Selective Gas-Phase Oxidation of Monochlorotoluenes over Modified Oxovanadium Systems Supported on Al₂O₃ and SiO₂

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Abstract: V-Mo-O/SiO₂ materials were prepared by the impregnation techniques and characterized by Scanning Electron Microscopy (SEM), FT-IR, Thermal analysis, N₂ adsorption/desorption and X-ray powder diffraction (XRD) to determine the phase structure and loadings of vanadium species. This material was tested for solvent-free catalytic oxidation of monochlorotoluene under chosen conditions. The results show that V-Mo-O/SiO₂ is an effective catalyst, exhibiting a conversion of monochlorotoluene and selectivity on monochloromaleic anhydride 75–85%, 24–32% respectively. Furthermore, the catalyst can be easily recovered and reused for 20-25 hours without a significant loss in its activity and selectivity. The oxidation rate and direction determined by the temperature (315-450 °C), proportions between the reagents (1:1–1:15 mol/L), bond dissociation energies, the effects of active components of catalyst, and contact time.

Keywords: Chlorotoluene; maleic anhydride; chloromaleic anhydrides; oxovanadium catalyst; chlorobenzaldehyde.

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INTRODUCTION

Catalytic systems based on vanadium oxides which are supported on different types of supporting agents are one of the most studied ones, because of their wide range of applicability in the petrochemical industry, especially in alkyl aromatic hydrocarbons and its chlorosubstituted derivatives’ conversion. Oxovanadium systems modified by Mo, Sr, Bi, Cu, Cr, and Co were prepared by co-precipitation, impregnation, and mechanical-chemical shifting for carrying out heterogeneous oxidation reactions of alkylaromatic chlorohydrocarbons, and the systems supported on carriers Al₂O₃, SiO₂, TiO₂, pumice, and coal showed higher performance among the received systems [1–4]. Depending on the specific oxide support vanadia catalysts may show different catalytic activity and selectivity due to the nature and the surface area of the support as well as the vanadium content, all of which are key factors in the formation of surface species [5–7]. Apart from this, vanadium oxide has also been explored for various other applications including pseudo-capacitors and cathode material in various conversion reactions. Notably, vanadium has displayed excellent catalytic activities in all forms, whether it has been employed as a supported active phase or in the form of mixed oxides prepared in combination with other ions; it displayed efficient catalytic properties as an oxidation catalyst [8, 9]. However, the zeal for finding a better performing catalyst for the selective oxidation of toluene and its chlorinated derivations still is an ongoing process.

In this respect, the present work is aimed at preparation and textural, structural and acid characterization as well as catalytic behavior in the gas phase selective oxidation of mono-CT of vanadium systems with different V₂O₅ loading, supported Al₂O₃ and SiO₂. Catalytic systems were prepared co-precipitation and they characterized by FT-IR, X-ray diffraction, N₂ adsorption/desorption, thermal analysis, and SEM. The effect of heat treatment and phase formation of the synthesized catalytic systems on their activity in the oxidation reactions was studied.

MATERIALS AND METHODS

The systems were mainly received by diluting vanadate or phosphate in oxalate or hydrochloric acid. The solution was evaporated for a short time and permeated on SiO₂ or Al₂O₃ and subsequently desiccated in air at 180–230 °C for an hour, further step being calcination in the fume cupboard at 270–380 °C for two hours, and lastly, calcination for an hour at 500 °C. Before the reaction the reagents were heated above than 100 °C, and then oxidation process was carried out. Kinetic regularities of heterogeneous catalytic oxidation of chlorinated alkyl aromatic hydrocarbons studied [2,3]. Probable scheme of mechanism, kinetics and mathematical models of the oxidation processes were proposed. The influence of
initial, intermediate products and reaction yields on the kinetics of oxidation reactions were revealed.

Phase identification and quantification: Phase properties (cell parameters, crystallite size, and lattice strain), are offered by the crystal structure of synthesized catalytic systems, determined by the Bruker manufactured (Germany) D2 Phase X-ray powder diffraction analyzer.

Surface area ($S_{\text{BET}}$, m$^2$/g) and pore size (cumulative volume $V$, cm$^3$/g; diameter $d$, Å) information of catalytic systems were obtained from the adsorption-desorption isotherm of nitrogen at its liquid temperature (-196 °C), using a Gas Adsorption Surface Porosimeter (Thermo Scientific, Italy). Prior to the measurements, all samples were degassed to 0.1 Pa. Brunauer–Emmett–Teller (BET) surface areas were calculated assuming a cross-sectional as 0.164 nm$^2$ for nitrogen molecule.

Thermogravimetric analyses were carried out using NETZSCH STA 449F3 (Germany). Temperature was programmed from 25 °C to 900 °C at a heating rate of 10 °C min$^{-1}$. The weight of the nanopowder obtained was 0.6 g.

SEM and elemental analysis were carried out. This was used to determine the morphology of system and its elemental composition. Element analysis of the catalyst precursor components was performed on TruSpec Micro analyzer of Horiba company.

Selective oxidation mono–CT was carried out in a continuous flow fixed-bed reactor at an atmospheric pressure and in the temperature range of 370–480 °C. Chlorotoluenes were fed by means of a micro-feeder at 0.8 mL/h and the ratio CT/air ($O_2$) =1:20. The catalyst was pre-treated at the reaction temperature for 1 h in a $F_{\text{air}} = 25$ cm$^3$/min. An analysis of reagent and product composition was carried out using Agilent 7820A (Agilent Technologies, USA) Gas Chromatography equipped a flame ionization detector (FID) and HP5 column.

The values of CT oxidation rate, $r_{\text{CT}}$, were obtained from conversion (X) values, according to the equation, $r_{\text{CT}}=XF/W \times 100$, where $W$ is catalyst weight, and $F$ is feed rate of CT (mol/h).

**RESULTS AND DISCUSSION**

**Characterization of Catalysts**
The morphology and particle size of the synthesized catalysts were characterized using SEM. The SEM micrographs of the pre-calcined (300 °C) catalyst V-Mo-O/SiO$_2$, where V:Mo=1:1–1:5, are shown in Figure 1. It was observed that the morphology of the synthesized catalysts
is not well defined, and the surface appears to be rugged without any obvious phase separation. The stoichiometric amount of elements was confirmed from the elemental analysis and found to be approximately in agreement with calculated value. The result of elemental analysis is given in Table 1. There is insignificant amount of calcium and sodium in the system which probably does not influence catalytic behavior in the system, as seen from Table 1.

![Figure 1. SEM of the catalysts V-Mo-O/SiO$_2$ at 300 °C.](image)

**Table 1.** Elemental characterization of VMoO/SiO$_2$ (V:Mo=1:2).

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atom %</th>
<th>Comp %</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na K</td>
<td>0.43</td>
<td>0.39</td>
<td>0.58</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>Si K</td>
<td>28.62</td>
<td>21.26</td>
<td>61.23</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Mo K</td>
<td>9.59</td>
<td>6.46</td>
<td>21.97</td>
<td>MoO</td>
</tr>
<tr>
<td>Ca K</td>
<td>0.21</td>
<td>0.11</td>
<td>0.30</td>
<td>CaO</td>
</tr>
<tr>
<td>V K</td>
<td>8.92</td>
<td>3.66</td>
<td>15.93</td>
<td>V$_2$O$_5$</td>
</tr>
<tr>
<td>O</td>
<td>52.23</td>
<td>68.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td></td>
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</tbody>
</table>

Figure 2 shows X-ray diffraction patterns of mixed oxides of phosphorus silica, with different ratio of vanadium oxide pre-calcined at 300 °C. Both oxovanadium (33.3%), and vanadium pentoxide (28.3 %) in the catalytic system were found, and vanadium is included of the monoclinic structure.
The thermal stability of the synthesized catalyst with different % loading of vanadium oxide systems were studied using TGA analysis. Temperature was programmed from 25 °C to 900 °C at a heating rate of 10 °C min⁻¹. It was observed that almost all synthesized catalysts are thermally stable, yielding a maximum loss of weight of 31.97 % at 895 °C the catalyst; VMoO/SiO₂ (V:P=1:5) was the least stable while VMoO/SiO₂ (V:P=1:2) was the most thermally stable catalyst with a least weight loss % just 18.4 % at the same temperature among the synthesized systems. A graphical illustration is given in Figure 3.

Figure 3. TGA curves of the synthesized catalyst V-Mo-O/SiO₂.
The surface and porous properties of the attained catalytic systems were studied and a plot for V-Mo-O/SiO₂ system was shown in Figure 4. The values for surface area, porous radius, and radius/diameter are respectively, 12 m²/g, 0.7mL/g, 344 Å for V-Mo/Si system.

Figure 1: B.E.T plot of V-Mo-O system based on SiO₂

Catalytic test

It is defined that chlorotoluenes (CT) form π- and σ-complexes while adsorption on a surface of heterogeneous catalysts (V-Mo-O/SiO₂, etc.) which turns into maleates and desorption yields maleic anhydride (MA) and its chloro derivatives. Oxidation process of CT takes place on the redox mechanism and a series-parallel pattern was revealed [3, 8]. The reaction scheme for the p-chlorotoluene showed below in Scheme 2.

Scheme 2: Conversion of chlorotoluenes to maleic anhydrides and chlorobenzoic acids.
Note: X=H, Y=Cl or X=Cl, Y=H.

The oxidation processes of chlorinated alkyl aromatic hydrocarbons investigated both on a fixed bed and fluid-bed layer of catalyst. Although the process of heterogeneous catalytic
oxidation of chlorotoluenes took place with a higher conversion in a fixed bed but it showed higher selectivity fluid-bed layer of the catalyst. We also determined that when vanadium/phosphorus/oxide system (V-Mo/Si etc.) was deactivated both on a fixed bed and fluid-bed layer of catalyst, but deactivation rate and time was almost twice lower on the fluid-bed layer of catalyst.

An effect of active components of these catalysts on the oxidation reaction was also studied. CT performs 75–92% conversion at a V:Mo=1:2–1:3 ratios, the yields of chloromaleic anhydride (CMA) was 24-32%. The yield of chlorobenzaldehyde begins to increase at V:P=1:4–1:5 ratios. According to the obtained results usage of the catalytic systems based on V: P=1:2–1:3 are considered purposeful for further researches.

Although the oxidation reaction begins from 350 °C, we determined that the yields of main products are negligible. By increasing temperature both the conversion of the CT and yield of CMA begins to enhance, and at 420 °C temperature it shows the maximum (24–32%), and simultaneously, yields of maleic anhydride (MA), chlorobenzaldehyde and chlorobenzoic acid (CB acid) decreases. By the further rise of temperature CT conversion continues to increase, but also yields of the main products at its maximum begin to decrease and this happens by way of their exposing deep oxidation process that verified by increasing of CO\textsubscript{2} yield as it is seen from the reaction scheme.

CONCLUSION

In conclusion, it has been determined that oxovanadium systems modified with molybdenum or phosphorus, and supported on SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} (V-Mo-O/SiO\textsubscript{2}) are the most active and selective catalytic systems in the gas phase selective partial oxidation of chlorotoluenes. The catalysts show excellent recyclability and reusability. The optimum reaction condition for the activity and selectivity for received catalysts was designated. Consequently, the p-chloro-substituted substrate, p-chlorotoluene, is much more reactive than the m-chloro-substituted counterpart.

REFERENCES


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Anahtar kelimeler: Klorotoluen; maleik anhidrit; kloromaleik anhidritler; oksovanadyum katalizörü; klorobenzaldehit.
