

CATALYTIC OXIDATION OF N-HEPTANE ON IMMOBILIZED MANGANESE-CONTAINING POLYMER CATALYST

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Abstract. Manganese nanoparticles with varying percent loadings (5 and 10 wt%) immobilized on poly-4-vinyl-pyridine have been prepared and used for neat O₂ oxidation of n-heptane mainly to the corresponding alcohols and, in lower amounts, aldehydes and ketones. The studies were carried out in the temperature range 298 – 408 K, molar ratios of heptane:oxygen= 1 : 3.38, and at atmospheric pressure. It was found that the non-crosslinked (MnP4VP polymer poly-4-vinylpyridine) and the crosslinked with N, N / methylene-bis-acrylamide metal-polymer catalyst MnP4VP/MBAA containing 5 wt.% Mn²⁺ exhibits the highest activity in the oxidation of n-heptane and can be reused in consecutive catalytic cycles.

Keywords: Supported catalysts, metal immobilization, n-heptane, liquid-phase oxidation.

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1. Introduction

Hydrocarbon's oxidation is an important industrial process due to the huge worldwide demand for oxidized products (Mishra *et al.*, 2018). From literature it is known that, C-H bond activation represents an efficient approach to molecular functionalization (Lakshman *et al.*, 2011).

Controlled oxidation using activated catalytic materials has been found efficient for the oxidation process (Lašič Jurković *et al.*, 2019; Tiziani *et al.*, 2003; Sussich & Cesàro, 2000).

In this paper, we will discuss n-heptane oxidation ability by using metal polymer complex catalysts.

n-Heptane (n-C₇H₁₆) is an important surrogate fuel component used, together with iso-octane, for the octane rating of gasoline as well as a surrogate to represent linear alkanes in diesel fuels and to approximate the combustion behavior of complex, real fuels (Pelucchi *et al.*, 2014; Dagaut *et al.*, 1995). n-Heptane oxidation is often of great interest, as their strong negative temperature coefficient (NTC) behavior makes it a valuable reference hydrocarbon for the modeling of longer straight-chain alkanes (Ferris *et al.*, 2019).

Prior research on alkane oxidation has shown that the rate of reaction depends on catalyst structure (Hicks *et al.*, 1991). As reported in (Herbinet *et al.*, 2012) the most of research projects of oxidation of n-heptane were carried out under conditions of high-

temperature (typically above 800 K), and relatively little attention was paid to the low-temperature oxidation, especially regarding the characterization of oxygenated reaction products (Walker & Morley, 1997).

Previously, research results show that low and medium temperature oxidation of n-heptane involves carbonyl compounds for which evaluated kinetic data is available for the first oxidation steps but often limited to atmospheric conditions at much lower temperatures and also evaluated kinetic data is missing for the reactions of large radical carbonyl species at medium temperatures (Ahmed *et al.*, 2007).

In recent years, research in the field of homogeneous catalytic oxidation of hydrocarbons by molecular oxygen has been developing in two directions: the free-radical chain oxidation catalyzed by transition metal complexes and the catalysis by metal complexes that mimic enzymes (Matienko *et al.*, 2009; Williams & Nozaki, 2019). The number of oxidative reactions catalyzed by coordination compounds of transition metals has expanded significantly (Dasireddy *et al.*, 2018; Bae & Lakshman, 2008; Tušar *et al.*, 2012).

Well-defined metal nanoparticles deposited on inert well-defined supports allow better catalytic activity and selectivity. Moreover, such catalysts can be easily removed from the reaction media and recycled. In heterogeneous catalysis, manganese based compounds are used as selective catalysts for a wide range of catalytic applications (Tušar *et al.*, 2012; Tušar *et al.*, 2010; Khusnutdinov *et al.*, 2012).

On the other hand, Polymer Chemistry has dominated our daily lives through its application in all kinds of materials thanks to the ingenuity of polymer chemists and material scientists (Nyanhongo *et al.*, 2011; Takata *et al.*, 2005). In this regard, the main direction of our laboratory is focusing on to obtain polymer based metalcomplexes catalysts.

In manganese-containing compounds, Mn can exist in various oxidation states; therefore, manganese compounds exhibit different reactivity in reactions, in particular with organic substances (Pombeiro & Guedes da Silva, 2019; Van der Vlugt & Meyer, 2007; Roesky 2010). Observation of the system of liquid-phase oxidation of individual, carbonyl complexes in the presence of metalpolymer complexes will permit us to identify the regularities of the running processes (Suleymanova *et al.*, 2017; Suleymanova *et al.*, 2021; Mishra & Kumar, 2003).

In this paper, polymer based catalyst has been reported in which manganese-containing complex immobilized on quaternized non-crosslinked and cross-linked polymer poly-4-vinylpyridine (P4VP) (Centi *et al.*, 2021; Hodnett, 2000; Punniyamurthy *et al.*, 2005; Khusnutdinov *et al.*, 2012).

2. Experimental Section

Manganese and its salts are known to be active in various oxidation reactions. The aim of our research was to prepare a manganese immobilized polymer heterogeneous catalysts and evaluate it in the oxidation of n-heptane. In that regard, supported metal catalyst was tested in the oxidation of n-heptane under mild reaction conditions and this research is focusing on to assess the catalytic activity and recyclability of the Mn polymer complexes for the partial oxidation of n-heptane (Tagiev *et al.*, 2020; Tagiev *et al.*, 2020). The study was divided in two stages. Firstly, Poly (4-vinylpyridine) was quaternized with benzyl chloride. Secondly, for the formation of immobilized Mn containing polymer complexes, $MnCl_2 \cdot 4H_2O$ was added to polymer solution and studied

in aqueous phase. Additionally, herein we used quaternized non cross-linked and cross-linked P4VP polymer.

2.1 The quaternization of Poly (4-vinylpyridine)

To obtain Mn containing polymer catalyst, the polymer was quaternized (Tagiev *et al.*, 2020; Tagiev *et al.*, 2020). In this regard, solution of the P4VP (1 g of P4VP: 100 ml of C₂H₅OH) were heated to 333 K and at this temperature benzyl chloride in amounts of 10 - 60% of the dissolved polymer was added to the solution, and stirred for 6h, in a three-necked flask equipped with a stirrer. At the end of the process, P4VP samples quaternized to various degrees. The quaternized polymer was precipitated with 0.1N NH₄OH solution, washed with diethyl ether to remove the excess of benzyl chloride and dried in vacuum 10⁻² Pa at 313 K to constant weight.

2.2 Crosslinking of Poly (4-vinylpyridine)

Polymer was crosslinked by using following method: quaternized P4VP samples were crushed and dissolved in ethanol, 8-10% solutions were prepared, and crosslinking agent N, N / methylene-bis-acrylamide (30% in amount of P4VP) was added to the solution. Grinding and mixing were carried out for 1-3 min in a ball mill with a ball diameter of 0.8 cm. The particle size of the crushed mixture was in the range of 0.05-0.1 mm. Tablets were pressed with a diameter of 8 mm and a thickness of 0.2-0.4 mm from a mixture of MnP4VP and MBAA. These tablets were heated for 2-3 hours in evacuated to 10⁻² Pa quartz ampoules at 393-403 K.

2.3 Synthesis of P4VP-Manganese complexes

P4VP-Mn catalysts were prepared by adding 0.36 g MnCl₂·4H₂O into ethanol solutions of quaternized P4VP samples. The mixture was stirred for 3h in a 500 ml three-necked flask equipped with a stirrer. Then, the redox agent NaBH₄ was added to the solution. The precipitated MnP4VP complexes were washed with distilled water to remove the excess of Mn(II) cations and dried in a vacuum until totally dried at 313 K.

3. Results and Discussion

Since polymer supported metal systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we have decided to investigate the catalytic activity of manganese polymer complexes in the oxidation of n-alkanes in mild conditions.

Quaternized non-crosslinked and crosslinked manganese-containing polymeric (based on poly-4- vinylpyridine (P4VP) and N, N/methylene-bis-acrylamide (MBAA)) catalytic systems for the oxidation of n-heptane to obtain heptanol 1; 2; 3; 4, heptanal and heptanone were synthesized and characterized. It has been established that manganese-containing complexes formed in the catalytic reaction are responsible for the oxidation of n-heptane by oxygen (Fig. 1, Fig. 2). As can be seen from Figures 1 and 2, the conversion of the initial product increases when temperature is rising which is associated with the formation of by-products, but this leads to decreasing in the yields of the target products (alcohols). In this regard, it is considered to conduct n-heptane oxidation process on the above catalysts at low temperatures 25-45⁰C respectively.

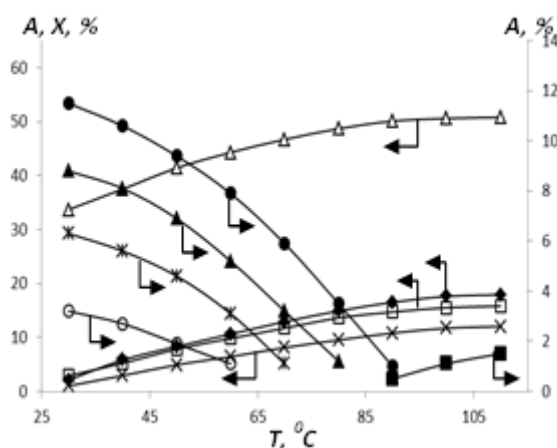


Fig. 1. Experimental results of the liquid-phase oxidation of n-heptane over MnP4VP catalysts: Δ -conversion of heptane; \bullet -heptanol 3; $*$ -heptanol 4; \blacksquare - mixtures of acids; \square -heptanone 4, 3; \circ -heptanol 1; \blacktriangle -heptanol 2; \times -heptanal; \blacklozenge -heptanone 2; A-yields of products and X-conversion of n-heptane

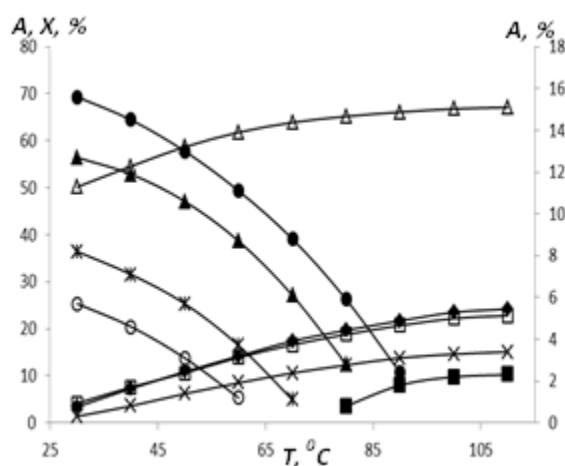


Fig. 2. Experimental results of the liquid-phase oxidation of n-heptane over MnP4VP/MBAA catalysts: Δ -conversion of heptane; \bullet -heptanol 3; $*$ -heptanol 4; \blacksquare -mixtures of acids; \square -heptanone 4, 3; \circ -heptanol 1; \blacktriangle -heptanol 2; \times -heptanal; \blacklozenge -heptanone 2; A-yields of products and X-conversion of n-heptane

3.1. Characterization

The structure and phase composition of the prepared catalysts was determined by X-ray diffraction analysis (XRD; D2-Phaser Bruker diffractometer), FT-IR spectroscopic analysis (FT-IR spectroscopy Nicoletisio VSA), scanning electron microscopy (SEM and EDS on Sigma VP. Carl Zeiss Jena), The products of the catalytic testing were analyzed using a Agilent 7890B Gas Chromatograph (GC) with column HP-5 with a gas carrier velocity (H₂ and N₂) of 1.2 ml/min and a pressure of 5.41 psi (pound-force per square inch) (Tagiev *et al.*, 2020).

3.2. Catalytic testing on the n-heptane oxidation

The properties of the obtained catalyst samples MnP4VP and MnP4VP/MBAA were studied in the oxidation reaction of n-heptane by oxygen in a laboratory stationary reactor in a variable temperature regime (the reaction temperature was varied in different experiments). The reaction was carried out at heptane/oxygen molar ratios = 1: 3.38. The temperature in different experiments was varied within the range of 25–110°C at atmospheric pressure, respectively. n-Heptane (5 ml) and the catalyst MnP4VP or MnP4VP/MBAA (0.8 cm³) were loaded into the reactor. The molar ratio of n-heptane to catalyst was 0.038: (0.0012- 0.006). The reactor was placed on a magnetic stirrer brand "MS-5" with heating. The identification of the obtained data was carried out on the Agilent 7890B gas chromatograph with column HP-5 with a gas carrier velocity (H₂ and N₂) of 1.2 ml / min and a pressure of 5.41 psi (pound-force per square inch). Reaction kinetics studies show sustained catalytic activity and high selectivity for a manganese immobilized poly-4-vinyl-pyridine under mild conditions.

4. Conclusions

The direct methods for the conversion of alkanes to the desired products by heterogeneous catalysis have a distinct economic advantage. Sampling-gas chromatograph analysis have been implemented and calibrated in order to identifying and quantifying chemical species formed during the course of the experiments. Experimental results have been obtained with n-heptane: oxygen mixtures at equivalence ratios of 1: 3.38. In this blank experiment, a significant n-heptane conversion was obtained at 313K.

According to our research, it was found that the duration of the catalyst activity under the above mentioned conditions was 72 hours. After the indicated time, the yield of n-heptane oxidation products decreases, and hence efficiency of catalyst is decreasing.

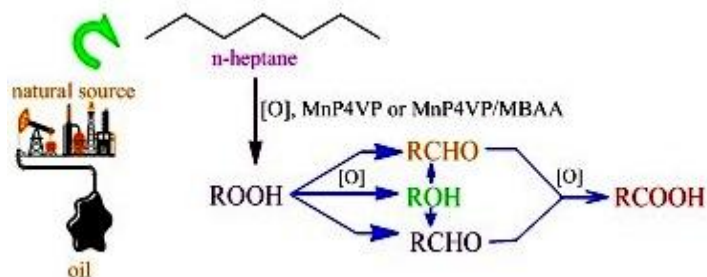


Fig. 3. Graphical abstract of n-heptane oxidation with non-crosslinked and crosslinked MnP4VP and MnP4VP/MBAA

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