Influence of hydrotalcite preparation conditions on its physico-chemical properties

Miroslava Mališová[a], Michal Horňáček[a], Pavol Hudec[a],
Jozef Mikulec[b], Vladimír Jorík[c], Elena Hájeková[a]

[a]*Department of Organic Technology, Catalysis and Petroleum Chemistry,*
Faculty of Chemical and Food Technology, Slovak University of Technology,
Radlinského 9, 812 37 Bratislava, Slovakia
[b]*Research Institute of Petroleum and Hydrocarbon Gases, Vlčie Hrdlo, 820 03 Bratislava, Slovakia*
[c]*Department of Inorganic Chemistry, Faculty of Chemical and Food Technology,*
Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia
mamiroslava@gmail.com

Abstract: The aim of the research was to prepare and characterize hydrotalcite synthesized under different preparation conditions. The most common hydrotalcite preparation is the co-precipiaton method. The preparation process strongly influences the catalytic properties of hydrotalcite; therefore, optimal conditions have to be determined. During the study, seven samples of the catalyst were prepared in the pH range from 8 to 12 and the synthesis temperature range from 25 to 55 °C. Based on several catalyst properties, optimal synthesis pH 10 was found. Ideal temperature of the preparation was determined to be 35 °C, but the temperature does not have a significant effect on the catalyst properties.

Key words: hydrotalcite, preparation conditions, co-precipitation, catalyst

Introduction

Several types of layered double hydroxides (LDH) were studied for various applications depending on their crystallinity and catalyst properties. LDH synthesis dates from 1930, when precipitation was used to prepare samples (Sato et al., 1988). A wide range of applications of this special layered structure have been studied. For example, oil adsorbents, sorption agents for industrial, sensors in electrochemistry and flame retardants in polymer nanocomposites (Cavani et al., 1991, Salomão et al., 2013).

Hydrotalcite (HT) belongs to the group of LDH, also known as anionic clays. In comparison to cationic clays, anionic clays are not very common in nature but their preparation in laboratory is much easier. The most widely used HT is magnesium-aluminum type with the chemical formula $[M_n^{2+}M_m^{3+}(OH)_{2(n+m)}]_m^+[A_x^-]_{m/x} \cdot {}_yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations and A_x is the interlayer anion. An identical formula was found for the natural mineral hydrotalcite (Nishimura et al., 2013). Layered structure is based on rotation of positively charged octahedral layers and interlayer space. Charge balancing anions and water molecules occupy the interlayer space (Baskaran et al., 2015). The range of metal cations from the positive charge layer is relatively wide and is determined by their size, which should be similar to that of Mg^{2+} for divalent cations and that of Al^{3+} for trivalent cations (Basąg et al., 2016).

Scheme 1 shows a simplistic representation of the hydrotalcite structure (Baskaran et al., 2015).
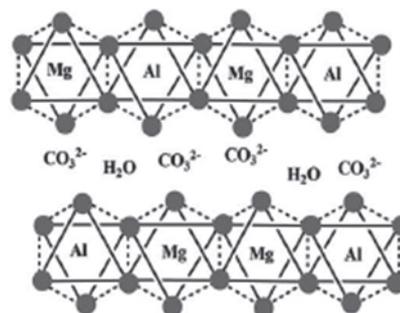
Scheme 1. Simplistic representation of hydrotalcite structure (Baskaran et al., 2015).

Synthesis

Co-precipitation is the most common method to prepare LDH like hydrotalcite. There are two different way of preparation: co-precipitation at variousable pH and at constant pH values. At constant pH, preparation is based on addition of NaOH solution to maintain the pH value constant during the whole time of preparation. In the variable pH method, a solution containing salts of the cations (divalent and trivalent) is added to an alkaline solution containing the anion to be interlayered. With the increasing concentration of alkaline metals, pH decreases. Co-precipitation is usually carried out at relatively low temperatures, usually up to 55 °C,

to prevent secondary formation reaction of simple hydroxides (Salomão R, et al., 2013).

Hydrotalcite application

Thanks to its special layered structure, hydrotalcite can be used for a variety of applications such as base, redox and photo-catalyst, as well as adsorbents. As a base catalyst, hydrotalcite can catalyze a wide range of reactions such as aldol condensation, hydroxylation, isomerization and others. Nowadays, many studies deal with hydrotalcite use as an adsorbent to reduce emissions of NO_x and SO_x because of its large sorption capacity. Hydrotalcite has drawn attention also as a catalyst to produce biofuels as it is very effective for transesterification of vegetable oils to produce biofuels. Easy preparation by co-precipitation, which is quick and not complicated, as well as its great catalyst properties are its advantage.

Experimental

One of the most common methods to prepare hydrotalcite was used to prepare seven samples. First solution (A) was Na_2CO_3 ($c = 0.5$ mol/dm³) dissolved in 1 L of deionized water. Solution of metal nitrates (solution B) prepared from $Mg(NO_3)_2$ and $Al(NO_3)_3$ with the concentration of 1.0 mol/dm³ was slowly added (10,44 ml/min) to solution A for 1 hour. Preparation of hydrotalcite samples was realized in the pH range from 8 to 12 and temperature range from 25 to 55 °C. The pH value was kept constant by addition of NaOH solution with the concentration $c = 3.0$ mol/dm³. Addition of NaOH was controlled by a pH electrode measuring the pH value throughout the reaction. Temperature was monitored by a temperature sensor connected to a heating plate. Each sample aged for 24 hours. After the solution sedimentation, the sediment was washed with at least 2 L of distilled water and filtered. Drying was carried out for 1−2 hours at 80 °C. After the preparation, all samples were stored in an airtight container and subsequently calcined at 150 °C and 450 °C. Prepared samples were used for further measurements.

Crystalline phase identification and phase purity determination of the prepared samples were carried out by XRD analysis using a STOE THETA-THETA diffractometer, with CoKα radiation, scan range of 2.90 ° − 90.00 ° 2Θ and at the step size of 0.02 °.

Surface characteristics were measured by physical adsorption of nitrogen at –196 °C using ASAP-2400 (Micromeritics). Overnight evacuation of the samples at 150 °C and 450 °C preceded the adsorption analysis. Specific surface area, S_{BET}, was obtained using the conventional BET isotherm ($p/p_0 = 0.05 − 0.30$). The surface of mesopores, S_t, and the volume of micropores, V_{micro}, were calculated from the t-plot using the Harkins–Jura master isotherm. The value of the total pore volume, V_a, was determined from adsorption data at relative pressure $p/p_0 = 0.99$. From desorption branches of the isotherms, pore size distribution was calculated using the BJH method.

Temperature programmed desorption of carbon dioxide as a probe molecule (TPD-CO_2) was carried out in equipment with a TCD detector. The catalyst amount of 200 mg (grain of 0.4−0.71 mm) was placed in a quartz reactor. Before the TPD experiment, the catalysts were activated at 450 °C for 80 minutes in helium flow (75 mL/min). Subsequently, the catalysts were cooled down to 25 °C and treated with CO_2 flow (99 % purity, 50 mL/min) for 30 minutes. The weakly adsorbed CO_2 was removed by flushing the sample with helium (110 mL/min) at 25 °C for 80 minutes. Desorption of CO_2 was measured by heating the catalyst from 25 °C to 500 °C at the heating rate of 5 °C/min in helium flow. The amount of basic sites was calculated from the area of CO_2 desorption peaks with help of calibration using a known amount of CO_2 desorbed from $MgCO_3$ decomposition.

SEM images were taken using field emission JEOL JSM-7600F SEM at the accelerating voltage of 5 kV and working distance of 4.5 mm.

Result and Discussion

Seven samples of aluminum-magnesium hydrotalcite were prepared for the study under various synthesis conditions. Temperature of the synthesis as well as pH were varied for each sample. Table 1 presents symbols of individual samples together with their preparation conditions. All samples were prepared with the same amount of metal nitrates and Na_2CO_3 solution.

Tab. 1. Samples preparation conditions.

Sample	pH of synthesis	Temperature of synthesis [°C]
HTT/10/25	10	25
HTT/08/25	8	25
HTT/09/25	9	25
HTT/12/25	12	25
HTT/10/45	10	45
HTT/10/55	10	55
HTT/10/35	10	35

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Temperature was controlled by means of a temperature sensor connected to a heating plate while pH was maintained at a constant value during the reaction by NaOH solution. Designation of the samples was as follows: HTT/pH/temperature.

Specific surface area – BET
One of the most important properties of a catalyst is its specific surface area. It tells us about the catalyst adsorption capability. With the increasing specific surface area, hydrotalcite gains better properties for the catalysis of various reactions.

The determined specific surface areas of samples calcined at 150 °C and 450 °C with different preparation pH can be seen in Table 2. HTT/10/25 prepared at pH 10 shows the highest specific surface area and pore volume at both calcination temperatures.

A graphical comparison of the samples prepared at 25 °C and calcined at 150 °C and 450 °C with different pH can be seen in Figure 1. A significant increase in the specific surface area for the sample prepared at pH 10 can be observed.

Tab. 2. Determined surface area of samples with different preparation pH.

Sample	150 °C		450 °C	
	S_{BET} [m²/g]	V_a [cm³/g]	S_{BET} [m²/g]	V_a [cm³/g]
HTT/08/25	27	0.127	175	0.279
HTT/09/25	38	0.177	177	0.411
HTT/10/25	131	0.468	236	0.759
HTT/12/25	24	0.078	86	0.256

Based on Table 2 it is clear that from the point of view of surface area, optimal pH for hydrotalcite preparation is 10. In Table 3, calculated specific surface areas of samples prepared at pH 10 can be seen. The range of preparation temperature was from 25 to 55 °C and after the preparation, samples were calcined at 150 °C and 450 °C. It can be seen that the sample of HTT/10/35 synthesized at 35 °C shows the highest specific surface area compared to other samples.

However, in Figure 2 it can be seen that the synthesis temperature does not significantly affect
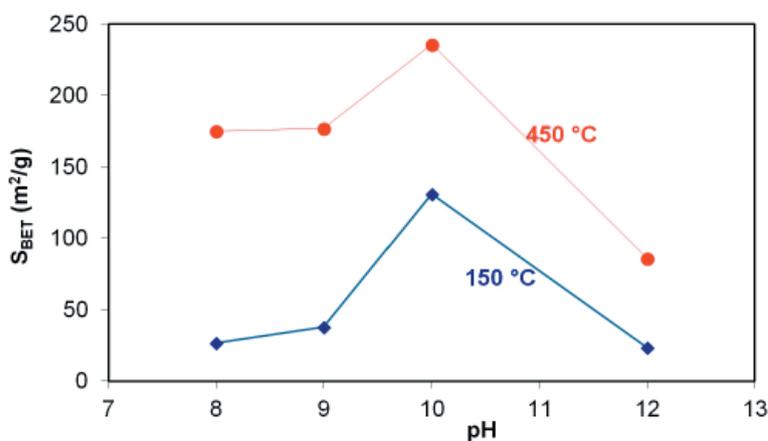
Fig. 1. Comparison of samples prepared with different pH calcined at 150 °C and 450 °C.
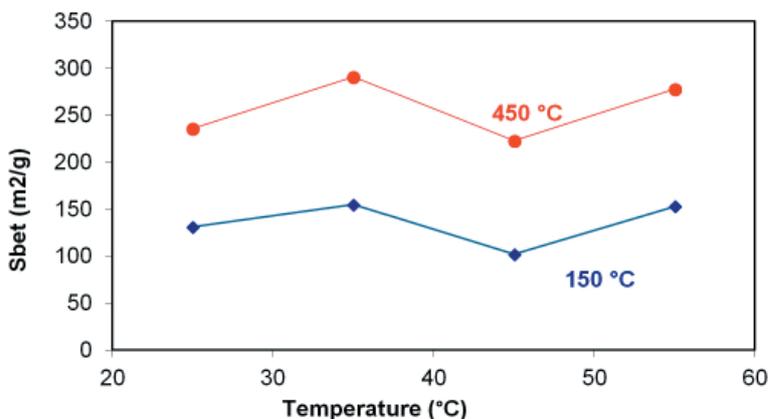
Fig. 2. Comparison of surface area of samples prepared at different synthesis temperatures and calcined at 150 °C and 450 °C.

Tab. 3. Determined surface area of samples with different preparation temperatures.

Sample	150 °C		450 °C	
	S_{BET} [m²/g]	V_a [cm³/g]	S_{BET} [m²/g]	V_a [cm³/g]
HTT/10/25	131	0.468	235	0.759
HTT/10/35	<u>155</u>	0.630	<u>291</u>	0.856
HTT/10/45	102	0.457	223	0.721
HTT/10/55	153	0.620	278	0.907

the specific surface area of hydrotalcite; however, four samples are not enough to make a conclusion whether the preparation temperature affects the specific surface area at all.

XRD

Influence of preparation temperature and synthesis pH on hydrotalcite properties has been investigated also by X-ray diffraction. XRD patterns of samples prepared at constant calcination temperature of 450 °C and different preparation temperatures are shown in Figure 3. This calcination temperature was chosen because hydrotalcite layered structure changes to mixed metal oxides structure. Higher calcination temperatures caused destruction of the layered structure and led to the formation of spinel structure.

The XRD pattern shows typical peaks of mixed metal oxide structure consisting of a symmetrical and sharp peak with high intensity at low 2θ angle (8−10) and asymmetric broad peaks at high 2θ angle. These
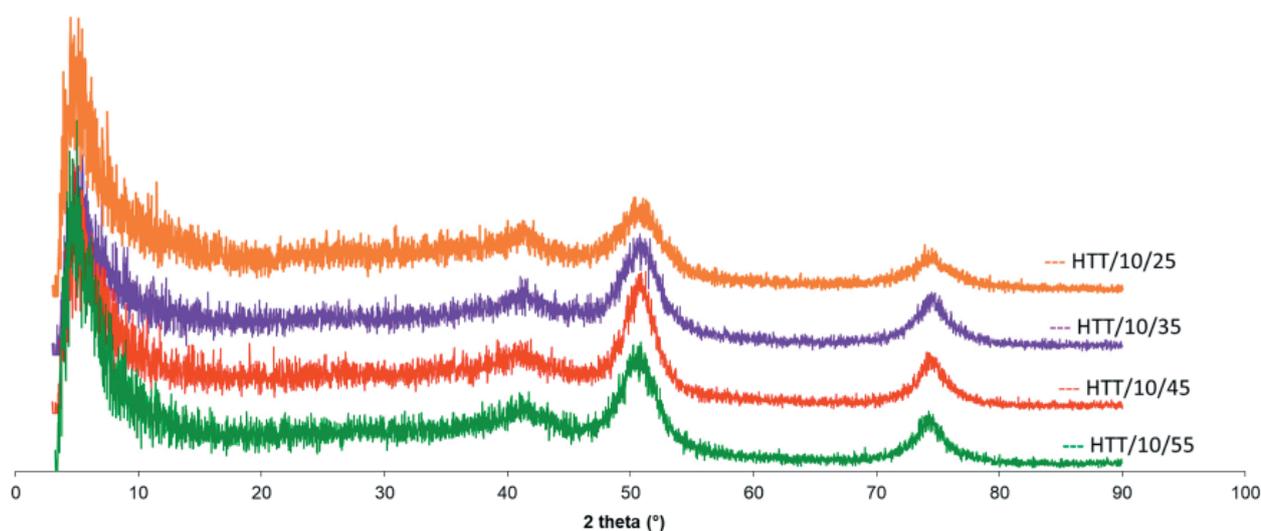
Fig. 3. XRD patterns of samples prepared at constant pH calcined at 450 °C.
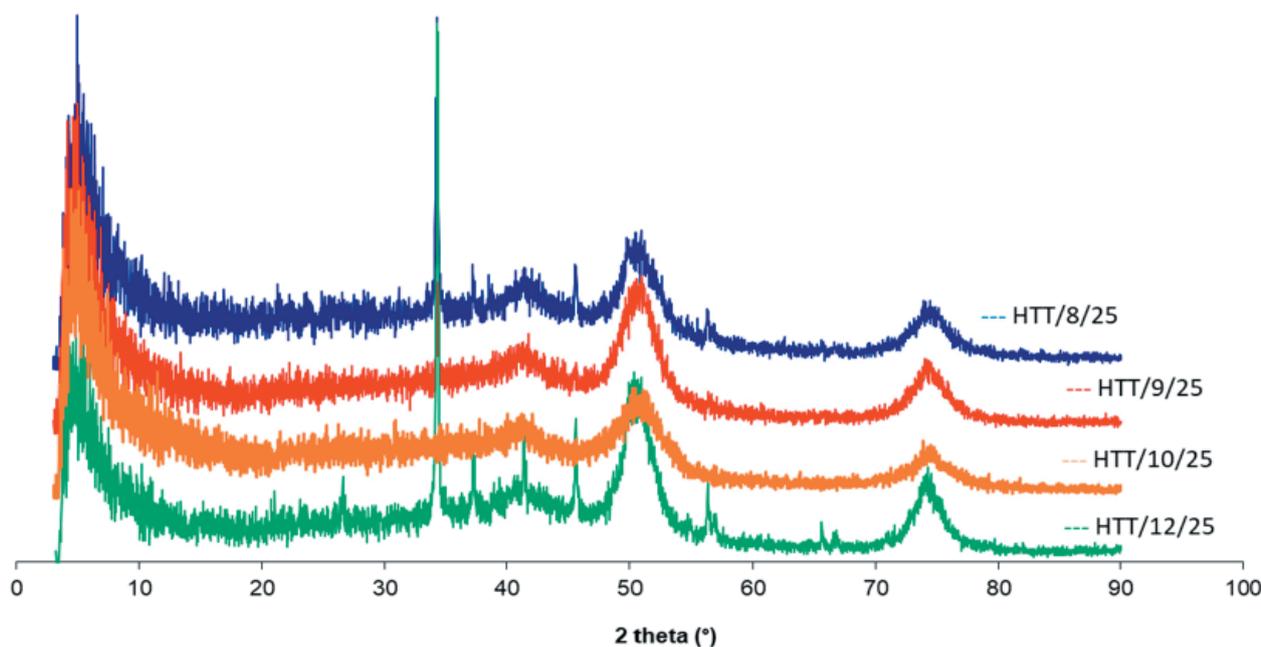
Fig. 4. XRD patterns of samples prepared at constant temperature and calcined at 450 °C.

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diffraction patterns indicate good crystallinity of the prepared hydrotalcite (Wiyantoko et al., 2015). The influence of synthesis temperature on crystallinity is small which can be seen as just a little difference between the intensity of each peak.

In Figure 4, XRD pattern of samples prepared at constant temperature (25 °C) but different synthesis pH can be seen. Samples were calcined at the temperature of 450 °C. The XRD pattern also shows typical peaks of mixed metal oxide structure. In the sample prepared at pH 12, intense reflection at 2θ values of 35 ° and several smaller reflections in the 2θ range of 25 ° − 70 ° can be seen. These peaks can be attributed to $NaNO_3$ crystals and their presence may be caused by insufficient sample washing during filtration. Filtration of HTT/12/25 (pH 12) is difficult probably due to the crystal size of the prepared sample. The influence of synthesis pH on the crystallinity of hydrotalcite is considerably higher than that of the preparation temperature. In the 2θ range from 30 ° to 45 °, there are not very intense peaks in samples HTT/08/25 and HTT/12/25 prepared at pH 8 and 12, which are not characteristic peaks for mixed oxides structure.

SEM

Based on XRD, differences between the sample crystals obtained under different preparation conditions are minimal. Crystallinity of the prepared samples was in line with the characteristic reflections from the XRD pattern. (Wiyantoko et al., 2015) Figure 5 shows a SEM image of HTT/10/25 prepared at 25 °C and pH 10, which proved to be the best preparation conditions. The image shows very thin crystals. The morphology of prepared hydrotalcite was formed by accumulation of nanoparticle aggregates (Wang et al., 2012).

Adsorption-desorption isotherm

The following graphs show the adsorption-desorption isotherms of samples calcinated at 150 °C and 450 °C. Based on their shape, mesoporous texture of the samples can be seen. As a result of capillary condensation, a hysteresis loop is formed caused by a different mechanism of pores filling and emptying. These hysteresis loops are formed due to the presence of mesopores. Distribution of mesopores is in average 5—50 nm, some are up to 70 nm when it comes to macropores. The volume of micropores was evaluated using the t-plot and it was found to be negligible; specific surface area of mesopores, S_t, was practically the same as S_{BET}. When comparing the effect of preparation temperature on the adsorption isotherm, the total pore volume is slightly increased in the sample prepared at 35 °C. The effect of calcination temperature can also be seen at greater pore volumes at higher calcination temperatures, which is positive for the catalyst properties.

Temperature-programmed desorption of CO_2 (TPD-CO_2)

Hydrotalcite belongs to basic catalysts. With increasing basicity, catalytic properties of hydrotalcite are better. TPD-CO_2 was used to determine basicity of all hydrotalcite samples calcined at 450 °C. As it can be seen in the previous section, after calcination at temperatures below 450 °C, hydrotalcite structure changes from layered to mixed metal oxides. Table 4 shows calculated values based on CO_2 desorption measurements. Sample prepared at pH 10 and at 35 °C achieved the highest basicity. The strong basicity in mixed oxides is connected to the presence of alkaline metals. (Fraile et al., 2015).

In Figures 7 and 8, dependence of the measured signal from the calcination temperature can be
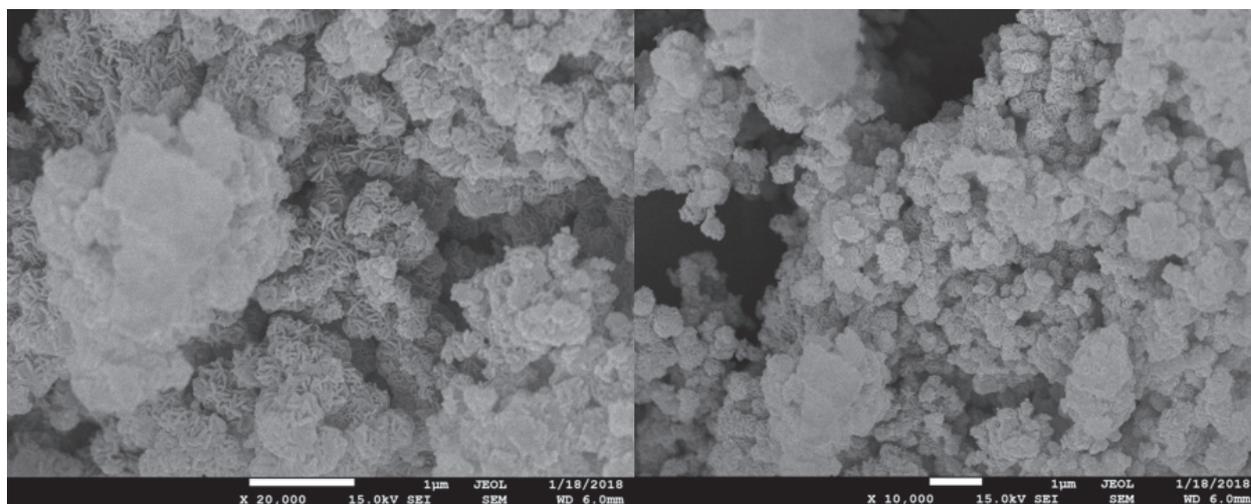
Fig. 5. SEM image of sample HTT/10/25 prepared at pH 10 and preparation temperature of 25 °C.

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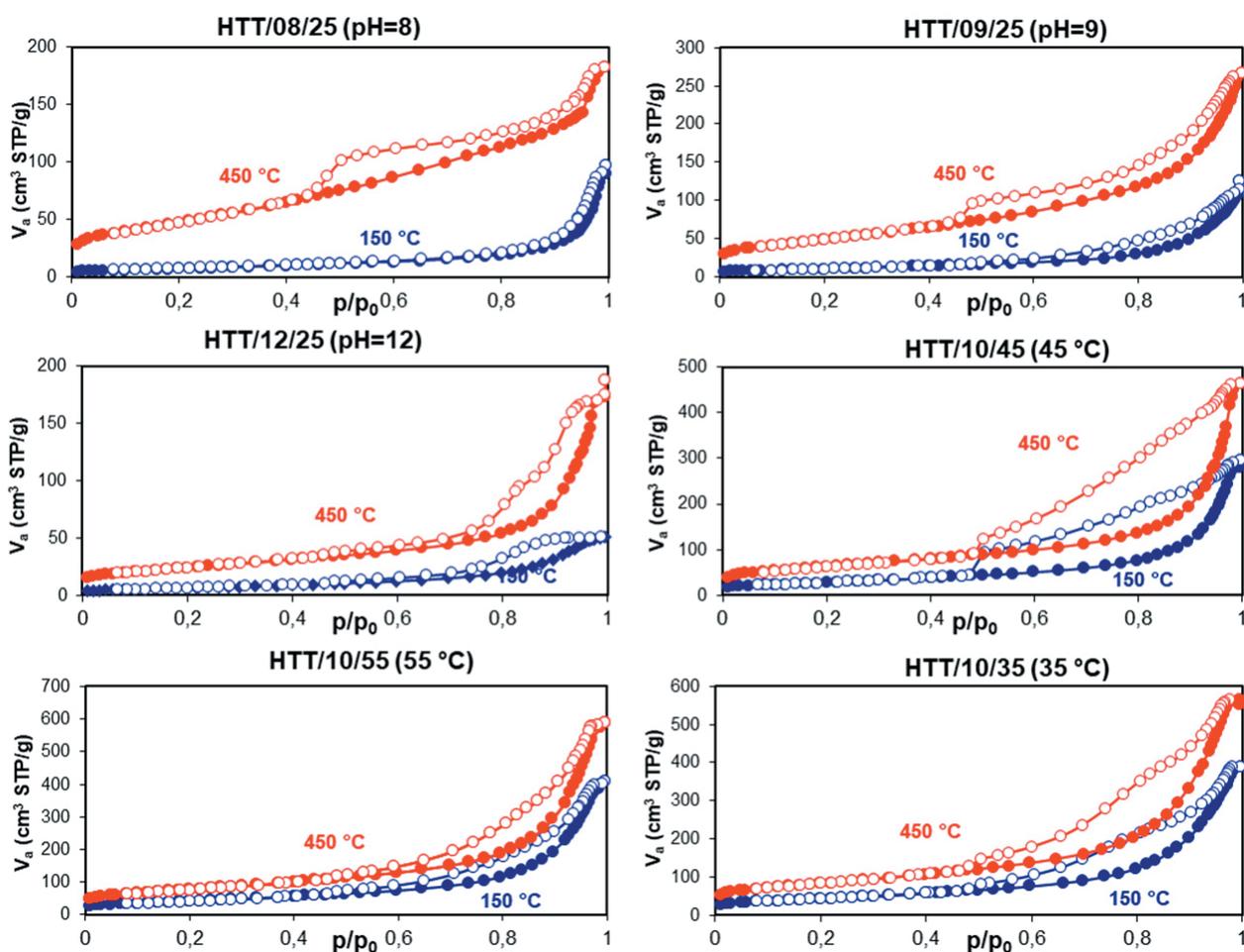
Fig. 6. Adsorption-desorption isotherms of prepared samples.

Tab. 4. Calculated values of basicity based on CO_2 desorption measurements.

Sample	HTT/10/25	HTT/08/25	HTT/09/25	HTT12/25	HTT/10/45	HTT/10/55	HTT/10/35
mmol CO_2/g	1.04	1.35	1.10	0.92	0.78	1.38	<u>1.44</u>

seen. Through the calcination of hydrotalcite, basic centers are formed. At temperatures below 100 °C, weak basic centers are visible. At higher calcination temperatures, from 100 °C to 200 °C, medium-basic sites, and at temperatures above 200 °C, strong basic sites occur (Navajasa et al., 2018). The sample prepared at pH 8 shows an intense maximum in the area of weak basic centers, which can be seen in Figure 7. In contrast, the HTT/10/25 sample does not reach such high intensity as the HTT/08/25 sample, but its signal indicates the presence of medium-basic or strong basic sites. In case of preparation temperature effect on sample basicity, high maximum in sample HTT/10/35 can be seen in the area of weak basic center, but high signal at other temperatures indicates the presence of medium-weak and strong basic sites. In Table 4, a comparison of basicity of all samples is shown, sample HTT/10/35 has the highest basicity among all samples.

Conclusion

Because of its wide range of application and easy preparation, hydrotalcite is an interesting substance. Preparation of hydrotalcite at different preparation temperatures and pH values provides information on the influence to hydrotalcite properties. Preparation by co-precipitation is the most common method to prepare this catalyst with the required structure to catalyze basic reactions. Basicity of hydrotalcite is one of the key properties. Preparation pH can influence basicity as it can be seen for sample HTT/10/35 prepared at pH 10, where basicity reached the highest value of all samples. In case of specific surface area, sample HTT/10/25 prepared at pH 10 showed the highest surface area. Preparation temperature does not have any significant effect on the specific surface area. Hydrotalcite is a mesoporous material as indicated by the hysteresis loop. In case of samples
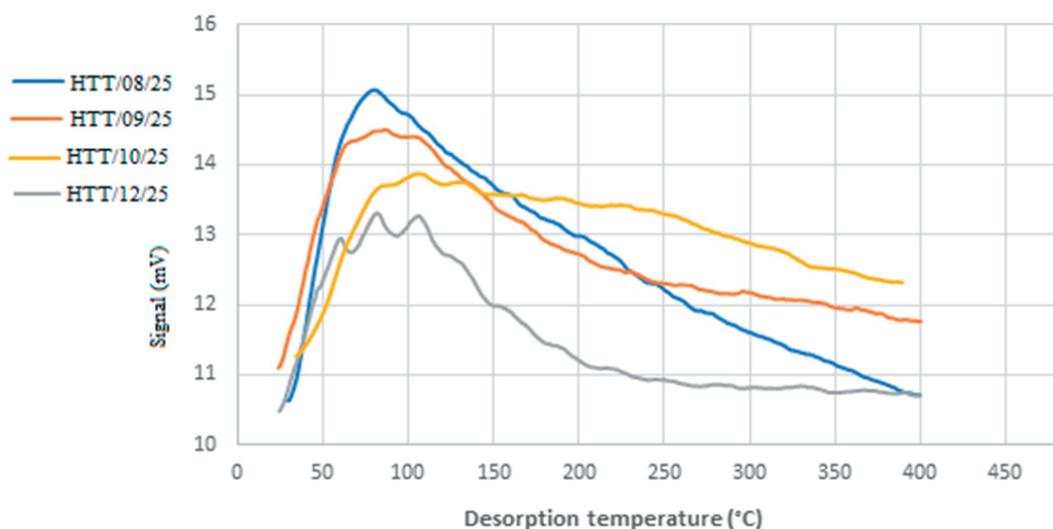
Fig. 7. Desorption curve of samples prepared at different pH.
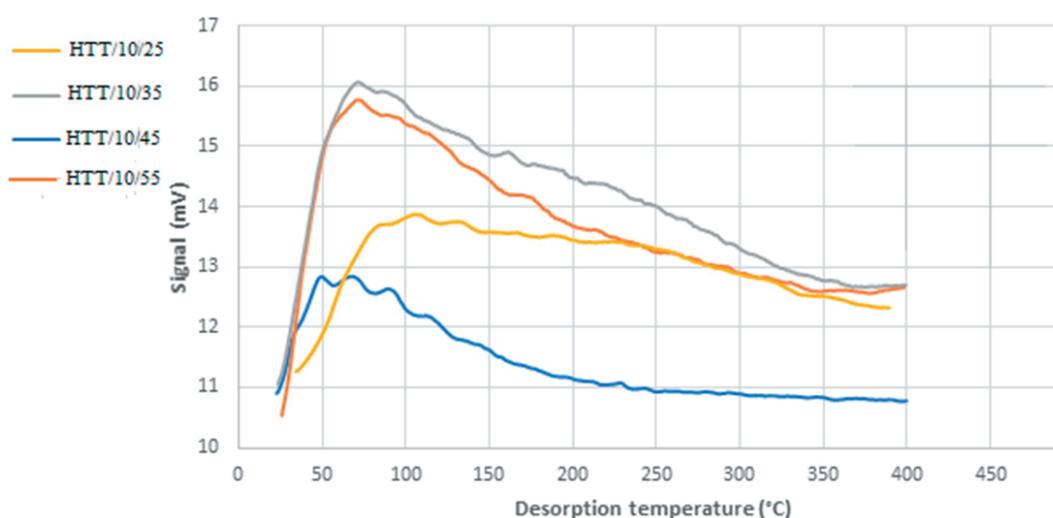
Fig. 8. Desorption curve of samples prepared at different temperatures.

prepared at 35 °C, higher pore volume can be seen. With higher pore volume, the sorption capacity of hydrotalcite increases, which is important when it is used as an adsorbent to reduce NO_x and SO_x emissions from industry. XRD patterns showed good crystallinity of prepared samples with peaks typical for mixed metal oxide structure. In sample HTT/12/25 prepared at pH 12, high intensity peaks can be seen which was attributed to $NaNO_3$ crystals present due to insufficient washing of sample during filtration.

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