Preparation of $\alpha$-MoO$_3$ from H$_3$PMo$_{12}$O$_{40}$ precursor: synthesis of 1,2-cyclohexanediol from cyclohexene over $\alpha$-MoO$_3$-TiO$_2$ catalyst

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Abstract

A series of $\alpha$-MoO$_3$-TiO$_2$ mixed oxides were prepared by calcining a mixture of the heteropolyacid H$_3$PMo$_{12}$O$_{40}$ and TiO$_2$ at temperatures ranging from 350 °C to 600 °C. The mixed oxides thus prepared were characterized and tested for the oxidation of cyclohexene by the oxidizing mixture H$_2$O$_2$/CO$_2$. FTIR and XRD characterizations showed that the Keggin structure of H$_3$PMo$_{12}$O$_{40}$ was preserved for calcination temperatures below 400 °C. Above 450 °C, Keggin’s structure collapses. XRD analysis revealed that as the calcination temperature increased, more orthorhombic $\alpha$-MoO$_3$ was formed. Analysis of the reaction mixture by GC-MS showed that oxidation by the H$_2$O$_2$/CO$_2$ mixture leads to 1,2-cyclohexanediol as the main product and to 2-cyclohexene-1-one and 2-cyclohexene-1-ol as minor products. Oxidation by H$_2$O$_2$/CO$_2$ mixture proved to be more effective than H$_2$O$_2$ alone and CO$_2$ alone. The conversion (69.4%) and the 1,2-cyclohexanediol selectivity (93.2%) obtained over $\alpha$-MoO$_3$-TiO$_2$ mixed oxides, higher than that obtained with TiO$_2$ monoxide and $\alpha$-MoO$_3$ monoxide, suggest a synergistic effect between TiO$_2$ and $\alpha$-MoO$_3$. This efficient and stable catalyst after reuse can be developed for the synthesis of diols.

1. Introduction

The partial oxidation of saturated and unsaturated hydrocarbons is a very important process in organic synthesis due to the importance of the products obtained as valuable commercial intermediates [1–5]. Among the unsaturated hydrocarbon compounds, cyclohexene has been the subject of great attention leading to many industrial applications [6]. It is a cheap chemical, an easily obtained raw material and can be oxidized into various oxygenated chemicals which are important intermediates for the production of drugs, pesticides, spices, surfactants, chemicals and polymers [7, 8]. Depending on the type of catalyst and the oxidant used in the reaction, the oxidation reaction can be carried out on the allylic position or on the double bond [9, 10]. Among the different products resulting from the partial oxidation of cyclohexene, diols have attracted more attention because they are basic intermediates for the synthesis of many useful products [11]. Several authors have reported the synthesis of diols using transition metal catalysts [12–14] and several oxidizing agents such KMnO$_4$, OsO$_4$ [15–17], alkylhydroperoxides [18–20], and peracids [21] have been used. Unfortunately, these oxidants used are harmful to the environment and moreover they increase the production costs due to the need for multiple purification steps. Therefore, a greener oxidant which can efficiently convert olefin to 1,2-diols by an organic solvent-free process is desired. Two other oxidants, namely hydrogen peroxide (H$_2$O$_2$) and molecular oxygen (O$_2$) are attractive due to their high active oxygen content and to their environmentally friendly processes [22–24]. Molecular oxygen is a desirable oxidant from a green chemistry perspective but unfortunately its direct application requires high temperature and pressure [25, 26] which usually requires a pre-activation step with a reducing agent to overcome this drawback and be able to operate under mild reaction conditions [25, 27, 28]. H$_2$O$_2$ has the advantage of carrying out oxidation reactions under milder conditions than O$_2$ gas. It is the suitable oxidizing agent due to its high active oxygen content and its environmental friendliness with only water as a by-product. However, its cost limits its application on an industrial scale. Increasing its efficiency can...
composite for its cost. The solution proposed in this work is to use it in a mixture with CO₂. When CO₂ is added to hydrogen peroxide, oxidation reactions are more efficient. The role of CO₂ as a soft oxidant has been observed in the oxidative dehydrogenation of ethylbenzene to styrene by restraining total oxidation [29]. This work concerns the synthesis of 1,2-cyclohexanediol from cyclohexene by a simple, safe and green method. The partial oxidation was carried out by the H₂O₂/CO₂ mixture as a mild oxidant without the use of solvent. The reaction was catalyzed by mixed oxides of titanium oxide and molybdenum obtained from 12-phosphomolybdic acid (H₃PMo₁₂O₴₀). It should be noted that it is possible to synthesize a multitude of polyoxometalates having different compositions and different structures by the choice of the cation, the central atom and the addendum atoms. But as the objective was to see the effect of the α-MoO₃ species on the synthesis of diols, heteropolymolybdates were selected because their calcination leads to the formation of the α-MoO₃ species. Among the family of heteropolymolybdates, the heteropolyacid H₃PMo₁₂O₴₀ (where the cation is the proton) was chosen and not one of its salts because the calcination of the salts gives, in addition to the α-MoO₃ species, oxides from the cations (see equation (1)).

\[
\text{H}_3\text{PMo}_{12}\text{O}_{40} \xrightarrow{\Delta 420 ^\circ \text{C}} 1/2\text{Mo}_3\text{O}_7 + 12\text{MoO}_3 + 1/2\text{P}_2\text{O}_5
\]

So the heteropolyacid was used to avoid the effect of the oxides of the cations on the reaction because in the case of the heteropolyacid (where the cation is the proton), the proton is eliminated in the form of H₂O which evaporates (see equations (3) and (4) in the manuscript).

This work can be considered as an alternative to harmful methods for the synthesis of vicinal diols.

2. Materials and methods

2.1. Materials

H₃[PMo₁₀O₄₀] x H₂O heteropolyacid, was obtained from Fluka AG, CH-9470 Buchs (99% purity). Aqueous solution of hydrogen peroxide (H₂O₂/H₂O 30/70 wt%) was purchased from WINLAB Ltd., UK. Titanium dioxide (TiO₂) and Cyclohexene (C₆H₁₀) with a purity > 99.5% was purchased from BDH. All other chemicals were of analytical grade and used as received.

2.2. Preparation of the catalysts

A series of α-MoO₃–TiO₂ have been prepared by calcining a mixture of 12-molybdo phosphoric acid and titanium oxide. The preparation procedure is as follows: 2.5 g of 12-molybdo phosphoric acid (1.4 × 10⁻³ mol) are dissolved in 10 ml of water at 40 °C. To this solution, 2.5 g of titanium dioxide (0.03 mol) are added and the resulting mixture is kept under stirring for 30 min. After homogenization, the mixture is heated to 70 °C until the water evaporates and a powder is obtained which is then dried in an oven at 80 °C for 12 h. The precursor salt obtained was calcined at the desired temperature for 6 h in a stainless steel reactor with an air flow of 6 l/h. Various samples calcined at different temperatures designated by HPMo/TiO₂-x (x = calcination temperature, varying from 350 °C to 600 °C) were prepared. The samples prepared are denoted (a) HPMo–seul–600; (b) HPMo/TiO₂–600; (c) HPMo/TiO₂–550; (d) HPMo/TiO₂–500; (e) HPMo/TiO₂–450; (f) HPMo/TiO₂–400; (g) HPMo/TiO₂–350.

2.3. Catalytic tests

The catalytic tests were carried out in a jacketed stainless steel reactor connected to a circulating water bath to adjust the temperature. The reactor is equipped with a manometer for pressure adjustment. The reaction mixture, consisting of 10 ml of cyclohexene, 20 ml of hydrogen peroxide (30% in aqueous solution), 5 ml of acetonitrile (solvent) and 0.5 g of catalyst is heated to 75 °C, under a pressure of 0.5 MPa of CO₂ with stirring. After 7 h of reaction, the mixture was cooled, centrifuged to separate the catalyst from the reaction mixture to be analyzed. The quantitative analysis was carried out using a gas chromatograph (PYE UNICAM) equipped with a flame ionization detector and a thermal conductivity detector. The qualitative analysis of the products was carried out by Gas chromatography–mass spectrometry (GC–MS) using a gas chromatograph (Thermo Trace GC Ultra A1 3000) equipped with a capillary column TR-5 MS–SQC (30 mx 0.25 mm di, 0.25 μm phase thickness).

2.4. Characterization of the catalysts

The infrared analyzes were carried out with a GENESIS II–FTIR infrared spectrometer in the 4000–400 cm⁻¹ range using KBr pellets. X-ray diffraction (XRD) analyzes were performed using a Rigaku Ultima IV x-ray diffractometer using Cu-Ka radiation. The thermogravimetric analyzes (TGA) were performed by means of a Netzsch thermogavimetric analyzer model TGA SAT 449 F3, transmission electron microscopy (TEM) JSM-7600F (JEOL Ltd., Japan), TEM micrographs were performed on a JEOL JEM-2100F field emission electron
microscope (JEOL, Japan) with an accelerating voltage of 110 kV. Surface morphology of the catalysts were determined by means of a Scanning Electron Microscopy (SEM) on a JEOL, Japan) with an accelerating voltage of 100 V and a beam current of 30A.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. FTIR analysis

Samples of the prepared catalyst series were characterized by FTIR. In order to identify the compounds present in solids calcined at different temperatures, it is useful to examine the FTIR spectra of as received TiO₂, uncalcined bulk HPMo and uncalcined HPMo/TiO₂. The results obtained are shown in figure 1. FTIR spectrum of the as received TiO₂ (figure 1(a)) exhibits two peaks, one at 530 cm⁻¹ and the another at 655 cm⁻¹ and are assigned to O=Ti=O bonding in anatase [30–32]. The spectrum of uncalcined HPMo (figure 1(b)) is consistent with that reported in the literature for keggin structure [33]. The Keggin structure is characterized by the main peaks observed around 1064 cm⁻¹ (s=Mo–Oα), 964 cm⁻¹ (s=Mo–Oβ–Mo), 870 cm⁻¹ (s=Mo–Oβ–Mo), and 780 cm⁻¹ (s=Mo–Oα–Mo). The four typical HPMo bands are not masked by the titanium oxide bands and were easily observed (figure 1(c)). Thus the Keggin unit after being loaded onto the support (TiO₂) can be easily characterized.

Figure 2 shows the spectra of all catalyst samples subjected to calcination at different temperatures. As it can be seen, the calcination at 350 °C and 400 °C, does not induce significant modifications. In fact, the characteristic bands of the Keggin structure are still observed. From 450 °C to 600 °C, the effect of calcination is significant. The four characteristic bands of Keggin structure disappeared indicating the collapse of kegging structure. In contrast a narrow band at 993 cm⁻¹, assigned to the vibration of the Mo=O terminal bond, two bands, one at around 876 and the second at 820 cm⁻¹ assigned to the vibration of Mo–O–Mo bridging bonds appeared [34]. Two other bands one at 635 and the other at 510 cm⁻¹ were attributed to stretching and bending vibration of O=Mo–O group [34]. The results confirm the formation of the or-thorhombic molybdenum trioxide (α-MoO₃) when the calcination temperature exceeds 400 °C.

3.1.2. XRD analysis

Figure 3 indicates the XRD pattern of the products obtained by calcination at temperatures ranging from 350 °C to 600 °C under an air atmosphere for 6 h (figures 3(b)–(g)). In order to see the evolution of the products resulting from the calcination of HPMo at different temperatures, the uncalcined bulk HPMo precursor and the bulk HPMo calcined at 600 °C (HPMo-600) were also presented (figures 3(a) and (h)). HPMo-600 XRD pattern (figure 3(a)) show 2θ values at 12.81°, 23.51°, 25.75°, 27.37°, 29.17°, 33.69°, 35.55°, 39.04°, 46, 15°, 49.34°, 52.34°, 56.17°, 58.88°, 64.76° and 67.82°, which are assigned to the oriented planes (020), (110), (040), (021), (130), (131), (111), (150), (002), (230), (211), (112), (081), (062) and (270) respectively. These peaks confirm that calcination at 600 °C leads to the formation of the orthorhombic phase α-MoO₃ (α-MoO₃)
As for the effect of the calcination temperature between 350 °C and 600 °C on the products formation, it can be seen that the HPMo-x samples progressively transform into orthorhombic α-MoO₃. It is also noted that the higher the calcination temperature, the stronger the intensity of the α-MoO₃ product peaks. It should be noted that the intense and sharp diffraction peaks observed, suggest that the as-synthesized α-MoO₃ product is well crystallized. None of the h-MoO₃ or β-MoO₃ phases were observed. In fact, it is well known that the crystal structures of MoO₃ exist in three phases. A thermodynamically stable orthorhombic phase α-MoO₃ and two metastable phases namely hexagonal h-MoO₃ and monoclinic β-MoO₃. The two metastable phases are generally obtained at low temperature. Nevertheless, their transformation into orthorhombic α-MoO₃ depends on the calcination temperature, the calcination duration and the calcination atmosphere (air, Ar...).
3.1.3. TEM analysis

TEM studies were carried out to confirm the structure already observed by XRD, samples of HPMo-TiO$_2$-x after calcination at temperatures ranging from 350 $^\circ$C to 600 $^\circ$C. Two samples, the HPMo-TiO$_2$–350, calcined at the lower temperature (350 $^\circ$C) and the other, the HPMo-TiO$_2$–600 calcined at the higher temperature (600 $^\circ$C) were examined by TEM (figure 4). For the HPMo-TiO$_2$–350 sample (figure 4(a)), the image shows a mixture of two types of nanoscale particles. The first type is almost cubic in shape and about 150 nm in size and appear to be those of the Heteropolyanions crystallites which preserved its Keggin structure at this calcination temperature (350 $^\circ$C). The second type of particles with almost spherical shapes and whose size varies between 110 and 120 nm are those of TiO$_2$. As for the HPMo-TiO$_2$–600 sample (figure 4(b)), the image also shows a mixture of two types of nanoscale particles. The almost total disappearance of cubic particles (HPMo) and the appearance of new particles of hexagonal or orthorhombic shapes should be noted. These new particles can be attributed to the solid MoO$_3$. These TEM images confirm the results obtained by XRD.

3.1.4. SEM analysis

SEM analysis was used to investigate the surface morphology of HPMo/TiO$_2$–350 and HPMo/TiO$_2$–600 catalysts, and SEM micrographs of these two solids are shown in figure 5. The micrograph of HPMo/TiO$_2$–350 (figure 5(a)) reveals a solid composed of two types of irregularly shaped microparticles. The micrograph shows large aggregates scattered over small particles, which appear to be HMPo crystallites scattered over a larger number of irregularly shaped particles which can be attributed to TiO$_2$. The HPMo/TiO$_2$–600 sample (figure 5(b)) shows smaller aggregates scattered on the small particles which can be attributed to MoO$_3$ crystallites.
3.1.5. Thermogravimetric analysis

In order to determine the possible compounds which can form during the action of the temperature on the HPMo-TiO₂-x catalysts, thermogravimetric analyzes (TG) were carried out in the range of temperatures going from 25 to 700 °C with a speed heating of 10°C min⁻¹. The TG profile of uncalcined HPMo-TiO₂ sample and HPMo-TiO₂-x samples is shown in figure 6. The profile of uncalcined HPMo/TiO₂ TG (figure 6(a)) almost resembles that of typical TG from Bulk HPMo, as observed in previous work. work [35] where uncalcined HPMo heteropolyacid was shown to exhibit two stages of mass loss. The first stage takes place between 25 and 140 °C and corresponds to the loss of water of hydration (13-hydrates) (equation (1)). This first step is followed by a plateau between 140 °C – 270 °C corresponding to anhydrous acid (equation (2)). The second stage takes place between 270 °C – 420 °C, and it corresponds to the loss of structural water (1.5H₂O) (equation (3)). For temperatures above 420 °C, HPMo decomposes to its oxides P₂O₅ and MoO₃ (equation (4)). For the calcined solids, it should be noted that when the calcination temperature increases from 350 to 400 °C (figures 6(b) and (c)), the amount of water of hydration decreases, which indicates a decrease in the HPMo content on the HPMo/TiO₂ catalyst. For solids calcined at 450 °C and 500 °C (figures 6(d) and (e)), the TG profile indicates a very low HPMo content. It should be recalled that at the same time as the loss of water of hydration and structure of HPMo occurs, there is also the loss of water physisorbed and chemisorbed on the TiO₂. For the latter, the first weight loss observed in the 25 °C – 200 °C range is due to the elimination of water molecules physically adsorbed on TiO₂. The second weight loss observed between 200 and 550 °C can be attributed to the elimination of chemisorbed water molecules [36]. Beyond 600 °C, a progressive weight loss is observed for all the samples. This weight loss has been mentioned in several research works published in the literature. Indeed, a study by thermogravimetric and differential thermal (DTA) analyzes of MoO₃-TiO₂ composite [37] showed that a rapid weight loss was observed at 674 °C. According to the authors this indicates the final stability of the MoO₃-TiO₂ composite. Another study by TGA and (ATD) comparing the stability of pure TiO₂, pure MoO₃ and TiO₂ doped with 20% MoO₃ heated up to 1200 °C has been reported [38]. The results obtained show that there is no significant thermal change for the TiO₂ sample. On the other hand, the curve of the pure MoO₃ sample showed an endothermic peak at approximately 790 °C corresponding to the melting of molybdenum oxide. According to the authors, it is from this temperature that the evaporation of MoO₃ begins, as indicated by the mass on the TG curve. Although the endothermic peak of MoO₃ melting in the MoO₃-TiO₂ sample was not clearly observed, evaporation was visible. In another research work, Tg analysis of TiO₂ doped with 2.5% MoO₃ [39] showed weight loss above 750 °C. According to the authors, this corresponds to the sublimation of MoO₃ from TiO₂.

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\begin{align*}
H_3PMo_{12}O_{40}·13H_2O & \xrightarrow{25°C-140°C} H_3PMo_{12}O_{40} + 13H_2O \\
H_3PMo_{12}O_{40} & \xrightarrow{140°C-270°C} H_3PMo_{12}O_{40} \\
H_3PMo_{12}O_{40} & \xrightarrow{270°C-420°C} H_3PMo_{12}O_{38.5} + 3/2H_2O \\
H_3PMo_{12}O_{38.5} & \xrightarrow{>420°C} 1/2P_2O_5 + 12MoO_3
\end{align*}
\]
3.2. Catalytic activity

The oxidation of cyclohexene by H$_2$O$_2$ (30% aqueous solution) in the presence of CO$_2$ was carried out at 75 °C for 4 h on HPMo/TiO$_2$–600 catalyst. Analysis by means of GC-MS (Scheme 1) showed that 1,2-cyclohexanediol (diol) was obtained as the major product and the products 2-cyclohexen-1-one (cyone), with 2-cyclohexen-1-ol (cyol) were obtained as minority products. Cyclohexene oxide and other oxygenated by-products were observed in trace amounts.

3.2.1. Effect of oxidizing agent

In order to choose the suitable oxidizer among the environmentally friendly ones, we have performed the oxidation by O$_2$ and H$_2$O$_2$. The oxidation was performed at 75 °C for 7 h on an HPMo/TiO$_2$–600 catalyst (Table 1). In the case of oxidation by O$_2$, the results obtained under pressure of 0.5 MPa of O$_2$ gave a conversion of 39% and a selectivity of diols of 9.4%. Whereas in the case of oxidation by H$_2$O$_2$ (at 30%), the oxidation leads to a conversion of 59% and a very good selectivity for diols (92.4%). As for oxidation by CO$_2$, the conversion produced under these operating conditions is minimal. This is expected because the carbon dioxide molecule is very thermodynamically stable. Activating it requires more energy. Given the very good selectivity obtained in the oxidation state by H$_2$O$_2$, it was tempting to see the effect of carbon dioxide on the oxidation of cyclohexene by H$_2$O$_2$. The reaction was carried out under a pressure of 0.5 MPa of CO$_2$. The obtained results showed an improvement in the conversion and selectivity of the diols. The obtained values are 69.4% and 93.2%, respectively. Therefore, the H$_2$O$_2$ / CO$_2$ oxidation system was chosen to study the effect of various factors on the production of diols.

3.2.2. Effect of calcination temperature

The effect of the calcination temperature on the conversion and the selectivities was studied in the temperature range going from 350 °C to 600 °C. The samples were calcined in a stainless steel reactor with an air flow of 6 l/h. The results obtained (Figure 7) show that the conversion increases rapidly when the calcination temperature varies from 350 °C to 450 °C then it slows down beyond this temperature while continuing to increase. As for the selectivities, it should be noted that the selectivity of the diol increases rapidly, also when the temperature varies from 350 °C to 450 °C then it stabilizes beyond 450 °C. Conversely, the selectivity of Cyone and Cyol decreases rapidly when the temperature increases from 350 °C to 450 °C and then stabilizes in the range 450 °C–600 °C. It should be recalled that the characterizations by XRD and TG have shown that when the calcination temperature increases from 350 °C to 450 °C, the HPMo is gradually transformed into α-MoO$_3$. Beyond 450 °C, it is completely transformed into α-MoO$_3$. It is therefore clear that it is the α-MoO$_3$ species which has a significant effect on the conversion and the selectivities. Since this species, tested alone (calcination of HPMo alone at...
600 °C) gave a low conversion compared to the case where it is in the presence of TiO₂, it is obvious that there is a synergistic effect between α-MoO₃ and TiO₂ leading has a high conversion. With regard to the reduction in the selectivities in Cyone and in Cyol, this is explained by the fact that the deep oxidation reactions are favored in an acid medium. Indeed, in the 350 °C–450 °C range, the HPMo is gradually transformed but it still exists. Like all heteropolyanions, HPMo is a superacid with a very strong oxidizing power [40, 41]. So the presence of HPMo leads to further oxidation, i.e. the formation of Cyone. The Cyol decreases because it is oxidized to Cyone (deep oxidation). As for the selectivity of the diol, which decreases with the calcination temperature, this is explained by the fact that the more the calcination temperature decreases, the more the proportion of HPMo increases and consequently the acid character increases, which favors the dehydration reaction leading to the formation of the Cyone (scheme 2).

3.2.3. Activity of TiO₂ and HPMo
Before determining the best composition of the TiO₂--HPMo-600 catalyst in TiO₂ and HPMo for the production of the diol, it is useful to evaluate the activity of each of these solids compared to the mixed TiO₂--HPMo-600 catalyst. To do this, the three catalysts were tested under the same conditions, namely oxidation by H₂O₂/CO₂ under a pressure of 0.5 MPa of CO₂ with stirring for 7 h. The results obtained (figure 8) show that the mixed catalyst TiO₂--HPMo-600 is by far the best catalyst compared to solid TiO₂--600 and HPMo-600. Indeed, the conversion obtained by TiO₂--HPMo-600 is 69.4% while those obtained by TiO₂ and HPMo are equal to 17.0%...
and 24.0% respectively. The diol selectivity obtained by TiO2-HPMo-600 is 93.2% while the selectivities obtained by TiO2 and HPMo are equal to 19.1% and 79.9% respectively. It is evident that a synergy effect between TiO2 and HPMo has occurred. Since the mixed oxide is more reactive, it would be useful to determine the optimal composition of TiO2 and HPMo for a good production of the diol. For this reason we have studied the effect of the mass fraction of HPMo on the conversion and the selectivity to diol.

3.2.4. Effect of mass fraction

The effect of mass fraction on conversion and selectivities has been studied in the mass fraction range from 0.1 to 0.9. The oxidation was carried out on the HPMo-TiO2-600 catalyst at 75 °C under a CO2 pressure equal to 0.5 MPa for 7 h. The results obtained (figure 9) show that when the mass fraction of HPMo increases from 0.1 to 0.5, the conversion increases from 56.0 to 69.4%. Beyond 0.5%, it decreases and reaches the value of 37% for the mass fraction of 0.9%. As for the variations of the selectivities, the results show that they remain almost constant in the fraction range from 0.1 to 0.5%. Beyond 0.5%, a slight decrease in the selectivity for diol and Cyone was observed. This slight decrease occurs in favor of that in Cyole. This is due to the fact that when the
mass fraction of HPMo increases, the acidity of the catalyst increases is therefore the reaction of dehydration of the diol and the reaction of protonation of Cyone leading to Cyol are favored (diagram 2). It should therefore be noted that the solid having the mass fraction 0.5 in HPMo is the best catalyst. The diol is obtained as a major product with a selectivity of 93.2% while Cyone and Cyol are obtained as minor products with a selectivity of 2.9% and 1.8% respectively. The epoxy was not detected.

3.2.5. Reusability
The reuse of catalysts is an important factor not only from an economic point of view but also from an environmental point of view. That is why it is important to study the regenerability of the catalyst and its catalytic stability catalysts after reuse. In this work, the TiO₂-HPMo-600 catalyst which proved to be the best catalyst was retested under the same conditions for the oxidation of cyclohexene. After recovery of the catalyst from solution, it was characterized by FTIR (figure 10) and by XRD (figure 11). The results show that the FTIR and XRD spectra before and after use are identical respectively. This shows that the catalyst is stable and can be reused. As for its catalytic activity, the results obtained are reported in table 2. It emerges from this table that the conversion
decreases slightly compared to the first use. Indeed, it went from 69.5% to 65.1%. On the other hand, the selectivity of diol and Cyol increased from 93.2% and 2.6% to 95.0% and 3.7%. This increase in alcohol selectivities occurs to the detriment of Cyone, which drops from 4.2% to 0.2%. This slight reduction in the conversion accompanied by a slight increase in the selectivity of the diol clearly shows that the TiO$_2$-HPMo-600 catalyst can find its application for the synthesis of diols.

4. Conclusion

In this work, a series of mixed oxides of $\alpha$-MoO$_3$-TiO$_2$ were prepared by calcining a mixture of the heteropolyacid H$_3$PMo$_{12}$O$_{40}$ and TiO$_2$ at temperatures ranging from 350 $^\circ$C to 600 $^\circ$C. The mixed oxides thus prepared were characterized and tested for the oxidation of cyclohexene by the oxidizing mixture H$_2$O$_2$/CO$_2$. The following points emerge from these results:

Characterizations by FTIR, XRD and TEM showed that the Keggin structure of H$_3$PMo$_{12}$O$_{40}$ completely collapsed at 600 $^\circ$C leading to a well-crystallized orthorhombic molybdenum trioxide ($\alpha$-MoO$_3$). None of the h-MoO$_3$ or $\beta$-MoO$_3$ phases were observed. Therefore, the pure $\alpha$-MoO$_3$ phase can be prepared by calcination of the precursor heteropolyacid.

Oxidation by the H$_2$O$_2$/CO$_2$ mixture is more effective than oxidation by H$_2$O$_2$ alone or by CO$_2$ alone. It leads to 1,2-cyclohexanediol as the main product and to 2-cyclohexene-1-one and 2-cyclohexene-1-ol as minor products.

The conversion and the selectivity in 1,2-cyclohexanediol obtained by TiO$_2$-HPMo, much higher than those obtained with TiO$_2$ alone and HPMo alone, suggest a synergistic effect between TiO$_2$ and HPMo.

After reuse, the TiO$_2$-HPMo catalyst still remains efficient and stable. This can consider it as a promising catalyst from an economic and environmental point of view for the synthesis of diols.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contribution

Tahani Saad AlGarni provided materials and performed characterizations, Naaser A.Y. Abduh performed the experiments and analyzed the experimental data, Abdullah Al Kahtani provided materials and funding, Ahmed Aouissi designed and wrote the article. All authors have read and accepted the published version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.
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