Cobalt Oxide Nanoparticles Supported on γ-Alumina as Catalysts in the Selective Oxidation of Alcohols in Aqueous Phase

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In this work, cobalt oxide nanoparticles supported on γ-alumina were prepared and were well characterized by scanning electron micrograph (SEM) and X-ray diffraction patterns. These were employed as catalysts for the oxidation of alcohols to aldehydes or ketones with tert-butylhydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) as the oxidant in the liquid phase. For these cobalt oxide nanoparticles supported on γ-alumina, acetonitrile as the solvent was employed. The research results showed that oxidant and the catalyst type influenced the conversion percent of alcohols oxidation. TBHP was found to be better oxidant than H_2O_2 since higher conversion percent of alcohols were observed when TBHP was employed. The catalytic activity of 10%Co_3O_4/nano-γ-alumina was superior to that of 5% and 15% Co_3O_4/nano-γ-alumina catalysts. Under the optimum reaction conditions, the catalytic system of 10%Co_3O_4 nanoparticles supported on γ-alumina gave about 82.3% conversion percent of cyclohexanol.

Key words: Oxidation, γ-Alumina, Nanoparticles, Co_3O_4, Alcohols.

Oxidation reactions are among the most important transformations in synthetic chemistry and offer an important methodology for the introduction and modification of functional groups. Therefore, the oxidation of alcohols by metal oxides to the corresponding carbonyl compounds is a worthwhile goal[1,2]. In this way, chemists have used different kinds of metal salts and oxides in the form of homogeneous catalysts [3,4] or supported metal ions and supporting oxometal catalysts as heterogeneous systems[5,6].

Many different oxidants were used for the oxidation of alcohols such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), $KMnO_4$, MnO_2, CrO_3 and so on. Most of these oxidizing reagents which can be used in a research laboratory in stoichiometric amounts are expensive or toxic[1,7]. Thus, the advantages of environmentally friendly oxidizing agents, such as H_2O_2 and O_2, have been extensively studied. H_2O_2 is attractive for producing active oxidation species in aqueous solution, with H_2O as a by-product.

Supported metal oxide catalysts are frequently used as catalysts in partial oxidation reactions[8–10]. In these catalysts, Al_2O_3, TiO_2, SiO_2 and ZrO_2 are commonly used as the supports. Bulk oxides in general cannot be used in industrial processes as they impart poor thermal stability that lead to fast deactivation of the catalyst. Furthermore, it is also known that bulk Co_3O_4 leads to high combustion of organic molecules to carbon oxides[11]. Santra et al.[12] have studied the oxidation of benzyl alcohol with molecular oxygen in the presence of gold nanoparticles on mesoporous cerium-tin mixed oxide as catalyst. In another report, Tian and coworkers have employed RuO_2/TiO_2 nanobelt heterostructures for gas-phase selective oxidation of benzyl alcohol. The RuO_2/TiO_2 samples exhibited good activity for oxidation of benzyl alcohol[13]. However, to the best of our

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knowledge, there is no report for application of Co_3O_4 nanoparticles supported on γ-alumina for partial oxidation of alcohols with H_2O_2 and TBHP. In this work we report Co_3O_4 nanoparticles supported on γ-alumina as catalysts for partial oxidation of alcohols to the corresponding carbonyl compounds in the liquid phase.

EXPERIMENTAL

Instrument and Reagents

Powder X-ray diffractions were performed by a Siemens D 5000. Specific surface area was measured by BET techniques in liquid N_2 temperature by a Strohlien. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV scanning electron microscopes (SEM). The reaction products of oxidation were identified by GC-MS (Finnigan TSQ-7000) and were analyzed by GC (Shimadzu 8A). All the reagents were commercial grade obtained from Merck. None of the oxidation products were found in the alcohols before the oxidation reaction.

Preparation of the Catalysts

Aluminum nitrate {$Al(NO_3)_3.9H_2O$}, aqueous ammonia {$NH_3.H_2O$} and deionized water were used as starting chemicals. Two hundred milliliters of deionized water was taken in a 2 l capacity round-bottom flask and stirred well using magnetic stirrer. Then, aluminum nitrate (1.5 M) solution and (10.4 M) solution of aqueous ammonia were added to 200 ml of deionized water drop by drop to precipitate Al cations in the form of hydroxides. The temperature was maintained ~55 °C during precipitation/digestion experiment. The pH after precipitation was found to be in the range of 5.4-6.4. The precipitates were further digested at 55 °C for 1 h. After the alumina gel was formed, it was filtered and washed by distilled water. Then, (0.5 M) cobalt nitrate $Co(NO_3)_2$ aqueous solution was added to the alumina-gel. This gel was stirred and homogenized and was placed in an oven under temperature of 100 °C for 24 h. The mixture was then heated 2 °C/min till the temperature reached 600 °C and the mixture was kept at this temperature for 4 h.

Experimental Procedure

In a typical procedure, a mixture of 0.2 g catalyst, 15 ml solvent and 20 mmol cyclohexanol was stirred under nitrogen in a 100 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 15 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) or H_2O_2 (30% in H_2O) was added as oxidizing reagents. The resulting mixture was then refluxed for 6 h under N_2 atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by GC. Products identification was done with GC-MS and confirmed by comparison of their retention times with authentic commercial samples of these compounds.

RESULTS AND DISCUSSION

Characterization of the Catalysts

The XRD pattern presented in Figure 1 indicates that γ-alumina nanoparticles are formed. There is no significant change in the XRD pattern with 10 wt.% Co_3O_4 nanoparticles supported on γ-alumina which confirms that Co_3O_4 dispersed through pores does not change the γ-alumina structure.

Scanning electron micrograph (SEM) of a typical sample of 10% Co_3O_4/nano-γ-alumina is shown in Figure 2. It is clarified from Figure 2 that the sizes of the particles are in the ranges of 40-80 nm. This result was coincident with the particle sizes calculated from the Scherrer equation. Similar images were obtained for the other catalysts. Specific surface area measured with BET method was 186 m^2/g for γ-alumina and 164 m^2/g for 10% Co_3O_4/nano-γ-alumina. This reduction in specific surface area for the supported Co_3O_4 may be an indication of encapsulation of Co_3O_4 in the nano-γ-alumina pores.

Catalytic Oxidation of Cyclohexanol

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of alcohols[14], this oxidant was found to cause minimal destruction of the cobalt oxide catalysts, and to give better activity of the catalysts. The performance of the set of samples prepared as catalysts for the oxidation of alcohols was tested with TBHP. The solvent of acetonitrile was employed for the catalysis, since all the reagents dissolved and gave the highest yields of the products. At first, the reactivity of a model compound, cyclohexanol, was examined under a variety of experimental condition (Table 1). In all reactions were produced only one

Table 1. Results of the cyclohexanol oxidation using Co_3O_4/nano-γ-alumina as catalysts

Catalyst	Oxidant	Conversion (%) cyclohexanol	Product selectivity (%) cyclohexanone
5% Co_3O_4/ γ-Al_2O_3	H_2O_2	53.2	100
5% Co_3O_4/ γ-Al_2O_3	TBHP	64.7	100
10% Co_3O_4/ γ-Al_2O_3	H_2O_2	69.7	100
10% Co_3O_4/ γ-Al_2O_3	TBHP	82.3	100
15% Co_3O_4/ γ-Al_2O_3	H_2O_2	61.8	100
15% Co_3O_4/ γ-Al_2O_3	TBHP	72.5	100
γ-Al_2O_3	H_2O_2	21.8	100
γ-Al_2O_3	TBHP	25.6	100

Reaction condition: 0.2 g catalyst, cyclohexanol 20 mmol, oxidant 15 mmol, solvent of acetonitrile, reflux temperature, reaction time 6 h.

Table 2. Effect of the 10% Co_3O_4/nano-γ-alumina catalyst in the oxidation of different alcohols

Alcohols	Conversion (%)	Selectivity (%)	Products
2-Propanol	75.3	100	2-Propanon
Benzyl alcohol	71.8	100	Benzaldehyde
Isobutylalcohol	66.9	100	Isobutanal
1-Butanol	58.4	100	1-Butanal

product (cyclohexanone) therefore, selectivity (%) is 100 with respect to it. The research results showed that three kinds of catalysts could catalyze cyclohexanol oxidation with TBHP. The activity of the catalysts was as follows: 10% Co_3O_4/nano-γ-alumina > 15% Co_3O_4/nano-γ-alumina > 5% Co_3O_4/nano-γ-alumina. In the presence of 10% Co_3O_4/nano-γ-alumina, conversion percentage of cyclohexanol was 82.3% with TBHP as an oxidant and acetonitrile as the solvent. Contrastive experiment results show that cyclohexanol oxidation with TBHP did not occur in the absence of the catalyst under the same reaction condition. In addition, unsupported γ-alumina has shown lower catalytic activity than the supported catalyst.

Influences of Reaction Time on Cyclohexanol Oxidation Reaction

In this experiment, the change in conversion percentage of cyclohexanol in the presence of *tert*-butylhydroperoxide oxidant and 10% Co_3O_4/nano-γ-alumina catalyst was monitored and plotted with respect to time (Figure 3). The reaction was carried out at reflux temperature for 6 h with 0.2 g catalyst and 20 mmol cyclohexanol
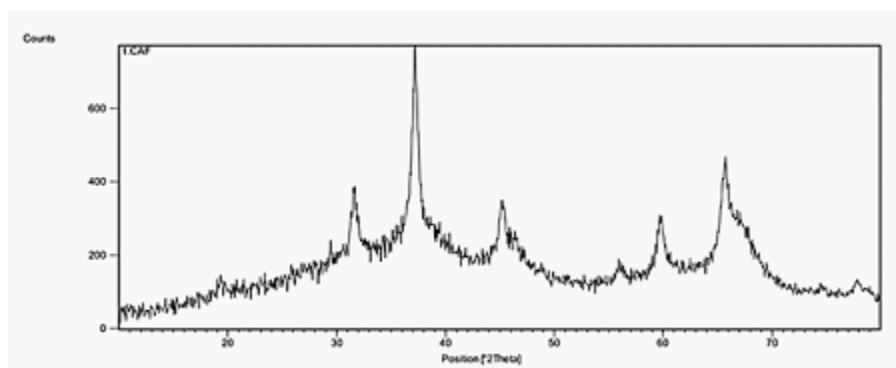
Fig. 1. XRD patterns of 10 wt.% Co_3O_4/nano-γ-alumina

and 15 mmol TBHP in a round bottom flask and some samples was drawn out at regular intervals and analyzed by GC. Figure 3 shows that the conversion of cyclohexanol increases continuously until 82.1% as time increases and
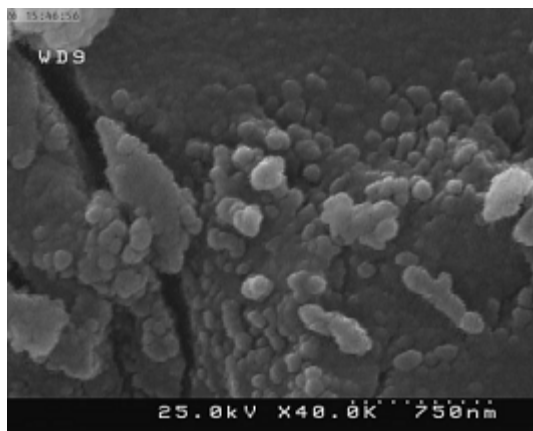

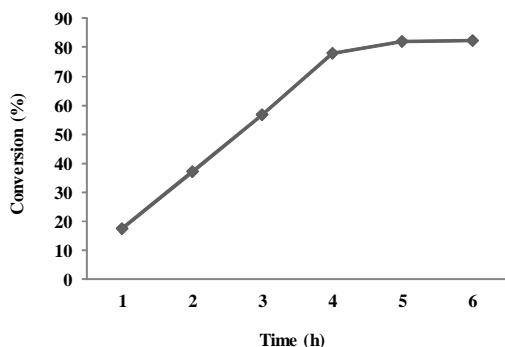**Fig. 2.** SEM photograph of 10% Co_3O_4/nano-γ-alumina

Fig. 3. The effect of reaction time on cyclohexanol conversion
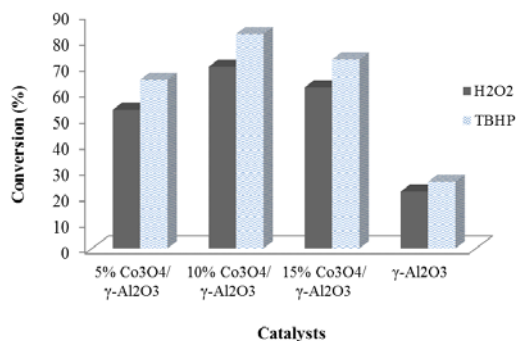

Fig. 4. The effect of oxidant type on cyclohexanol conversion in the presence of acetonitrile as the solvent.

then remains constant after 5 h, therefore duration about 5-6 h is proper reaction time.

Influences of the Loading Amount of Cobalt Oxide on Cyclohexanol Oxidation Reaction

For investigation of the loading effect Co_3O_4 on the conversion and selectivity of the products three catalysts were tested. In Table 1, details of the conversion and selectivity of the products for each catalyst are shown. It is observed that maximum conversion occurs with the catalyst of 10% Co_3O_4/nano-γ-alumina. It is known that cobalt oxide can be highly dispersed on γ-alumina at 10 wt.% loading. A drop of conversion of cyclohexanol of the catalyst with higher loadings than 10 wt.% is possibly due to a more reduction of the specific surface area of the catalyst. Under these reaction conditions, the order of catalytic activities is as follows:

10% Co_3O_4/nano-γ-alumina > 15% Co_3O_4/nano-γ-alumina > 5% Co_3O_4/nano-γ-alumina.

Influences of Substrates and Oxidant Type on Cyclohexanol Oxidation Reaction

Figure 4 shows that the reactivity of the cyclohexanol toward oxidation with TBHP and H_2O_2 on Co_3O_4 nanoparticles supported on γ-alumina catalysts depend on type of oxidant. *tert*-butylhydroperoxide (TBHP) was found to be a more convenient oxidizing reagent due to weaker O-O bond than hydrogen peroxide (H_2O_2).

In this study, experiments on various selected alcohols were performed and the comparisons with respect to conversion and product selectivity are represented in Table 2. Higher conversion was obtained for cyclohexanol on 10% Co_3O_4/nano-γ-alumina catalyst using *tert*-butylhydroperoxide oxidant. Table 2 shows that the reactivity of the alcohols toward oxidation with TBHP and H_2O_2 on 10% Co_3O_4/nano-γ-alumina catalyst depends on the particular structure of the substrate.

CONCLUSION

In this study, a γ-alumina was prepared, and then its role in the catalytic activity of the cobalt oxide nanoparticle in the oxidation reaction of cyclohexanol in the liquid phase was investigated. The characteristics of catalysts that were prepared using the XRD, SEM and BET were investigated. In addition, the catalytic activity of

the cobalt oxide nanoparticles supported on γ-alumina in oxidation of cyclohexanol with *tert*-butylhydroperoxide (TBHP) as well as hydrogen peroxide (H_2O_2) as the oxidant and in the liquid phase were studied which revealed that TBHP oxidant was better than H_2O_2. In addition, methanol, ethanol and acetonitrile were used as the solvent. Due to its high polarity and the creation of reactive oxygen species in the reaction medium, acetonitrile was far better than other solvents. Finally, the oxidation of different alcohols was analyzed using optimum conditions that became clear that various alcohols showed different percentage of conversion that was based on the type of alcohols structure.

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