

The influence of amount of copper of modified vermiculites on catalytic properties in SCR-NH₃

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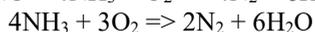
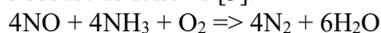
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Abstract. Vermiculite was prepared by modifications with nitric acid, pillaring with Al oligocations and polymer (polyamide), impregnation with Cu. Obtained products were used as catalysts in SCR-NH₃ process. All modifications increased catalytic performance compared to base vermiculite which was used as a reference. Sample pillared with polymer and impregnated with 5%wt. Cu showed best catalytic properties in the process, compared to other polymer and Cu modified samples.

1 Introduction

Nitrogen oxides, referred as NO_x, are one of the main pollutants deriving from fuels combustion. They are connected with admixtures and impurities in fuels or may occur as a product of side reactions. The negative impact of NO_x on the environment cannot be neglected since they are the cause of acid rains and degeneration of ozone layer. The main product of fuel combustion is nitrogen monoxide (NO), which undergoes oxidation to NO₂ in contact with oxygen from the atmosphere. Subsequently, nitrogen dioxide reacts with water, hence the nitric acid is created, which is one of the components of acid rains. Moreover, NO_x in general take part in the formation of smog and also are one of the greenhouse gases [1].

Hence the need to reduce emission of such pollutants, and that is where SCR comes to the aid. There are two ways of such reduction [2]: modification of combustion process and conversion of flue gases. Nowadays SCR is the most effective and most widely used method of NO_x removal from flue gases emitted by stationary sources. It is a process where NO_x are reduced to molecular nitrogen and water, with the aid of various catalysts. NO_x reduction takes place when the gases pass through the catalyst chamber in the installation, while reductants, such as ammonia or urea, are mixed with the gases (injected into the stream) prior. Main reactions occurring in SCR are as follows [3]:



SCR process utilizes reducing agents such as anhydrous ammonia, aqueous ammonia and urea. Thanks to the use of catalyst, NO reduction process can be maintained at lower temperatures (300-400°C compared to ~1000°C as in non-catalytic process).

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Typical industrial catalysts for this process are vanadium (V) oxide promoted with tungsten (IV) oxide on the carrier made of titanium (IV) oxide set on the monolith. The highest activity for such catalyst is at temperatures ranging from 250 to 400°C. In energetic installations, it is most commonly placed after the boiler and before the precipitator. However, such placement exposes the catalyst to harmful effects of various dusts and sulfide (IV) oxide, which reduces its lifetime [3]. Hence the need to study new catalysts with suitable properties for SCR process. So far, activated carbons and clay minerals are thoroughly studied to meet the conditions of a good SCR catalyst. Vermiculite and montmorillonite seem to be most suitable candidates thanks to their properties and ease of modification. It is also proved, that the addition of transition metals, such as Fe and Cu have great impact on catalytic properties [4]. Clay minerals, as layer materials can undergo numerous modifications, where the most important one, apart from acid activation, is pillaring with various agents, such as oligocations (Keggin ions) or polymers. Introduction of oligocations is a well known process, that leads to increase of the distance between layers. Because of such improvement, additional agents can be placed inside the material, hence giving or improving catalytic properties [5]. Since carbon (in form of activated carbon), gives very good catalytic results in SCR process [6], a polymer (polyamide) was used to introduce it into the vermiculite. The purpose of such modification was to check the impact of carbon, in other form than activated carbon which is already used as catalyst, on catalytic properties in the process.

2 Experimental and results

2.1 Sample preparation

Base material, natural vermiculite supplied by Sigma-Aldrich Company, has undergone various modifications, which purpose was to give/improve catalytic properties. All modification steps are shown in Figure 1.

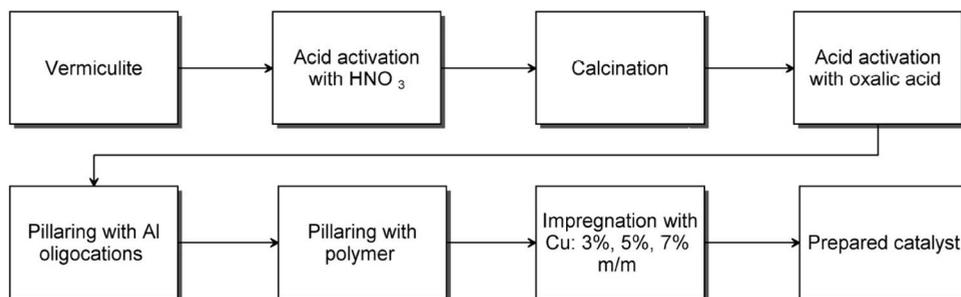


Fig.1 Preparation of samples

The first step of modification was the acid activation with 20% solution of nitric acid. Process was carried out at the acid boiling point under constant stirring for one hour. Activated material was filtrated, washed with distilled water to neutral pH. Then, vermiculite was calcined at 600°C for 4 hours. The next step was acid activation with 0.12M solution of oxalic acid, at 80°C under constant stirring for 3 hours (then filtrated, washed with distilled water and dried for 24 hours at 80°C) followed by pillaring with Al oligocations. Pillaring agent was prepared by slow addition of 0.4M NaOH to 0.4M solution of AlCl₃, under constant stirring for 24 hours. OH/Al ration was equal 2.4. After that, the pillaring solution was left to age in room temperature for 72 hours. Pillaring process was carried out under the following conditions: pillaring solution was slowly added to the activated vermiculite suspension of 2%wt. in distilled water, in an amount of 12 mmol of Al per 1 g of vermiculite, for about 24

hours. Pillared vermiculite was subsequently washed with distilled water until disappearance of chloride ions and dried for 24 hours at 80°C. Furthermore, Al-modified vermiculite was additionally pillared with polymer (polyamide). 5%wt. solution was added into Al-pillared vermiculite and stirred constantly for 24 hours at room temperature. Then it was filtrated and dried for 24 hours at °C. The final step was the incipient wetness impregnation. The Cu ions precursor, Cu(NO₂)₂, was added as a 3, 5 and 7%wt. solution in respect to vermiculite mass. Material was dried for 24 hours at 80°C, hence the prepared catalyst was obtained.



Fig.2 Modified vermiculite before (A) and after (B) pillaring

2.2 Catalytic tests

Prepared samples were tested as catalysts in the selective catalytic reduction of NO_x with ammonia. All tests were performed on AGH University of Science and Technology, Kraków, Poland. Parameters of SCR process were as follows:

- the reaction gas - 800 ppm NO, 800 ppm NH₃, in He with 3% v/v addition of O₂;
- gas velocity - 100ml/min;
- reaction temperature - 150 - 400°C;
- mass of the catalyst - 200mg;
- gas flow controller - ABB Uras-14;
- Concentration of gases in product stream measured every 65 seconds by NDIR (nondispersive infrared sensor) (Hartmann and Braun).

NO conversion was calculated based on formula:

$$\text{NO Conversion [\%]} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} * 100\% \quad (1)$$

Table 1 explains the preparation of samples and assigned symbols.

Table 1. Parameters of prepared samples

| Sample | V | VN20 | VN20g | VN20g3 | VN20g5 | VN20g7 |
|-------------------|---|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Acid activation | - | HNO ₃ 20% |
| Cu impregnation | - | - | - | 3% | 5% | 7% |
| Al-pillaring | - | + | + | + | + | + |
| Polymer pillaring | - | - | + | + | + | + |

Table 2 shows the results of catalytic tests performed at 150, 200, 250, 300, 350 and 400 °C in the form of N₂O concentrations at the outlet and NO conversions.

Table 2. N₂O concentration and NO conversion at given temperatures

| Parameter | Temperature [°C] | Sample | | | | | |
|--|---------------------|--------|------|-------|--------|--------|--------|
| | | V | VN20 | VN20g | VN20g3 | VN20g5 | VN20g7 |
| N ₂ O Concentration [ppm] | 150 | 12 | 38 | 155 | 187 | 323 | 214 |
| | 200 | 14 | 48 | 165 | 191 | 340 | 232 |
| | 250 | 15 | 68 | 172 | 200 | 352 | 255 |
| | 300 | 27 | 103 | 175 | 206 | 356 | 265 |
| | 350 | 17 | 112 | 176 | 234 | 393 | 297 |
| | 400 | 29 | 177 | 188 | 213 | 362 | 260 |
| NO Conversion [%] | 150 | 0.5 | 0.5 | 7.1 | 8.2 | 1.6 | 2.0 |
| | 200 | 3.0 | 15.2 | 16.1 | 10.0 | 19.6 | 15.7 |
| | 250 | 6.9 | 55.6 | 61.4 | 32.4 | 51.0 | 51.1 |
| | 300 | 8.9 | 90.1 | 93.1 | 66.2 | 80.0 | 82.6 |
| | 350 | 9.3 | 98.2 | 92.7 | 93.4 | 94.3 | 92.6 |
| | 400 | 12.4 | 60.5 | 61.5 | 64.4 | 60.3 | 61.2 |

2.3 Discussion

As can be seen in general in Figures 5 - 11, which were prepared based on Table 2, the biggest difference in N₂O concentration at the outlet, as well as NO conversion, occurs between non-modified (or only activated) vermiculites and modified ones. It is connected with enhancing catalytic properties via acid activation and pillaring. Base vermiculite (V), shows minimal, practically insignificant ability to catalyze SCR process (maximum NO conversion 12.4%), thus this sample is considered only as a reference. As a general rule for all modified vermiculites, with temperature increase, NO conversion rises, up to 350 °C, then slightly goes down at 400 °C. It means, that 350 °C is an optimal temperature for those catalysts.

Catalytic performance for polymer-modified samples with addition of Cu, varies between temperatures. Generally lower performance (compared to sample VN20) at 250 - 350 °C range, may be caused as a result of covering the active phase by polymer chains [7]. In case of montmorillonite, pillaring with the same polymer improved catalytic properties. Addition of Cu, increases the NO conversion in following orders: 7% > 5% > 3% at 250 and 300 °C; 5%, 3%, 7% at 350 °C. It is visible especially at 350 °C, where NO conversion for Cu-modified samples is highest for VN20g5 (as compared with all polymer-modified ones), which is 94.3%. These results correspond to Chmielarz et al. research [8-9], where NO conversion higher than 80% was reported. Studies for other layered materials, also show promising results, high levels of NO conversion, at various temperatures (usually ~350 °C). This parameter, obtained for PILCs (pillared interlayered clays) modified with copper goes up to almost 100% at 350 °C [10]. Polymer-modified sample (VN20g) shows best NO conversion at 250 and 300 °C, however at 350 °C it is only slightly lower (as well as catalysts with addition of Cu) than sample VN20 without further modifications.

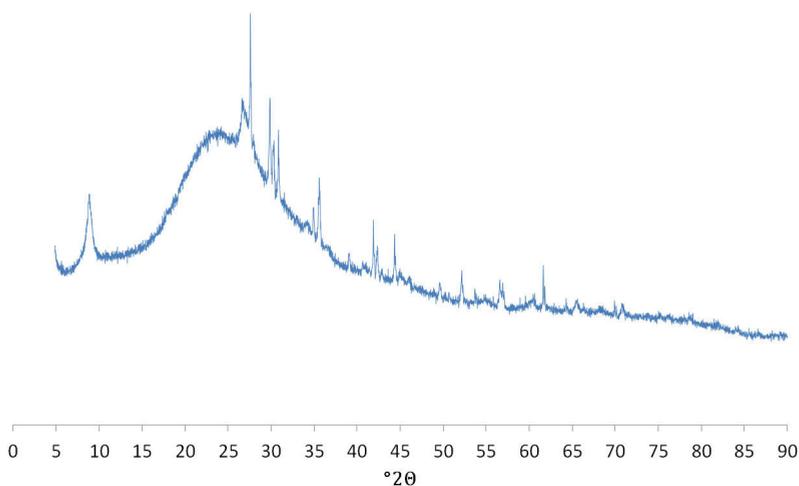
Table 3. S_{BET} of obtained samples

| S_{BET} | Sample | | | | | |
|-----------------------|--------|------|-------|--------|--------|--------|
| | V | VN20 | VN20g | VN20g3 | VN20g5 | VN20g7 |
| m^2/g | 5 | 6 | 7 | 2 | 3 | 2 |

Table 3 shows specific surface area (S_{BET}) of obtained samples. Nitrogen physisorption on catalysts was performed using ASAP 2020 Micromeritics instrument after degassing at 105 °C for 24 h at 1 Pa vacuum. The adsorption–desorption isotherms of nitrogen at –196 °C were treated by the standard Brunauer–Emmett–Teller (BET) procedure. S_{BET} for p/p_0 range = 0.05–0.25 was calculated [11]. These results show slight increase in S_{BET} of samples modified only via acid activation and pillared with polymer. However, addition of copper seems to decrease specific surface area. This is caused simply by deposition of copper species on the surface, and, what is also possible, partially inside the pores. Hence the lower parameter. Additionally, as shown in Fig 3, partial subsidence of the structure has occurred, which is indicated by amorphous part in XRD diffractogram.

Figure 4, which is an UV-Vis spectra of modified samples, gives information about Cu modification. According to Chmielarz et al. [9], the absorption band centered at 225 nm, here observed for each Cu-impregnated sample, is attributed to isolated Cu^{2+} species. Additional absorption band, reported around 360 nm, and attributed to charge-transfer between Cu^{2+} and oxygen in oligonuclear $[\text{Cu-O-Cu}]_n$ species has not been observed, thus indicating that only Cu^{2+} species exist in prepared samples [9].

According to Chmielarz et al. [8], vermiculites are stable materials in tested temperatures, as compared to activated carbons, which undergo oxidation to CO_2 at elevated conditions.

**Fig. 3.** XRD pattern for acid activated vermiculite (VN20)

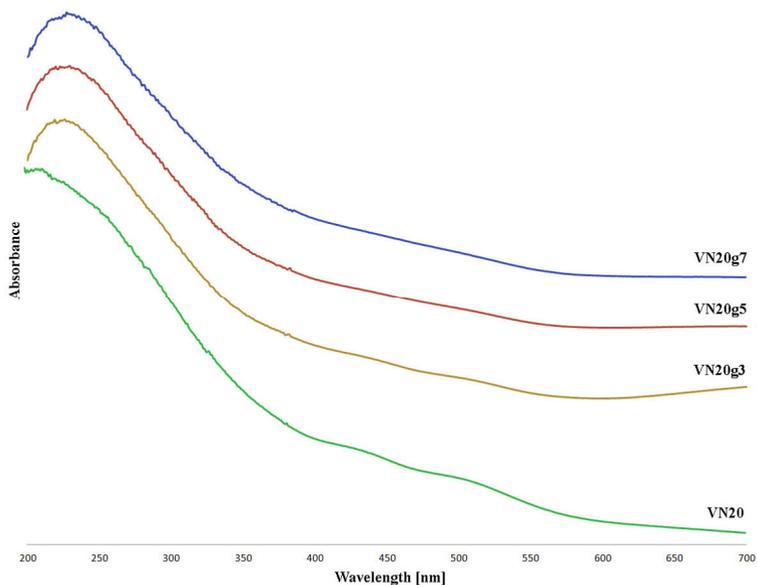


Fig. 4. UV-Vis spectra of base sample VN20 (not modified with Cu) and samples VN20g3, VN20g5 and VN20g7, impregnated with Cu, respectively 3, 5 and 7% wt.

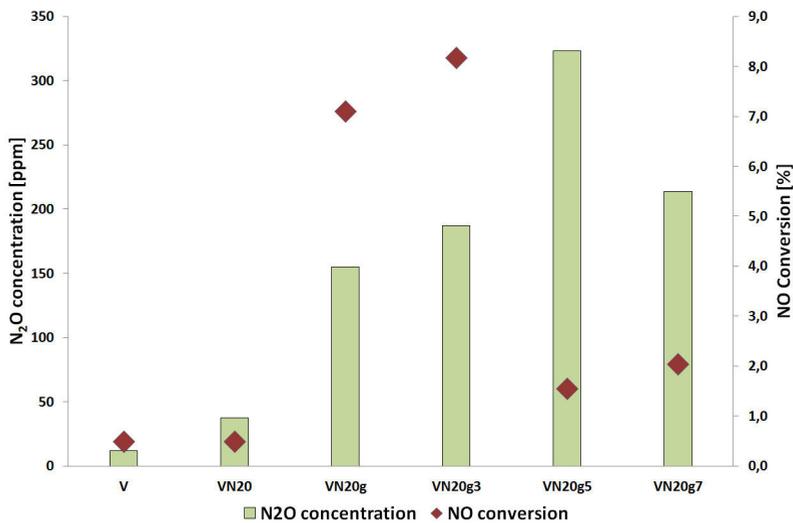


Fig. 5. N₂O concentration at the outlet and NO conversion at 150°C

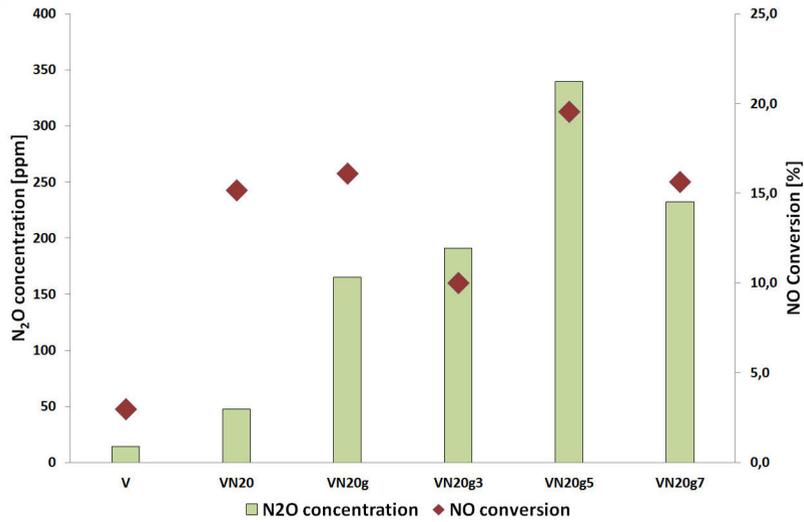


Fig. 6. N₂O concentration at the outlet and NO conversion at 200°C

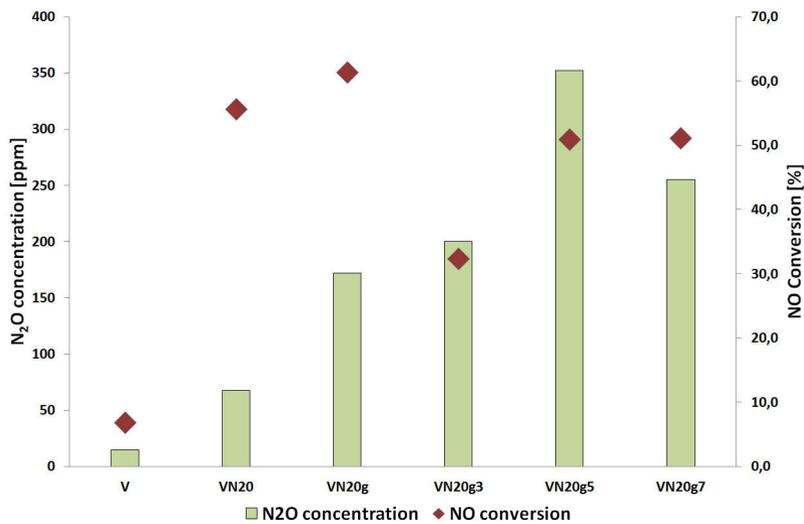


Fig. 7. N₂O concentration at the outlet and NO conversion at 250°C

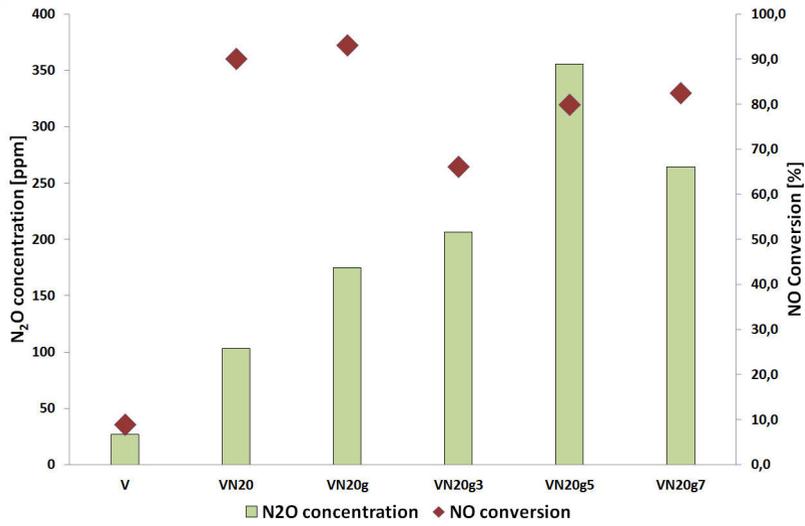


Fig. 8. N₂O concentration and at the outlet NO conversion at 300°C

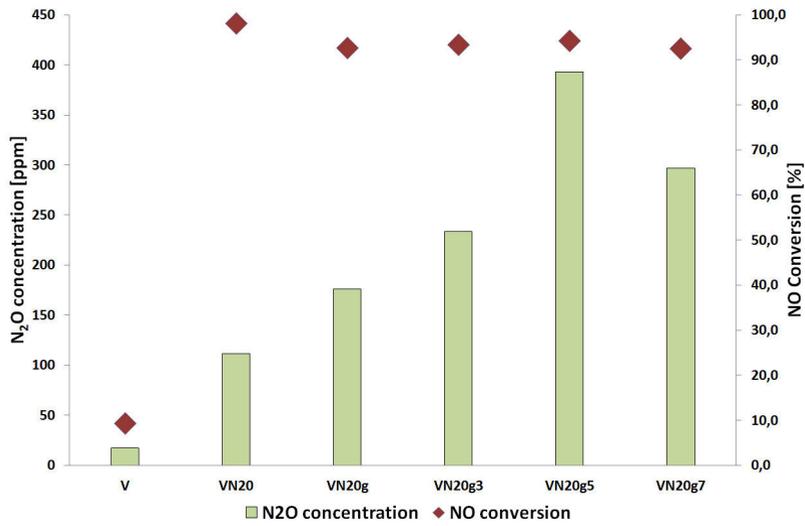


Fig. 9. N₂O concentration at the outlet and NO conversion at 350°C

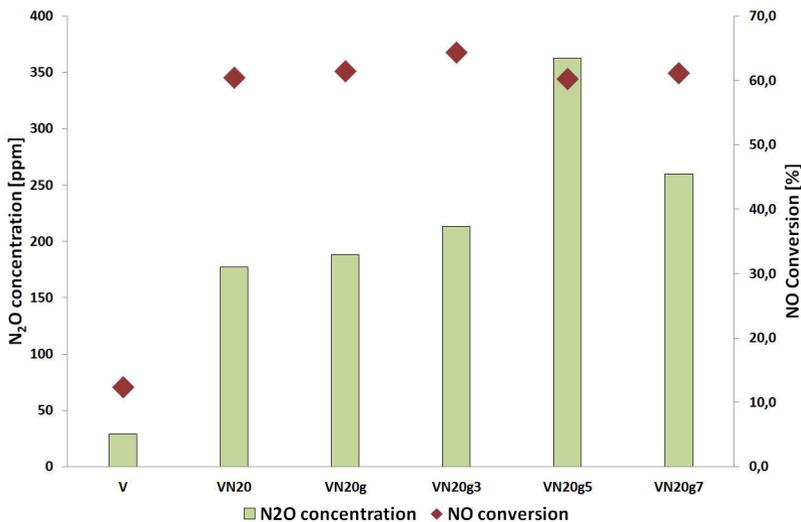


Fig. 10. N₂O concentration at the outlet and NO conversion at 400°C

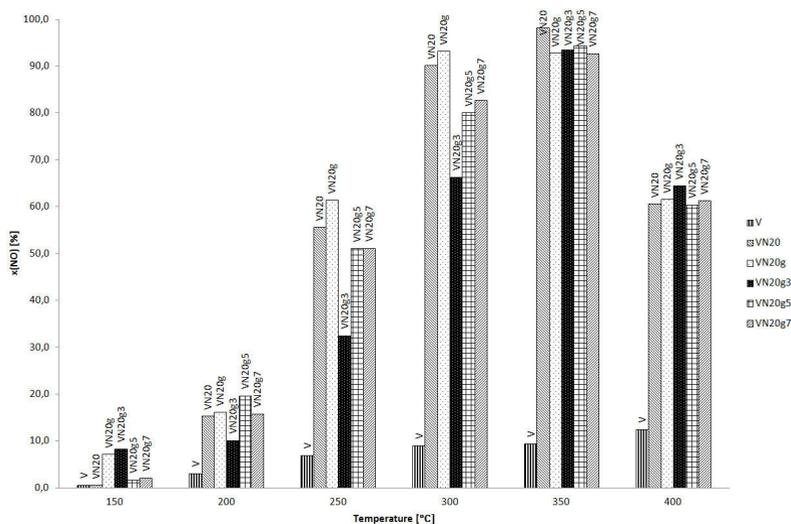


Fig. 11. NO conversion of all samples at temperatures ranging from 150 to 400 °C

3 Conclusion

The aim of this work was to study the influence of the copper amount on catalytic properties of modified vermiculites. Raw supplied vermiculite was modified by acid activation with nitric acid, pillaring with Al oligocations and polymer (polyamide), as well as impregnation with Cu.

Catalytic tests have shown promising results. Polymer, and Cu-modified samples perform well at 350 °C; NO conversions are the highest among all temperatures (94.3% for VN20g5,

92.6% for VN20g7). Modification with Cu slightly improves catalytic performance of polymer-modified vermiculites at this temperature.

Due to partial subsidence of the structure, the dependence of Cu-modification with other modification cannot be clearly described. Cu species decreased specific surface area, because of their deposition on the surface. Pillaring itself increases S_{BET} , however it may also allow the penetration of pores with active material.

The work was supported by AGH 11.11.210.213.

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