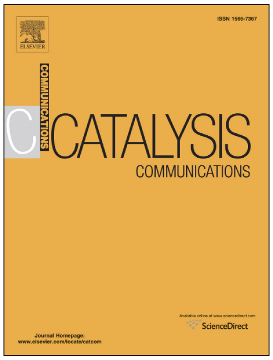

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Selective aerobic oxidation of toluene to benzaldehyde on immobilized CoO_x on SiO_2 catalyst in the presence of N-hydroxyphthalimide and hexafluoropropan-2-ol

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Abstract

A cost-effective method for the selective oxidation of toluene to benzaldehyde was developed based on immobilized CoO_x on SiO_2 catalyst with predominating cobaltous ions in the presence of N-hydroxyphthalimide (NHPI) and hexafluoropropan-2-ol (HFIP) using ambient molecular oxygen at room temperature. A toluene conversion of 91% and a selectivity to benzaldehyde of 68% were realized. HFIP was confirmed to work as a restraining agent against the further oxidation of benzaldehyde to benzoic acid on the immobilized CoO_x/SiO_2 catalyst in the presence of NHPI and HFIP.

Keywords: Toluene; Molecular oxygen; Selective oxidation; Benzaldehyde; Cobalt oxide; Immobilization.

1. Introduction

Benzaldehyde presents increasing and versatile applications in perfumery, pharmaceutical and agricultural industries, and it is generally produced by chlorination of toluene followed by saponification. Benzaldehyde is also obtained as a by-product of benzoic acid produced industrially, which proceeds by a liquid-phase oxidation of toluene catalysed by cobalt ions using molecular oxygen and acetic acid as oxidant and solvent, respectively [1-3]. However, some long-standing problems remain unsolved in the present mass production of benzaldehyde, such as chlorine contamination of the oxidative end-point, serious corrosion of the equipment, environmental pollution, and the poor space-time yield, which have motivated the academic and industrial perspectives to seek a simple, elegant, cost-effective and benign method for the production of benzaldehyde [1,3].

Vapor-phase oxidation of methylbenzene to benzaldehyde is favourable in a continuous operation with a high production capacity and a waiver of separation of catalyst, which is encountered in the homogeneous reaction [1,4-7]. However, the substrate conversion is generally controlled at a low level to avoid overoxidation to benzoic acid and deep oxidation products, such as CO_x [1,4]. The heterogeneous photocatalysis was used to probe aerobic oxidation of toluene to benzaldehyde in consideration of its environmentally benign characteristics, but its transformation efficiency must be markedly enhanced till the practical application can be considered [8, 9]. Liquid-phase oxidation of toluene can prevent the production of CO_x and other small molecular products. Unfortunately, benzoic acid is found as the predominating product because the desired benzaldehyde is much more easily oxidized than toluene [3]. An important progress was recently made by Pappo's group in the highly selective formation of benzaldehyde from toluene by aerobic oxidation using a cobalt acetate/N-hydroxyphthalimide (NHPI) in the presence of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), where a yield of more than 95% for benzaldehyde was realized using molecular oxygen at room temperature [10, 11]. It was found that the spontaneous oxidation of benzaldehyde at room temperature can be completely suppressed by HFIP. However, benzaldehyde was totally converted into benzoic acid in acetonitrile or acetic acid under the same conditions. Furthermore, the H-bond donor-acceptor interaction between benzaldehyde and HFIP was detected by ^{13}C NMR spectra, and the strong H-bonding was supported by their computational studies [10, 11]. Based on well-established chemistry of Ishii and co-workers [10] for the conversion of toluene into benzoic acid (Scheme S1), the authors contributed the highly efficient transformation from toluene to benzaldehyde to the role of HFIP, which prevents the subsequent oxidation of benzaldehyde to benzoic acid by inhibiting the cleavage of the aldehydic C-H bonds. In spite of the unprecedented achievement of

Pappo's group in the transformation from methylbenzene to benzaldehyde, there are still some barriers that need to be removed if this transformation has to be applied industrially, including the separation of cobalt acetate and NHPI and the usage of the expensive solvent HFIP, which will be inevitably consumed during its use and recycling.

In this work, cations of cobalt, manganese and cerium were supported on porous silica, and the resulting transition mixed metal oxide catalysts were used to catalyze the aerobic oxidation of toluene to benzaldehyde in the presence of NHPI and the solvent HFIP. The role of HFIP was compared to that of acetic acid, acetonitrile and ethanol, and its inhibiting mechanism in the benzaldehyde oxidation to benzoic acid was investigated based on the immobilized cobalt oxide on SiO_2 catalyst.

2. Experimental section

2.1. Catalysts preparation

CoO_x/SiO_2 catalyst was prepared by the incipient wetness impregnation method. Typically, the calculated cobaltous acetate (>99.5%, SinoPharm) was dissolved in deionized water, and 2 g of dried SiO_2 (370 m^2/g, SinoPharm) was added to the above solution with continuous stirring. The obtained mixture was dried at 393 K for 12 h followed by calcination for 4 h at 673 K in static air. MnO_x/SiO_2 and CeO_x/SiO_2 catalysts were prepared by a similar method using manganese and cerium acetate, respectively, as the corresponding precursor.

2.2. Sample characterization

Atomic absorption spectroscopy (AAS, PerkinElmer, PE-2100) was used to determine the actual Co loading in the prepared CoO_x/SiO_2 sample. An accurate amount of sample was grinded and dissolved in a solution of hydrofluoric acid, and then diluted roughly to 5 ppm for analysis.

N_2 adsorption–desorption was conducted at 77 K on a Micromeritics ASAP 2010 micropore analysis system. About 100 mg of the sample was degassed in vacuum at 393 K for 2 h before adsorption. The BET equation was used to determine the specific surface area (m^2/g) of the samples, and the BJH method to calculate the pore volume (cm^3/g) and average pore diameter (nm).

Powder XRD spectra were acquired by a Bruker D8 Advance X-ray diffractometer using Cu K_α monochromatic radiation source (λ=0.15406 nm). The 2θ degree scans covered the range 10 - 80º with a step of 0.02 º. The applied voltage and current were 40 kV and 40 mA, respectively.

TEM images were obtained using a Tecnai 12 electron microscope to determine the morphology and mean Pt particle size of the catalyst samples. The latter were dispersed in deionized water by means of ultrasonic bath for 15 min after careful grinding. The HRTEM analysis was carried out using a Tecnai G2 F30 S-TWIN electron microscope.

FT-IR spectra were recorded on a TENSOR 27 spectrometer with a resolution of 4 cm^{-1} in the 400~2000 cm^{-1} range. The self-supporting wafer diluted by KBr was prepared with a sample concentration of 1%.

The laser Raman spectra (LRS) of the samples were obtained at room temperature in air on an invia Raman microscope spectrometer (RENISHAW) equipped with a CCD detector. The 532 nm line of an Ar^+ laser was used as the excitation source with an intensity of 10 mW.

The UV-Vis/DRS spectra were recorded on a Cintra10e UV-Vis spectrometer equipped with a diffuse reflectance attachment. $BaSO_4$ was used as a reference. All spectra were recorded at room temperature under ambient gas atmosphere. A sample holder was used to support the wafer of a sample of ~ 100 mg.

XPS measurements were performed on an ESCALAB250Xi electron spectrometer. Monochromatic Al $K\alpha$ (1486.6 eV, 15 kV) was used as incident radiation. The obtained binding energies were determined with an overall resolution better than 0.05 eV. The C 1s binding energy from adventitious hydrocarbon was used as a charge reference, and this was fixed at 284.8 eV.

2.3. Catalytic activity measurements

The catalytic performance of the synthesized immobilized transitional metal oxides was evaluated towards the aerobic oxidation of toluene. The reaction was carried out in a Schenk tube (10 ml) at room temperature under an O_2 atmosphere (>99.9%, 1 atm). In a typical reaction, 0.50 mmol of toluene, 0.005 g of catalyst, 0.050 mmol of NHPI and 1 ml of HFIP were introduced into the Schenk tube, and the rest of the tube was repeatedly purged by O_2 (99.9%) before measurements. The resulting mixture after 4 h of reaction was analyzed by off-line GC (SHIMADZU GC-2014) equipped with a SGE AC-10 capillary column and a flame ionization detector.

In a scale oxidation, 100 mmol of toluene, 1.0 g of catalyst (2 mmol/g), 10 mmol of NHPI and 200 ml of HFIP were added into a three-necked flask. The reaction was carried out at room temperature for 4 h under continuous magnetic stirring after a careful displacement of the gaseous place of the flask using O_2 (99.9%). The reaction mixture was filtered to recycle the immobilized catalyst, and the liquid part was analyzed by GC. The recycled catalyst was repeatedly washed using anhydrous ethanol followed by drying in static air at 120 ^{o}C for 10 h. The solvent HFIP was recycled by distillation.

3. Results and discussion

3.1. Textural and structural properties

The SiO_2 (silica gel, 370 m^2/g, 7.5 nm) carrier was used to deposit the cobalt acetate by the incipient wetness impregnation, and the resulting CoO_x/SiO_2 catalyst (2 mmol/g) exhibited excellent textural properties and a high degree of dispersion of cobalt oxide on the support (Fig. S1, Table S1 in ESI). The content of cobalt ions in the catalysts was determined by ICP-OES, and this was found well agreeing with the nominal Co loading (Table S2).

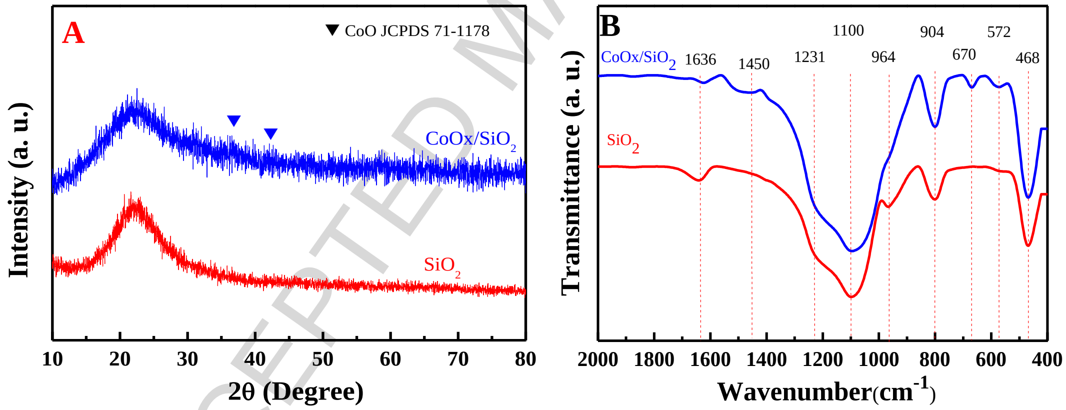


Fig. 1. Powder XRD patterns (A) and FT-IR spectra (B) of support SiO_2 and of the synthesized CoO_x/SiO_2 catalyst (2 mmol/g).

Powder XRD, FT-IR, Raman and UV-Vis/DRS were adopted to investigate the phase of cobalt oxide in the synthesized CoO_x/SiO_2 catalyst, and results are shown in Fig. 1 and Fig. S3 (ESI), respectively. Very weak XRD characteristic peaks at ca. 2θ degree of 36^{o} and 42^{o} were detected on the CoO_x/SiO_2 catalyst, which can be assigned to CoO with face-centered cubic CoO structure (JCPDS 71-1178), also suggesting a high dispersion degree of cobalt oxide on the support (Fig. 1a). A weak absorption peak located at ~1450 cm^{-1} in the FT-IR spectrum of CoO_x/SiO_2 catalyst recorded can be assigned to CoO species (Fig. 1B). However, the absorption peaks at 572 and 670 cm^{-1} can be attributed to the presence of a spinel Co_3O_4 phase [12,13]. The other absorption IR bands seen in the FT-IR spectrum are due to the support and its surface hydroxyls [14]. In consideration of a weak signal of CoO in FT-IR [12], this suggests that the prepared CoO_x/SiO_2 catalyst contained a considerable amount of CoO besides Co_3O_4.

In the Raman spectrum of CoO_x/SiO_2 catalyst (Fig. S2A, ESI), the characteristic bands observed at 478, 515, 616 and 685 cm^{-1} can be ascribed to the presence of the crystalline Co_3O_4 [15]. However, the bands centred at 460 and 670 cm^{-1} should be assigned to cobalt oxide, CoO [16]. The diffuse reflectance spectrum of the CoO_x/SiO_2 catalyst presented absorption bands at 521, 591 and 657 nm (Fig. S3B, ESI), which is an indication of the presence of Co^{2+} ions [13]. A weak shoulder at 765 nm might suggest the presence of Co_3O_4 spinel [13].

3.2. Surface oxidation states of cobalt

Fig. 2 compares the Co 2p XP spectrum of the CoO_x/SiO_2 catalyst with that of the bulk of Co_3O_4, which was prepared by thermal decomposition of cobalt acetate at 673 K in static air, and confirmed by XRD as a pure phase of Co_3O_4. The XP spectrum of the bulk Co_3O_4 was in line with the characteristics reported in the literature [19]. The Co 2p XP spectrum of the CoO_x/SiO_2 catalyst exhibits two main peaks at 781.6 and 797.5 eV, corresponding to the Co 2p3/2 and Co 2p1/2, respectively, with a spin-energy separation of 16.1 eV, which is in agreement with the XP spectra of CoO reported [19,20]. In addition, two shake-up peaks at 6.0 eV higher binding energy further confirmed the domination of the cobaltous ions on the surface of the prepared CoO_x/SiO_2 catalyst [20].

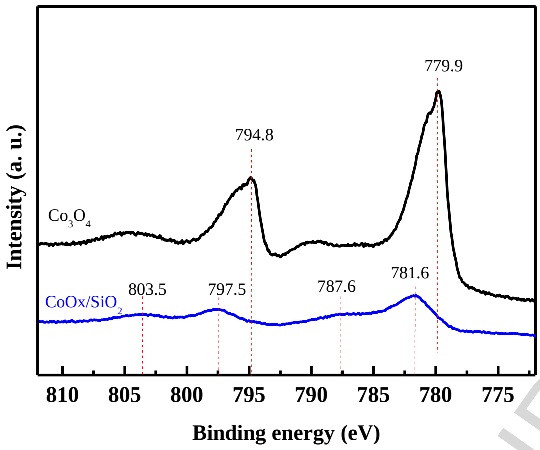


Fig. 2 Core level Co 2p XP spectra of the bulk Co_3O_4 and the synthesized CoO_x/SiO_2 catalyst.

3.3. Morphologies and elemental dispersion

The TEM image and elemental mapping of the CoO_x/SiO_2 catalyst are shown in Fig. 3 and Fig. S4 (ESI), respectively. It was found that CoO_x appears as nanoparticles of less than 5 nm in size, and homogeneously dispersed on the SiO_2 carrier, result which agrees with the XRD pattern shown in Fig. 3a. Fig. 3B presents a clear lattice spacing of ca. 0.25 nm, which can be assigned to the (111) crystal plane of CoO (JCPDS 71-1178). The energy dispersive spectrum of the CoO_x/SiO_2 catalyst confirmed cobalt oxide(s) as the sole species besides SiO_2 (Fig. S5, ESI). The STEM image and the elemental mapping images, further demonstrated that cobalt, oxygen and silicon were highly dispersed (Fig. S4A, B, ESI). In addition, the TEM images of CoO_x/SiO_2 catalyst with different loadings were compared and the results are shown in Fig. S6 (ESI). It was found that the mean particle size of CoO_x increased with increasing loading. A superfluous loading of CoO_x (4 mmol/g) led to a sharp increase in the size of cobalt oxide particle and an obvious aggregation.

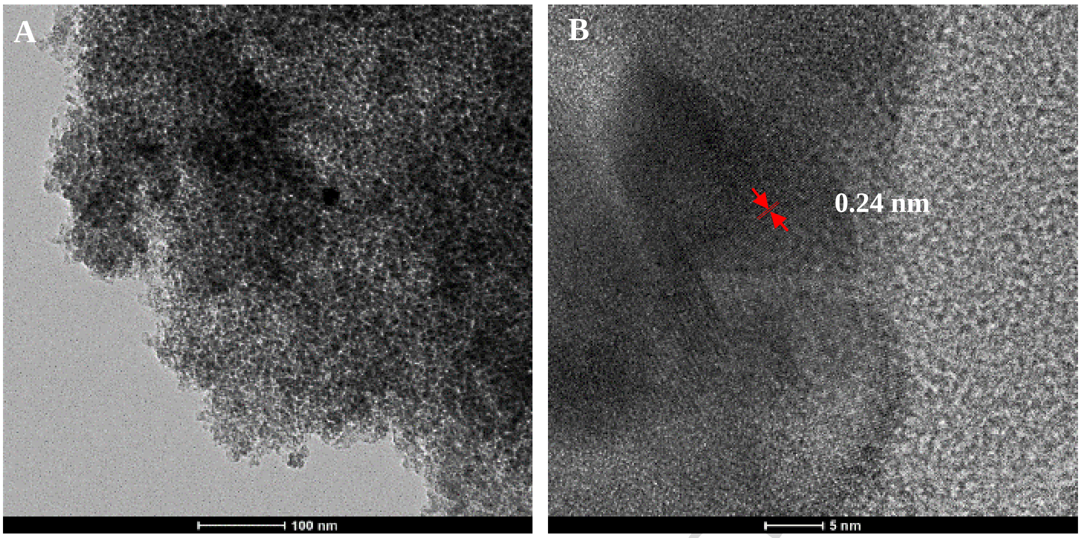


Fig. 3 TEM image (A) and HRTEM image (B) of CoO_x/SiO_2 catalyst.

3.4. Catalytic performance

Aerobic oxidation of toluene to benzaldehyde over the prepared catalysts was carried out at room temperature in the presence of NHPI and HFIP, and the results are shown in Table 1. No conversion of toluene is observed in the absence of CoO_x and NHPI (entry 1), indicating that autoxidation of toluene is negligible under the applied reaction conditions. Only CoO_x/SiO_2 catalyst was found inert for toluene oxidation under the conditions applied (entry 2). There is a toluene conversion of 0.6% detected when only NHPI was used as catalyst (entry 3), which suggests that NHPI itself can catalyze the oxidation of toluene to benzaldehyde, benzyl alcohol and benzoic acid, with a very low reactivity.

The supported CoO_x/SiO_2 catalyst (entry 4) exhibits a high toluene conversion (91.2%) in the presence of HFIP, which is similar to that observed in a homogeneous reaction by Pappo's group [10]. This shows that the immobilized cobalt oxide on silica and the homogeneous NHPI can synergistically catalyze the selective oxidation of toluene to benzaldehyde in the HFIP. However, ca. 68% of selectivity to benzaldehyde was detected, and this is lower than that observed by Pappo et. al. [10], indicating that the aerobic oxidation of toluene over the immobilized CoO_x catalyst could proceed in a different way than the homogeneous catalytic reaction. With respect to the CoO_x/SiO_2 catalyst, the MnO_x/SiO_2 presents a much lower reactivity (entry 5), and the supported cerium oxide catalyst shows a poor activity for toluene oxidation (entry 6). These results indicate that the immobilized cobalt oxide catalyst is more active for the selective oxidation of toluene to benzaldehyde under the applied reaction conditions. The immobilization of cobalt ions is favorable for the separation of the supported cobalt catalyst from the reaction mixture and the recycling of the solvent HFIP.

The effect of different solvents used on the selective oxidation of toluene to benzaldehyde in the presence of CoO_x/SiO_2, NHPI and dioxygen was investigated (entry 7-10). There is a much lower toluene conversion observed in 2,2,2-trifluoroethanol than that in HFIP (entry 7). With acetic acid as the solvent, the reaction proceeded to a relatively high toluene conversion, but a severely low selectivity to benzaldehyde is observed with benzoic acid as the predominating product (entry 8). Compared with the reactions in HFIP, 1,1,1-trifluoroethanol and acetic acid, lower toluene conversion (22%) was found in acetonitrile (entry 9). However, toluene was nearly converted in ethanol under the same conditions (entry 10). It is clear that, over the immobilized cobalt oxide catalyst, HFIP markedly promoted toluene conversion and the selective formation of the desired benzaldehyde. The dramatic enhancement in the selectivity to benzaldehyde was ascribed to the formation of a H-bond adduct between HFIP and benzaldehyde, which largely slowed down the abstract of the aldehydic C-H bond, and restrained the production of benzoic acid from benzaldehyde via a Ph(CO)• intermediate [10]. Certainly, the positive role of HFIP was also embodied in an obvious improvement of toluene conversion. The role of HFIP might be attributed to its promotional role on the activation of molecular oxygen by forming hydrogen bonds between them [21-23].

The SiO_2 support presented no reactivity under the applied reaction conditions (entry 11), and the non-supported Co_3O_4 gave a poor reactivity (entry 12). The prepared CoO_x/SiO_2 catalysts with loading between 0.5 and 4 mmol/g exhibit high toluene conversions and benzaldehyde selectivities (entry 4, 13-15), and the optimized reactivity was found at the loading of 2 mmol/g, which might be attributed to the chemical state (Fig. 2) and high dispersion degree of the cobalt ions on SiO_2 carrier (Fig. S6, ESI). The reaction was also performed in static air atmosphere on the optimized CoO_x/SiO_2 catalyst (entry 16), and a much lower reactivity was observed, suggesting that a high concentration of dioxygen will facilitate the transformation of toluene to benzaldehyde.

Table 1. Aerobic oxidation of toluene on supported CoO_x catalysts with NHPI in solvents at room temperature. [a]

Entry	Catalyst	Loading (mmol/g)	Starting material	Solvent	Conversion (%)	Selectivity (%)		
						Benzaldehyde	Benzyl alcohol	Benzoic acid
1	Blank [b]		toluene	HFIP	0	-	-	-
2	CoO_x/SiO_2 [c]		toluene	HFIP	0	-	-	-
3	Blank [d]		toluene	HFIP	0.6	41.7	14	44.3
4	CoO_x/SiO_2	2	toluene	HFIP	91.2	68.8	8.4	20.3
5	MnO_x/SiO_2	2	toluene	HFIP	26.0	62.3	30.7	1.7
6	CeO_x/SiO_2	2	toluene	HFIP	1.0	36.4	14.4	15.5
7	CoO_x/SiO_2	2	toluene	2,2,2-trifluoroethanol	30.4	53.9	16.6	21.6
8	CoO_x/SiO_2	2	toluene	acetic acid	75.2	3.2	0.5	93.5
9	CoO_x/SiO_2	2	toluene	acetonitrile	23.8	21.5	2.2	71.8
10	CoO_x/SiO_2	2	toluene	ethanol	1.3	2.2	0.0	97.8
11	SiO_2	-	toluene	HFIP	0	-	-	-
12	Co_3O_4	-	toluene	HFIP	7.0	62.1	23.4	1.9
13	CoO_x/SiO_2	0.5	toluene	HFIP	47.3	58.9	34.0	3.2
14	CoO_x/SiO_2	1	toluene	HFIP	69.2	63.9	27.2	6.2
15	CoO_x/SiO_2	4	toluene	HFIP	81.4	69.0	16.7	11.7
16	CoO_x/SiO_2 [e]	2	toluene	HFIP	48.4	61.5	34.0	2.5
17	CoO_x/SiO_2	2	benzyl alcohol	HFIP	99.8	19.2	-	80.6
18	CoO_x/SiO_2	2	benzaldehyde	HFIP	31.8	-	0	99.1
19	CoO_x/SiO_2 [f]	2	toluene	HFIP	92.2	69.7	9.5	19.2
20	CoO_x/SiO_2 [g]	2	toluene	HFIP	55.5	65.1	30.3	3.6

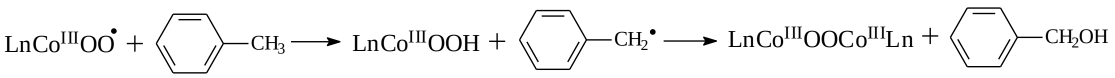
[a] Reaction conditions: toluene (0.50 mmol), supported oxide catalyst (2 mmol/g, 0.005 g), NHPI (0.05 mmol), O_2 (99.9%, 0.1 MPa), solvent (1 ml), 4 h. The composition of reaction mixture was analyzed by GC-FID.
[b] Without CoO_x/SiO_2 and NHPI.
[c] Without NHPI.
[d] Only with NHPI.
[e] Tested under air gas atmosphere.
[f] toluene (100 mmol), catalyst (2 mmol/g, 1.0 g), NHPI 10 mmol), O_2 (99.9%, 0.1 MPa), solvent (200 ml).
[g] evaluated using the catalyst recycled from entry 19.

The role of HFIP was further investigated by using benzaldehyde and benzyl alcohol as the raw materials, and the reactions were carried out under the same experimental conditions (entry 17, 18). The CoO_x/SiO_2 catalyst presented a high conversion of benzyl alcohol, up to 99.8% under the adopted experimental conditions, and the predominating product is benzoic acid besides 19.2% of selectivity to benzaldehyde. In the case of benzaldehyde, only 31.8% of conversion is observed and the benzoic acid is the exclusive resultant, indicating that HFIP can restrain the benzaldehyde transformation towards benzoic acid. However, the fact that part of benzaldehyde can be converted into benzoic acid under the same reaction conditions adopted in toluene transformation, clarified that HFIP cannot prevent the conversion of benzaldehyde to benzoic acid under the reaction conditions. This result can also explain why the observed selectivity to benzaldehyde on CoO_x/SiO_2 catalyst was 20% lower than that reported in homogeneous catalysis [10].

Benzoic acid was the sole product when benzaldehyde was used as the raw material under the adopted experimental conditions, suggesting that benzaldehyde can be directly converted into benzoic acid and the disproportionation of benzaldehyde into benzyl alcohol and benzoic acid (Cannizzaro reaction) could not occur. A low selectivity to benzaldehyde (19.2%), which is lower than benzaldehyde conversion (31.8%) when it is the starting material (entry 18), was observed when benzyl alcohol was used as the raw material under the same experimental conditions (entry 17), suggesting that benzyl alcohol can be directly converted into benzoic acid besides benzaldehyde. There was no toluene detected in the product mixture, indicating the absence of the disproportionation reaction of benzyl alcohol.

The effect of reaction time on toluene conversion and selectivity to benzaldehyde, benzyl alcohol and benzoic acid were investigated, and results are depicted in Fig. 4. At the beginning of reaction (0.5 h), benzaldehyde and benzyl alcohol are the predominating products, and there is little benzoic acid produced, which suggests that benzoic acid is not directly generated from toluene. There is a higher selectivity to benzaldehyde than benzyl alcohol at the initial stage of reaction, but 80% of benzyl alcohol is converted to benzoic acid when it is used as starting material (entry 17), which suggests that the desired benzaldehyde can be directly generated from toluene besides benzyl alcohol.

A competitive side reaction from toluene to benzyl alcohol can be suggested because ca. 40% of selectivity to benzyl alcohol was observed at the initial stage of reaction. However, research results reported by the groups of Pappo and Ishii clarified that the autoxidation of toluene does not proceed via benzyl alcohol in homogeneous catalysis [2, 10]. In fact, benzyl alcohol was found as an intermediate in the production of benzaldehyde from toluene by heterogeneous catalysis over transition metal oxides [24-27]. It was suggested the benzyl radical can react with the Co(III) hydroperoxide to produce the intermediate benzyl alcohol under the adopted experimental conditions, which is shown in Eq. (1):



(1)

The selectivity to benzyl alcohol monotonously decreased with reaction time, which can be ascribed to the competition between its generation from toluene and its further oxidation to benzaldehyde with reaction time. The generation and consumption of benzaldehyde also proceeded at the same time and an increasing trend was observed before 3.5 h of reaction, and the observed relatively high selectivity to benzaldehyde should be attributed to the inhibiting role of HFIP on benzaldehyde transformation to benzoic acid [10].

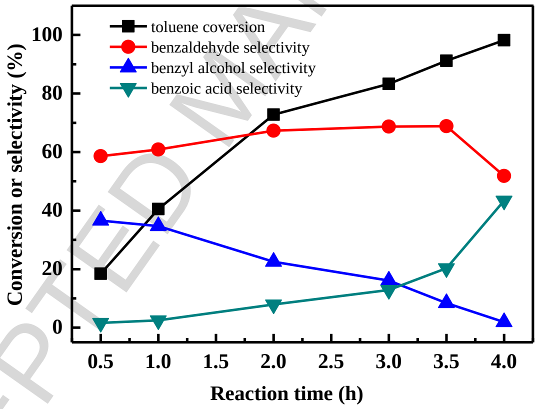


Fig. 4 Effect of reaction time on toluene oxidation at room temperature.

An enlarge-scaled reaction was carried out to probe the possibility of the further application of the catalyst, with 1 g of catalyst, 200 ml of HFIP and 10 mmol of NHPI, and catalytic results can be found in entry 19 of Table 1. A toluene conversion of 92.2% and a selectivity to benzyl alcohol of 69.7% are observed, which are similar to those observed in the Schenk tube over the same catalyst (1 ml of HFIP). About 91% of the solvent and 94% of the immobilized catalyst (CoO_x/SiO_2) were recycled. The results suggest that the recycling of the solvent and the immobilized catalyst are possible under the experimental conditions. However, toluene conversion was found a decrease when the used catalyst was evaluated in spite of an increased combined selectivity to benzaldehyde and benzyl alcohol (entry 20). The loss of catalytic activity can be partially ascribed to the loss of cobalt species in the used CoO_x/SiO_2 catalyst, since part of cobalt species was leached during the catalytic test (Table S2, ESI). Therefore, further investigations are required to decrease the loss of cobalt species and thus enhance reusability of the immobilized cobalt ions on SiO_2 catalysts. An immobilization of cobalt ions by coprecipitation or ion exchange instead of impregnation appears possible due to stronger interactions between the cobalt ions and the substrate.

4. Conclusions

CoO_x/SiO_2 catalysts were prepared by the incipient wetness impregnation method and the cobaltous oxide was found as the predominating phase on SiO_2. Toluene was selectively oxygenated to benzaldehyde on the prepared CoO_x/SiO_2 catalysts in the presence of NHPI and HFIP using molecular oxygen at room temperature. A high toluene conversion and a benzaldehyde selectivity up to 91.2% and 68.8%, respectively, were acquired. HFIP was observed to play an outstanding promotional role on the conversion of toluene to benzaldehyde and an obvious restraining role on the further oxidation of benzaldehyde to benzoic acid on the immobilized CoO_x/SiO_2 catalyst.

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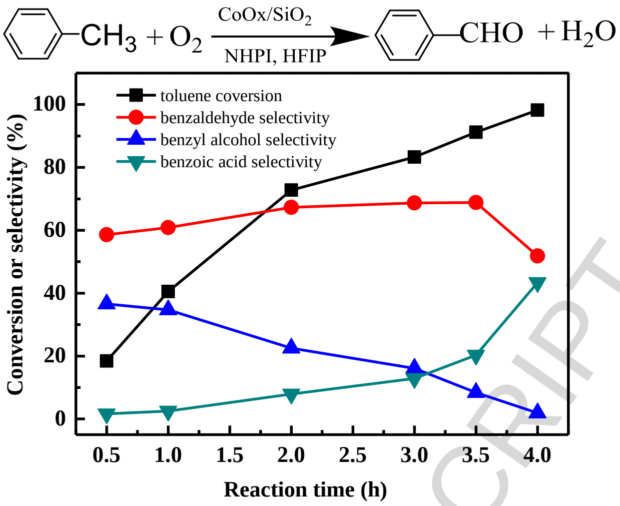
Graphical abstract



Highlights

- Immobilized CoOx catalysts were prepared with predominating cobaltous ions on SiO_2.
- The immobilized Co ions were active for toluene oxidation with NHPI in HFIP.
- A toluene conversion of 91.2% and a benzaldehyde selectivity of 68.8% were found.
- HFPI promoted the selective formation from toluene on CoO_x/SiO_2 with NHPI.