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FULL PAPER

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Highly selective aerobic oxidation of alkylarenes catalyzed by cobalt-based nanocatalyst in aqueous solution

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The catalytic aerobic oxidation of alkylarenes catalyzed by cobalt supported on a highly crystalline γ-Al_2O_3 support (Co/Al_2O_3 nanocatalyst) is reported. The catalyst was prepared by a co-precipitation method and characterized using scanning and high-resolution transmission electron microscopies, energy-dispersive X-ray spectroscopy, X-ray diffraction and surface area measurements. A wide range of alkylarenes were converted to corresponding ketones. The catalyst can be recovered by simple filtration is recyclable for up to six consecutive runs.

KEYWORDS
aerobic oxidation, alkylarenes, co/Al_2O_3 nanocatalyst, ketones

1 | INTRODUCTION

The oxidation reaction of alcohols is one of the most important transformations in synthetic chemistry that represents a significant methodology for the introduction and modification of functional groups. In this way, the oxidation of alkylarenes to their corresponding carbonyl compounds is of significant importance in organic chemistry, not only in academic research but also in the chemicals industry.[1–3]

In previous research, various catalytic procedures have been developed for the oxidation of alkylarenes using various oxidants, solvents and reaction conditions. In this view, environmentally benign procedures such as using green oxidants and heterogeneous recyclable catalysts are especially attractive for the oxidation of alkylarenes.

Due to the availability of oxygen in the air, and the fact that a by-product of oxidation in an atmosphere of oxygen is water, aerobic oxidation of alkylarenes using oxygen as the oxidant has drawn special attention in organic chemical synthesis.[4]

Until now various kinds of catalysts have been prepared for the aerobic oxidation of alkylarenes, and the catalytic activity, reaction mechanism, synthesis procedure and chemical character of such catalysts are different from each other. Based on the literature, the performance of metal-based catalysts such as Co,[5–9] Cu,[10,11] Mn[12] and Au[13] nanocatalysts in the aerobic oxidation of alkylarenes has been are widely reported.

Distinctive surface properties of metal oxide nanoparticles of definite shape and size have motivated the exploration of new synthesis strategies for nanostructured materials under controlled synthesis conditions. Therefore a convenient synthesis method for designing a nanomaterial having large surface area is highly attractive. Among the metal oxides studied in this context, Al_2O_3 is one of the most intensively investigated due to its wide-scale potential in catalysis, optics, electronics, adsorption and biomedical applications.[14,15]

Cobalt catalysts supported on alumina are important material systems in the field of heterogeneous catalysis. It has been reported that metal–support interactions may appreciably affect surface properties, and hence catalytic activities.[16,17] Especially, Co nanoparticles supported on Al_2O_3 substrates exhibit an attractive performance in oxidation reactions because of the favourable mechanical properties of the alumina support.[18–26] It has been reported that metal–support interactions can significantly improve the physical properties of the surface of a catalyst and hence the catalytic activity.

Supported metallic nanoparticles play an important role in nanoscience and nanotechnology. Moreover, the immobilization of nanoparticles on high-surface-area supports allows a higher stability and dispersity of the particles as well as a further exploitation of the special activity and recycling properties of catalysts.[27]

To the best of our knowledge, the performance of cobalt nanocatalysts supported on γ-alumina has not been investigated for organic synthesis reactions, especially for the oxidation of alkylarenes. Therefore, in continuation of our studies of the catalytic activity of various nanocatalysts in aerobic oxidation reactions,[28–34] herein the performance of a Co nanocatalyst supported on a highly crystalline γ-Al_2O_3 support is reported for the aerobic oxidation of alkylarenes to their corresponding ketones (Scheme 1).

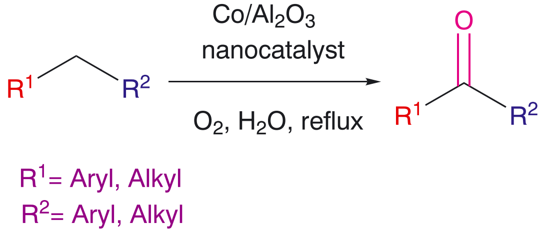
2 | EXPERIMENTAL

2.1 | General

Chemicals were purchased from Merck. All products were characterized by comparison of their spectroscopic data (NMR, IR) and physical properties with those reported in the literature. Yields refer to isolated pure products.

2.2 | Catalyst preparation

The nanocatalyst of cobalt oxide supported on Al_2O_3 (Co/Al_2O_3 nanocatalyst) was synthesized using a co-precipitation method. An aqueous solution of 0.5 M NaOH was added to a mixture of 0.5 M cobalt nitrate and aluminium nitrate under vigorous stirring at 50 °C. The obtained solution was aged at pH = 9 for 1 h, then filtered and washed with deionized water to remove the interfering ions. The sample was dried overnight at 100 °C and then calcined in air at 450 °C for 4 h. Also, a batch of Al_2O_3 support without Co content was prepared using the same method for supplementary analysis.



SCHEME 1 Aerobic oxidation of alkylarenes catalyzed by Co/Al_2O_3 nanocatalyst

2.3 | Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area of the catalyst was measured using the nitrogen adsorption–desorption method. The analysis was carried out using an automated gas adsorption analyser (Tristar 3020, Micromeritics). The sample was purged with nitrogen gas for 3 h at 300 °C using a VacPrep 061 degas system (Micromeritics).

X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer, Cu Kα monochromatized radiation source and a nickel filter (PANalytical X'Pert-Pro), in order to investigate the structure and crystallinity of the catalyst. The Scherrer equation was used to determine the average crystallite size of the sample. A flame atomic absorption spectrophotometer (GBC 906AA) was applied to determine the cobalt content of the catalyst.

The morphology of the prepared catalyst was analysed using scanning electron microscopy (SEM) with a JEOL JSM-6500F instrument, equipped with an energy-dispersive X-ray spectroscopy (EDS) analytical system to study the presence of various components of the catalyst. Transmission electron microscopy (TEM) analysis was also performed using a JEOL JEM-2100 (200 kV) microscope equipped with an EDS analytical system. The sizes of about 200 cobalt nanoparticles were measured in order to determine the size distribution and average particle size of the cobalt nanoparticles.

2.4 | General procedure

A heterogeneous mixture of alkylarene (1 mmol) and Co/Al_2O_3 nanoparticles (0.07 g) in water was stirred under oxygen atmosphere at reflux condition. The progress of the reaction was followed using TLC. After reaction completion, the catalyst was recovered by filtration, then washed with hot ethanol (2 × 5 ml), and dried for subsequent reaction runs. The filtrate was extracted with *n*-hexane. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure products.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

The XRD patterns of the cobalt nanocatalyst and the Al_2O_3 support are shown in Figure 1. The Co/Al_2O_3 nanocatalyst shows diffraction peaks at $2\theta = 37.60°$,

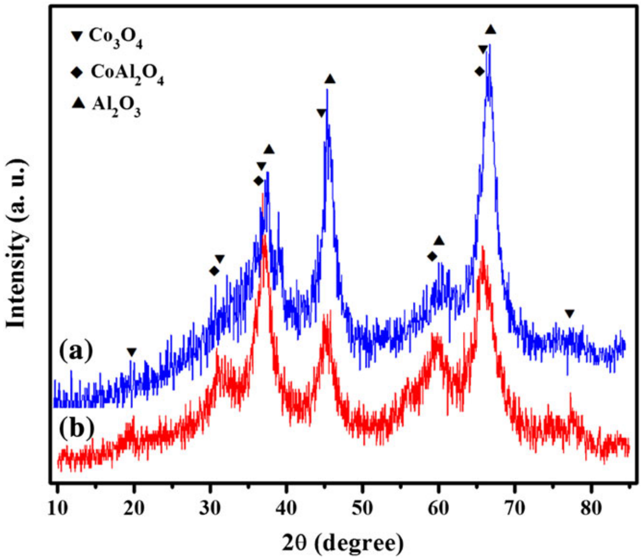


FIGURE 1 XRD patterns of (a) Al_2O_3 support and (b) cobalt nanocatalyst

45.79°, 66.76° and 85.02°, which are attributed to [110], [111], [211] and [300] planes of γ-Al_2O_3 (code no. 01-1303). The diffraction peaks at 19.04°, 31.35°, 36.94°, 44.92°, 59.51°, 65.41° and 77.56° respectively correspond to [111], [220], [311], [400], [511], [440] and [533] planes of cubic Co_3O_4 (code no. 01-074-1657). In addition, the XRD pattern of the cobalt nanocatalyst shows a distinct peak at 94.38° which is attributed to [731] plane of $CoAl_2O_4$ (code no. 03-0896). This peak indicates the incorporation of Co species into the structure of the Al_2O_3 support at calcination temperatures as high as 450 °C. The average crystallite size of Co oxide in the Co/Al_2O_3 nanocatalyst, calculated using the Debye–Scherrer equation, is about 11.1 nm.

Figure 2 shows the nitrogen adsorption–desorption profiles of the catalyst. The results show that the alumina support and the Co nanocatalyst exhibit adsorption–desorption isotherm profiles with hysteresis loops between $p/p^0 = 0.45$ and 0.9. Based upon the IUPAC classification, this type of isotherm is categorized as type IV, and ascribed to mesoporous structures. While the alumina support adsorption profile shows an H3-type hysteresis loop, which can demonstrate aggregates of nonuniform narrow slit-like pores of plate-like and/or cubic nanoparticles, the Co/Al_2O_3 sample shows an H2 hysteresis loop which is common for mesoporous carrier and catalysts. This type of hysteresis loop is attributed to aggregates and agglomerates of spheroidal particles with nonuniform size and shape pores.[35,36] As exhibited in Figure 2, the alumina support and the cobalt nanocatalyst display narrow pore size distributions with a maxima at 3 and 4 nm, respectively.

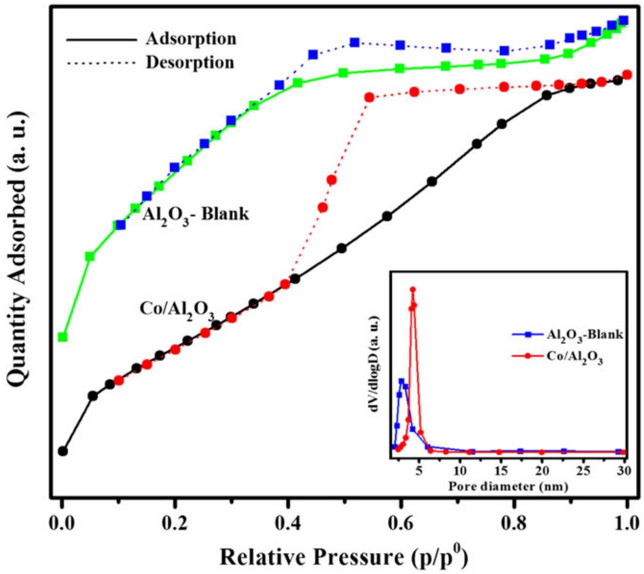


FIGURE 2 Nitrogen adsorption–desorption profiles of Co/Al_2O_3 nanocatalyst

Table 1 presents structural properties of the samples. The amount of Co in the catalyst analysed using atomic absorption spectroscopy is 9.6 wt%. The alumina support has a high BET surface area of about 270 $m^2\ g^{-1}$; however, after incorporation of Co content the BET surface area is decreased to about 252 $m^2\ g^{-1}$. Also, the decrease in the average pore size of the support is consistent with the pore size distributions of the samples in Figure 2.

Figure 3 displays SEM micrographs, TEM images and EDS results for the Co/Al_2O_3 catalyst. SEM analysis (Figure 3b,c) shows a uniform aggregate of nanoparticles with a diameter of about 21 nm. This result is in accordance with the type IV H2 hysteresis isotherm of the nitrogen adsorption–desorption experiment.

As shown in Figure 3(e), cobalt nanoparticles are dispersed on the alumina support with a particle size distribution of between 3 and 13 nm, and an average size of about 6.5 nm. The high-resolution TEM image of the catalyst (Figure 3g) exhibits reflections with *d*-spacing values of about 0.24 nm that can be attributed to Co_3O_4 (311) lattice plane.

TABLE 1 Structural properties of Al_2O_3 support and Co/Al_2O_3 nanocatalyst

Sample	Co content (wt%)[a]	Co crystallite size (nm)[b]	BET surface area ($m^2\ g^{-1}$)	Average pore size (nm)	Pore volume ($cm^3\ g^{-1}$)
Al_2O_3	0.0	—	269	2.8	0.21
Co/Al_2O_3	9.6	11.1	252	4.0	0.24

[a] Measured by atomic absorption method.

[b] Average Co crystallite size calculated by XRD.

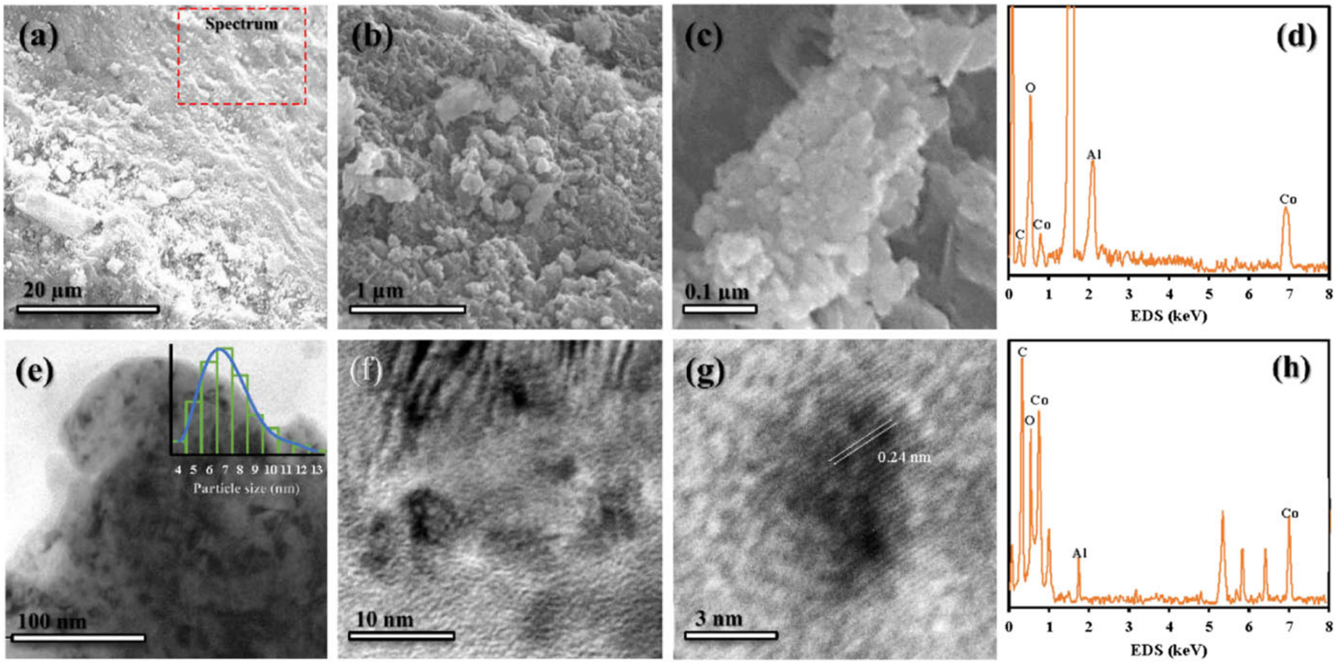


FIGURE 3 (a–c) SEM micrographs, (e–g) TEM images and (d, h) EDS results of Co/Al_2O_3 nanocatalyst

The EDS analysis shows a cobalt content of about 15.4 wt% on the surface of the catalyst. The higher Co loading in comparison to the nominal Co loading (10 wt%) could be due to the procedure of the synthesis of the catalyst. By considering the higher K_{sp} number of $Co(OH)_2$ (3×10^{-16}), in comparison to K_{sp} of $Al(OH)_3$ (3×10^{-34}), it can be suggested that with a gradual increase of the pH of solution during the co-precipitation procedure, the Co clusters tend to precipitate at higher pH values; this results in an increase in the amount of Co on the surface of the Co/Al_2O_3 catalyst.

3.2 | Catalytic activity

As presented in Table 2, the catalytic performance of the Co/Al_2O_3 nanocatalyst was studied for aerobic oxidation of ethylbenzene in various solvents such as water, ethanol, methanol, acetonitrile or DMSO, under oxygen atmosphere and reflux conditions. The obtained results demonstrated a high yield of 90% after 4 h of reaction in water solution. However, ethanol, as the second most active solvent, resulted in a yield of only 50% for a reaction time of 12 h. Therefore, water was adjudged as the most efficient solvent for the subsequent catalytic investigations.

TABLE 2 Optimization of reaction conditions[a]

Entry	Solvent	Condition	Catalyst (g)	Time (h)	Yield (%)[b]
1	CH_3CN	Reflux	0.07	12	25
2	DMSO	Reflux	0.07	12	20
3	CH_3CH_2OH	Reflux	0.07	12	50
4	Toluene	Reflux	0.07	12	10
5	*n*-hexane	Reflux	0.07	12	Trace
6	H_2O	Reflux	0.07	4	90

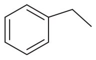
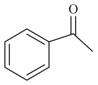
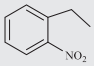
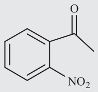
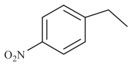
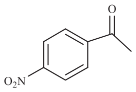
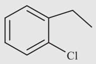
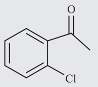
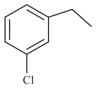
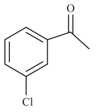
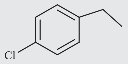
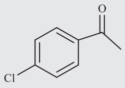
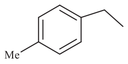
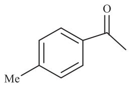
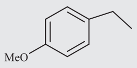
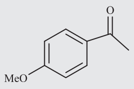
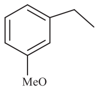
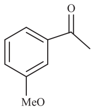
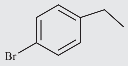
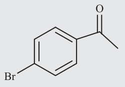
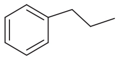
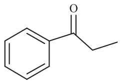
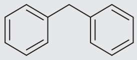
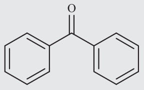
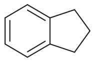
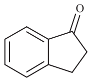
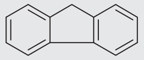
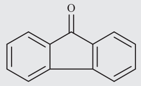
[a] Reaction conditions: ethylbenzene (1 mmol), O_2, reflux.

[b] Isolated yield.

Moreover, optimization of temperature and amount of catalyst was conducted. The best results were achieved in the presence of 0.07 g of catalyst in water under reflux condition (Table 2). Therefore, the reactions were performed in the presence of 0.07 g of Co/Al_2O_3 in water under reflux condition.

The scope of our procedure was investigated for the aerobic oxidation of various alkylarenes under oxygen balloon under optimized conditions (Table 3). As is evident from Table 3, alkylarenes were converted into the corresponding ketones in high yields under mild conditions. A wide range of ethylbenzene derivatives including those containing electron-donating and electron-withdrawing groups could be oxidized efficiently to the corresponding ketones with good conversions (Table 3, entries 1–10). All the reactions occurred with absolute selectivity for ketones and no other products were detected in the reaction mixture. Moreover, the oxidation of other cyclic arenes such as diphenylmethane and fluorene under the same reaction conditions afforded the corresponding ketones in high yields (Table 3, entries 12–14).

TABLE 3 Aerobic oxidation of alkylarenes catalyzed by Co/Al_2O_3 nanocatalyst[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			4	90
2			4	87
3			5	87
4			4	88
5			4	90
6			4.5	88
7			4	90
8			4	91
9			4.5	89
10			4	90
11			6.5	88
12			8	87
13			7	88
14			7	87

[a] Reaction conditions: alkylarenes (1 mmol), Co/Al_2O_3 nanocatalyst (0.07 g), in water at reflux conditions.

[b] Isolated pure products.

TABLE 4 Recyclability of Co/Al_2O_3 nanocatalyst

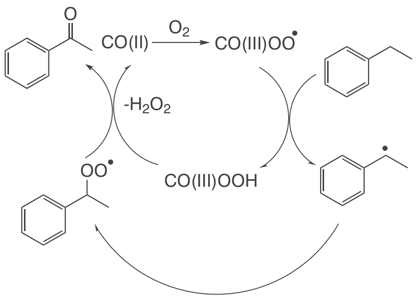
Run	1	2	3	4	5	6
Time (h)	4	4	5	5.5	5.5	7
Yield (%)[a]	90	90	89	88	85	80

[a] Isolated pure products.

Further studies were carried out to investigate the recyclability of the catalyst. As evident from Table 4, the aerobic oxidation of ethylbenzene was carried out six times in consecutive runs with only a slight decrease in the yield of products. After reaction completion, the catalyst was washed with hot ethanol, dried and stored for the subsequent reaction run.

A possible mechanism of the reaction is shown in Scheme 2. It possibly proceeds through the removal of a hydrogen atom from the benzylic position of the alkylarene by the Co/Al_2O_3 nanocatalyst.[5–7]

In order to show the merit of our method, Table 5 compares the results for the aerobic oxidation of alkylarenes catalysed by Co/Al_2O_3 nanocatalyst with those for some other reported catalysts. Compared with other reported catalysts, the Co/Al_2O_3 nanocatalyst promotes the reaction very effectively and gives the desired products in high yields in water. The catalyst can be recovered simply by filtration and can be reused in subsequent runs without significant decrease in its



SCHEME 2 Plausible mechanism of aerobic oxidation catalyzed by Co/Al_2O_3 nanocatalyst

TABLE 5 Comparison between Co/Al_2O_3 nanocatalyst and some other catalysts employed for aerobic oxidation of ethylbenzene

Entry	Condition	Catalyst	Time (h)	Yield (%)[a]	Ref.
1	[bmim]Br/100 °C	Co-pc	7	77	[5]
2	*o*-xylene/reflux	CoPc@cell	10	89	[6]
3	*p*-xylene/reflux	Co-NHAp	6	75	[7]
4	Acetonitrile/80 °C	$[CoTSPc]^{4-}/SiO_2$	24	39	[8]
6	H_2O/reflux	Co/Al_2O_3 nanocatalyst	4	90	This work

[a] Isolated yield.

activity. Reactions in the presence of some of other catalysts were performed in organic solvents. Moreover, other reported methods required longer reaction times and also excess amounts of base need to be used for reaction completion.

4 | CONCLUSIONS

We have discovered an efficient catalytic procedure for the aerobic oxidation of alkylarenes catalysed by Co supported on a highly crystalline γ-Al_2O_3 support (Co/Al_2O_3 nanocatalyst) in water. The Co/Al_2O_3 nanocatalyst demonstrated a good performance for the aerobic oxidation of various alkylarenes with O_2 as the oxidant. Moreover, the introduced nanocatalyst was easily separated from the reaction mixture with simple filtration and showed good recyclability and stability.

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