₂O₃ nanoparticles composites were prepared by precipitation and calcination at 500 and 700 °C. The acid-base centres on the catalyst surface were characterized by TPD (Temperature Programmed Desorption) method allowing to detect the molecules NH₃ and CO₂ desorbed from the surface when the surface temperature is increased. The temperature of surface and the peak from desorbed molecules suggest the strength of chemical bond between desorbed molecules and surface. Before desorption, the NH₃ and CO₂ are adsorbed on the surface of catalysts by chemisorption. The TPD method was supplemented with the laboratory analyses using XRD and SEM.

It has been found that the vermiculite/ α -Fe₂O₃ nanoparticles composite calcined at 500 °C has medium-strong base centres on the surface, although the pure vermiculite is a light acid and pure α -Fe₂O₃ is a neutral material. For this reason, it can be successfully applied to the depolymerization reaction in conversion to the styrene monomer. The calcination temperature 700 °C did not improve the basicity, but rather led to its suppression.

Keywords: Vermiculite, hematite, structural properties, acid-based centres, catalyst

1. INTRODUCTION

The clays are big technology importance due to their properties such as inertia, stability, reactivity, and catalytic activity. Significant representatives of clay minerals characterized by a layered 2:1 type structure. Vermiculites are very abundant and much cheaper in comparison with other clays. The 2:1 layers are composed of two tetrahedral and one octahedral sheet and interlayer space between them occupied by hydrated cations. Raw vermiculites are classified as mixed-layer phyllosilicates or interstratified phyllosilicates. Recently, interest in vermiculite as catalyst support has increased [1].

One of important properties of catalytic materials are acid-based centres on the surface of catalyst. In acid catalysis and base catalysis, a chemical reaction is catalysed by an acid or a base. According to Brønsted-Lowry acid-base theory, the acid is the proton (H⁺) donor and the base is the proton acceptor. And just basic centres are necessary for depolymerization of polystyrene to styrene monomer. During depolymerization, the polystyrene is cracking on the shorter compound as tri-, or dimers of styrene, styrene monomer and other cyclic compound such as toluene, xylene isomers, methylstyrene, etc. [2]. The presence of basic centres on the catalyst surface take the proton from compound structure, which lead to production of styrene monomer

from tri- and dimer of styrene. On the other site, acid centres on the catalyst surface give a proton to reaction and benzene or indene are produced in higher amount.

A temperature programmed desorption (TPD) technique is fundamental technique, which has been developed especially for catalysis. It can be used to study the interaction of reaction gases with solid surfaces, to evaluate active sites on catalyst surfaces and to understand the mechanisms of catalytic reactions including adsorption, surface reaction and desorption [3].

Adsorption of CO₂ is one of the best ways to study the basicity on the mixed oxides surface. CO₂ has been a strong bond (by chemisorption) to basic centres, which are represented by O²⁻ into the surface. Adsorption of CO₂ (as Lewis acid) on basic centres lead to creation of several form of carbonates - i.e. monodentate as strong basic centres, bidentate as medium-strong basic centres and bicarbonate as weak basic centres (see **Figure 1**).

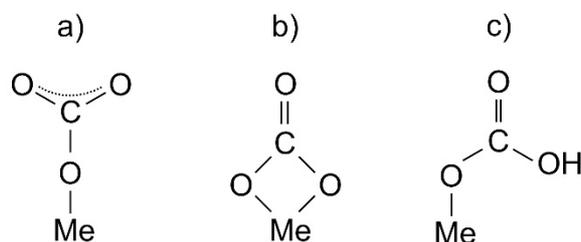


Figure 1 Bond between metal and CO₂ molecules: a) monodentate carbonates, b) bidentate carbonates and c) bicarbonates

Monodentate carbonate is formed on low-coordinated oxygen anions O²⁻ representing strongly basic centres. Bidentate carbonates are formed on metal-oxygen pairs Meⁿ⁺-O²⁻ (where n = 2 or 3). These pairs are designated as moderately strong basic centres. The formation of bicarbonate requires the presence of surface hydroxyl groups, which may be considered as weak bases in the mixed oxide materials investigated. In addition to the relatively strong bonding of CO₂ to the basic centres, CO₂ can be also weakly bond (by physisorption) to the acid centres, which are Meⁿ⁺ surface ions. Such complexes are formed only at equilibrium gas pressures. On the other hand, CO₂-cation complexes are not included in the TPD experiment due to their low stability [4].

The acidity of mixed oxides can be studied by adsorption of NH₃. NH₃ is a strong bond (by chemisorption) to acidic centres, which represent various surface Meⁿ⁺ ions. NH₃, such as a Lewis base, can provide a free electron pair on nitrogen to form relatively stable metal cation complexes. Furthermore, ammonia can interact weak bond (by physisorption) with basic centres on the oxide surface due to hydrogen bonds. Chemisorbed NH₃ interacts via a nitrogen pair with Lewis acid centres represented by unsaturated metal cations and, where appropriate, simultaneously interacts via a hydrogen bond with a nearby basic oxygen or hydroxyl group. Ammonia TPD is often used as the main method of characterizing the acid centre content. A small molecular size of ammonia allowed to penetrate all solid pores. Since most chemisorbed NH₃ interacts with acid centres on the oxide surface, their concentration can be determined by TPD. NH₃ complexes with basic centres are not included in the TPD experiment due to lower stability [4].

2. MATERIALS AND METHODS

2.1. Synthesis

Raw vermiculite from Palabora mine (Ver-P), South Africa was ball-milled in a cylindrical zirconium container for 15 min at 350 rpm and the fraction under 40 μm obtained by sieving was used for other synthesis.

Ver-P-500 was prepared by calcination at 500 °C for 4 h.

Ver-P/Fe-500 and Ver-P/Fe-700 were synthesized by mixing the dispersion of 4g Ver-P in 100 mL of deoxygenated distilled water with hematite nanoparticles under magnetic stirring for 3 h at 80 °C. Then the samples were filtered, washed with distilled water for several times, dried at 80 °C and calcined at 500 °C or 700 °C for 4 h. The hematite nanoparticles were prepared by the chemical precipitation method in the aqueous solution by dissolving 4g FeCl₃.6H₂O (precursor) in 100 mL of deoxygenated distilled water under magnetic stirring for 30 min at 80 °C. The precipitating agent, base solution of NaOH (30 wt.%), was added gradually drop wise to maintain a pH value of 11 to the dispersion of vermiculite.

2.2. Material characterizations

The temperature-programmed desorption of probe molecules NH₃ and CO₂ (NH₃-TPD, CO₂-TPD) was performed on a Micromeritics AutoChem 2950HP (Micromeritics Instrument Corp., USA) equipped by TCD detector. For TPD, approximately 100 mg of sample was placed in a quartz reactor. The reactor was heated (10 °C min⁻¹) to 500 °C and maintained for 10 min in flow of helium (99.9996, Linde gas) (25 ml min⁻¹). Subsequently, the sample was cooled down to 70 °C (10 °C min⁻¹) and saturated in flow of gas mixture (10 % CO₂ in He or 10% NH₃ in He) for 30 min. Then, the sample was purged in the flow of helium for 60 min in order to remove the physically absorbed molecules. The TPD experiment itself was carried out with a linear heating rate of 10 °C min⁻¹ in a flow of He (25 ml min⁻¹).

The pure vermiculite and catalysts α -Fe₂O₃/vermiculites were tested by X-ray diffraction for phase analysis. Elementary compositions were measured by X-ray fluorescence.

Phase composition and microstructural properties were determined using X-ray powder diffraction (XRD) technique. XRD patterns were obtained using Rigaku SmartLab diffractometer (Rigaku, Japan) with detector D/teX Ultra 250. The source of X-ray irradiation was Co tube (CoK α , $\lambda_1 = 0.178892$ nm, $\lambda_2 = 0.179278$ nm) operated at 40 kV and 40 mA. Incident and diffracted beam optics were equipped with 5° Soller slits; incident slits were set up to irradiate area of the sample 10 x 10 mm (automatic divergence slits) constantly. Slits on the diffracted beam were set up to fixed value 8 and 14 mm. The powder samples were gently grinded using agate mortar before analysis and pressed using microscope glass in rotational sample holder and measured in the reflection mode (Bragg-Brentano geometry). The samples rotated (30 rpm) during the measurement to eliminate preferred orientation effect. The XRD patterns were collected in a 2 θ range 5° - 90° with a step size of 0.01° and speed 0.5 deg.min⁻¹. Measured XRD patterns were evaluated using PDXL 2 software (version 2.4.2.0) and compared with database PDF-2 issued by ICDD, release 2015.

3. RESULTS

3.1. Temperature Programmed Desorption (TPD)

Temperature programmed Desorption of ammonia (TPD-NH₃) was used for the study to determine the distribution of acid centres. The amount of desorbed ammonia then correlates with chemisorbed NH₃ on the mixed oxide surface. Desorbed ammonia is record by TCD (thermal conductivity detector). This signal is named as TPD curves and TPD curves of acid centres are shown on **Figure 2** (left). First, pure vermiculite calcined at 500 °C (marked as Ver-P-500) was analysed. The ammonia desorption curve is observed in a wide temperature range, which indicates a wide distribution of acid sites. It can be seen two peaks around 100 - 200 °C and 250 - 350 °C, which correspond with weak acidic and medium-strong acidic centres, respectively. Other samples (marked as Ver-P/Fe-500 and Ver-P/Fe-700) has been one's peak caused to desorption of ammonia with maximum of peak around 150 °C. This peak corresponds with very weak acidic centres. Medium-strong acidic centres on pure vermiculite were probably covered by hematite in these samples, which was precipitated on the vermiculite surface.

Temperature programmed Desorption of carbon dioxide (TPD-CO₂) was used for the study to determine the distribution of basic centres. The TPD experiment was performed from 25 °C to 500 °C and TPD curves of basic centres are shown on **Figure 2** (right). First, pure vermiculite (marked as Ver-P-500) was analysed. The carbon dioxide desorption curve is observed in a wide temperature range, which indicates a wide distribution of basic sites. In contrast with ammonia desorption, there are only major peak of weak basic centres between 100 - 200 °C, whereas peak of medium-strong basic centres between 250 - 350 °C is bland. On the other hand, sample Ver-P/Fe-500 has distinctly high peak between 200 - 350 °C, which correspond to the high content of medium-strong basic centres on the surface. The last samples Ver-P/Fe-700 is contains only weak basic centres.

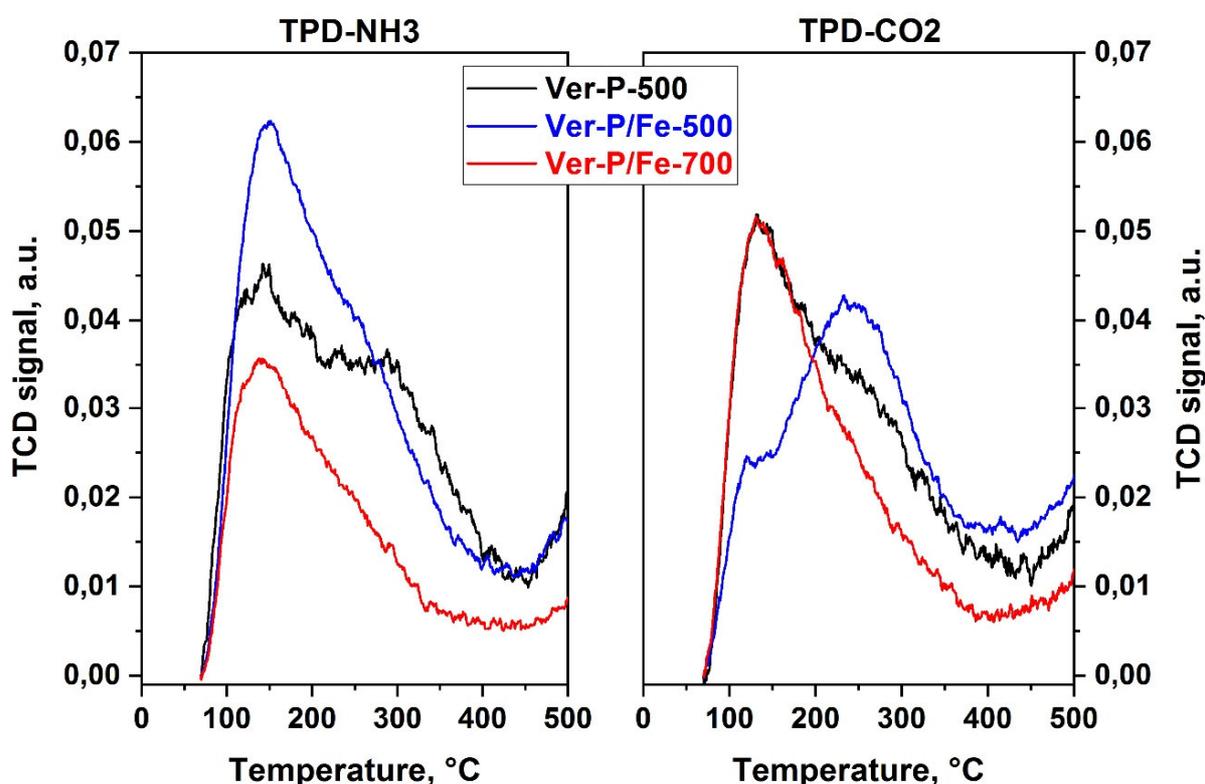


Figure 2 Acid (TPD-NH₃) and basic centres (TPD-CO₂) on the surface of vermiculite samples

3.2. X-ray Fluorescence (XRF)

Composition of prepared samples is listed in **Table 1**. Precipitation of hematite of vermiculite surface changes significantly composition of minerals. The iron oxide content increases three times, on the other site, content of another main oxides as magnesium oxide, alumina or silica decreases by one third.

For a better understanding of the formation or destruction of acidic and basic centres, it is necessary to look at the ratios between individual metals (Me²⁺ or Me³⁺) on the surface. The ratio between silica and alumina is around 5 (listed to **Table 2**), that is corresponding to the acidic centres on the surface, as discussed in zeolites theory [5]. But this was not confirmed with our TPD measurements, because Ver-P/Fe-500 has more basic than acidic centres. The other ratio for comparison is the ratio between magnesium oxide and alumina. The ratio is equal 3 for Ver-P-500 and Ver-P/Fe-500, which are sample with medium-strong basic centres. But for sample Ver-P/Fe-700 the ratio decreases to 2.4 and medium-strong basic and acid site were not detected. This results probably correspond with fact, that increasing content of magnesium oxide against alumina lead to creation of medium-strong basic centres which are created by Mg²⁺-O²⁻ [6].

Table 1 Composition of vermiculites samples analysed by XRF

	Ver-P-500 (wt. %)	Ver-P/Fe-500 (wt. %)	Ver-P/Fe-700 (wt. %)
SiO ₂	40.2	28.7	31.7
MgO	24.8	17.5	15.6
Fe ₂ O ₃	11.7	37.9	37.2
Al ₂ O ₃	8.4	5.9	6.4
K ₂ O	6.2	4.2	1.8
CaO	4.6	2.9	4.6
P ₂ O ₅	2.0	1.5	1.1
TiO ₂	1.8	1.0	0.8

Table 2 Ratio between individual oxides

	Ver-P-500	Ver-P/Fe-500	Ver-P/Fe-700
SiO ₂ /Al ₂ O ₃	4.8	4.9	4.9
MgO/Fe ₂ O ₃	2.1	0.5	0.4
MgO/Al ₂ O ₃	3.0	3.0	2.4

3.3. X-ray Diffraction (XRD)

Precipitations of hematite was performed correctly as seen in the XRD spectrum (see **Figure 3**).

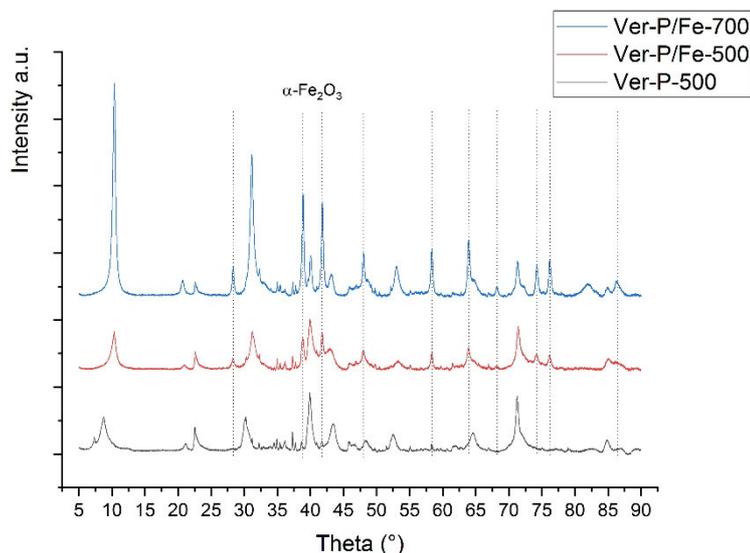


Figure 3 Diffraction patterns of the pure vermiculite and the vermiculite samples with hematite

4. CONCLUSION

The vermiculite/ α -Fe₂O₃ nanoparticles were prepared by precipitation and calcinated at different temperatures to the composites. Temperature Programmed Desorption show acid and base centre on surface of these nanocomposites, which can be marked as catalysts. The Ver-P-500 as a calcined pure vermiculite is a material

with wide distribution of acid and basic centres, although it has medium-strong acid centres. A very interesting finding is that although there is a lot of magnesium in the vermiculite structure, this magnesium does not participate significantly in the formation of basic sites. On the other hand, Ver-P/Fe-500 was presented as material with medium-strong basis centres. And these centres can be used as proton acceptor in catalysed reactions (e.g. depolymerization of PS). The formation of these centres is probably due to a significant decrease in alumina in the vermiculite structure. In the future, it would be appropriate to measure these basic centres using FTIR analysis. Finally, samples treatment by calcination temperature 700 °C has not any significant acid or basic centres, whereas lead to the higher crystalline hematite.

ACKNOWLEDGEMENTS

The work was supported from ERDF "Institute of Environmental Technology - Excellent Research " (No. CZ.02.1.01/0.0/0.0/16_019/0000853) and Student grant projects SP2019/91. „Experimental results were accomplished by using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2018098. The publication/presentation has been prepared using the results achieved with the infrastructure in open access regime within the project Efficient Use of Energy Resources Using Catalytic Processes (project code LM2015039) which was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic within the targeted support of large infrastructures. The project has been integrated into the National Programme for Sustainability I of the Ministry of Education, Youth and Sports of the Czech Republic through the project Development of the UniCRE Centre, project code LO1606.

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