Liquid-phase oxidation of cyclohexane over Co-TUD-1

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Cobalt was successfully incorporated into TUD-1 and characterized by means of X-ray powder diffraction, UV–Vis spectroscopy, N_2 adsorption and elemental analysis. The catalyst is highly efficient in the oxidation of cyclohexane with TBHP under solvent-free and mild oxidation conditions.

KEY WORDS: oxidation; cyclohexane; TBHP; mesoporous; Co-TUD-1.

1. Introduction

Cobalt is one of the principle metals used in the catalytic oxidation of cyclohexane to cyclohexanone [K] and cyclohexanol [A], intermediates in the manufacture of nylon-6 and nylon-6,6 [1,2]. Cobalt salts, molecular oxygen and temperatures above 150 °C are employed industrially, yielding conversions of ~4% with ~85% selectivity in mono-oxygenated products (i.e. a mixture of alcohol, ketone, and the intermediate cyclohexylhydroperoxide (CHHP), which is decomposed either directly or in a separate step to yield additional ketone and alcohol) [3,4]. Although in itself a successful process, the use of a homogeneous medium and solvents has several inherent disadvantages owing to the problems of product separation and the disposal of toxic solid and liquid wastes. The design of new and improved heterogeneous catalysts for the selective oxidation of organic substrates might offer an advantage as, in addition to the obvious ease of separation, they can operate in a solvent-free fashion.

In a recent study at our laboratory (based on earlier work by one of us) [5], cobalt acetate complexes were immobilized on a variety of carboxylate-modified silica supports and studied as catalysts for the oxidation of cyclohexane under solvent-free conditions using TBHP as oxidant. Significant improvements in the K/A ratio were achieved [6].

In the case of framework substituted cobalt (rather than grafted cobalt complexes) Sankar *et al.* [7] established that such cobalt is responsible for the catalytic activity in, e.g. Co-AlPOs and that there is a correlation between the degree of activity and the amount of oxidizable cobalt in the framework.

Combining these approaches by using a mesoporous carrier which has been derivatized with cobalt might generate interesting possibilities. One such carrier is the recently reported mesoporous silica family, TUD-1, characterized by high thermal stability and a three-dimensional, sponge-like structure with tunable pores resulting in high substrate accessibility [8]. These characteristics might be advantageous when compared to those of other microporous and mesoporous materials. Additionally, its synthesis method makes it particularly suitable to produce isolated and highly dispersed metal sites as evidenced by Ti-TUD-1 [8]. In this communication, we report the highly efficient solvent-free oxidation of cyclohexane over cobalt-incorporated siliceous TUD-1 using TBHP as oxidant.

2. Experimental

2.1. Synthesis

The synthesis of Co-TUD-1 with a Si/Co ratio of 100 has been carried out analogously to that of Ti-TUD-1 [9]. A clear synthesis mixture with a molar ratio composition of $SiO_2 : 0.01\ CoO : 0.5\ TEAOH : 1\ TEA : 11\ H_2O$ was prepared by adding a solution of 0.23 g cobalt(II) sulfate heptahydrate ($CoSO_4 \cdots 7H_2O$, Aldrich) in 5 mL of deionized water to 17.4 g of tetraethyl orthosilicate (TEOS, +98%, ACROS) and stirring for a few minutes. Subsequently, a mixture of 12.6 g triethanolamine (TEA, 97%, ACROS) with 5 mL of deionized water was added dropwise before finally adding 10.3 g of tetraethylammonium hydroxide (TEA-OH, 35% Aldrich). The mixture was aged at room temperature for 24 h, dried at 100 °C for 24 h and calcined at 600 °C for 10 h at a rate of 1 °C/min in the presence of air.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were recorded using CuKα radiation on a Philips PW 1840 diffractometer equipped with a graphite monochromator.

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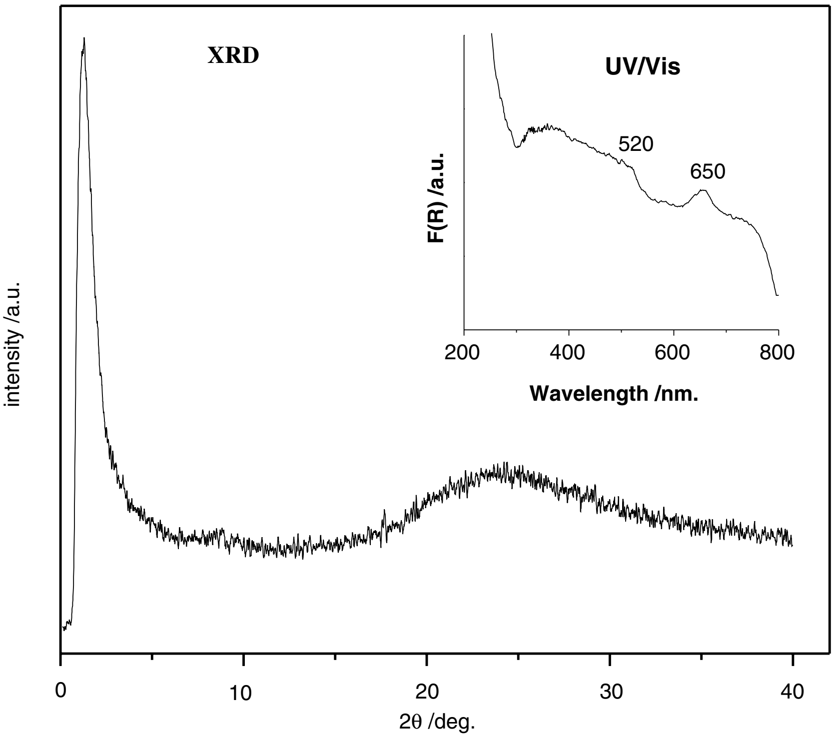

Figure 1. XRD pattern for Co-TUD-1. Inset, the UV–Vis spectrum for Co-TUD-1.

Nitrogen sorption isotherms were recorded on a Quantachrome Autosorb-6B at 77 K. Mesoporosity was calculated from the adsorption branch using the BJH model. Diffuse reflectance UV–Vis spectra were recorded using a CaryWin 300 spectrometer using $BaSO_4$ as reference. Samples were grounded carefully, heated overnight at 180 °C, and then scanned from 190 to 800 nm. Elemental analyses were carried out by using the technique of instrumental neutron activation analysis (INAA) [10].

2.3. Catalysis

In a typical cyclohexane oxidation experiment, a stock solution of TBHP in cyclohexane (30 wt%) was used as described earlier [6]. The catalyst Co-TUD-1 containing 0.1 mmol of the active metal (pre-treated in a flow of air for 24 h at 180 °C prior to the reaction) was added to the reaction mixture (consisting of 46.2 mmol cyclohexane (ACROS), 23.5 mmol TBHP (ACROS) and 3.6 mmol chlorobenzene (ACROS) as internal standard) in a two-necked round-bottomed flask (fitted with a reflux condenser and placed in a thermostated (70 °C) oil bath equipped with a magnetic stirrer). The course of the reaction was followed by analyzing the liquid samples on a GC (Agilent 6890 gas chromatograph) equipped with a split inlet (200 °C, split ratio 10.0) using a Sil 5 CB capillary column (50 m × 0.53 mm ID; constant flow of carrier gas N_2 4.0 mL/min) coupled to a FID detector. The concentration of carboxylic acid side products was determined by GC analysis from separate samples after conversion into the respective methyl esters [6,11]. Identification of the products was carried out using GC-MS. The evolution of molecular oxygen and its consumption was monitored volumetrically with an attached gas burette. The conversion of cyclohexane is defined in mol%, i.e. the moles of products formed divided by the initial moles of cyclohexane multiplied by 100. All mass balances were >92%.

3. Results and discussion

The XRD pattern of Co-TUD-1 is shown in figure 1. A single intensive peak at 0.1°–2.5° in 2θ, indicates that Co-TUD-1 is a mesostructured material. The absence of any other peaks shows that there are no bulk oxide phases of cobalt present. The UV-Vis spectrum of Co-TUD-1 is depicted as inset of Figure 1 and shows an absorption band centred at 650 nm with a shoulder around 520 nm. Both are attributed to the charge-transfer transition associated with an isolated Co(II) framework site in tetrahedral coordination [12,13].

Figure 2 shows the sorption isotherm for Co-TUD-1, which typical type IV adsorption behaviour, representing the mesostructured character. The surface area calculated using the BJH method was 620 m^2/g and the total pore volume was 0.73 cm^3/g. The pore size distribution for Co-TUD-1 (inset of Figure 2) showed a narrow distribution around 4 nm. Elemental analysis showed the Si/Co ratio in the calcined Co-TUD-1 as 108, which is very close to the theoretical ratio and

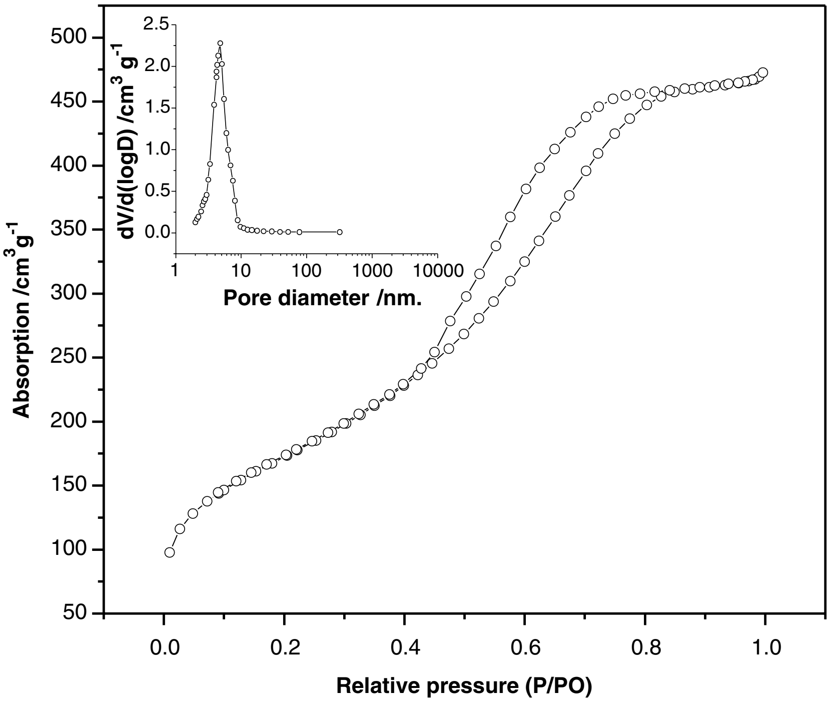

Figure 2. The N_2 sorption isotherm for Co-TUD-1. Inset, the pore size distribution for the same sample.

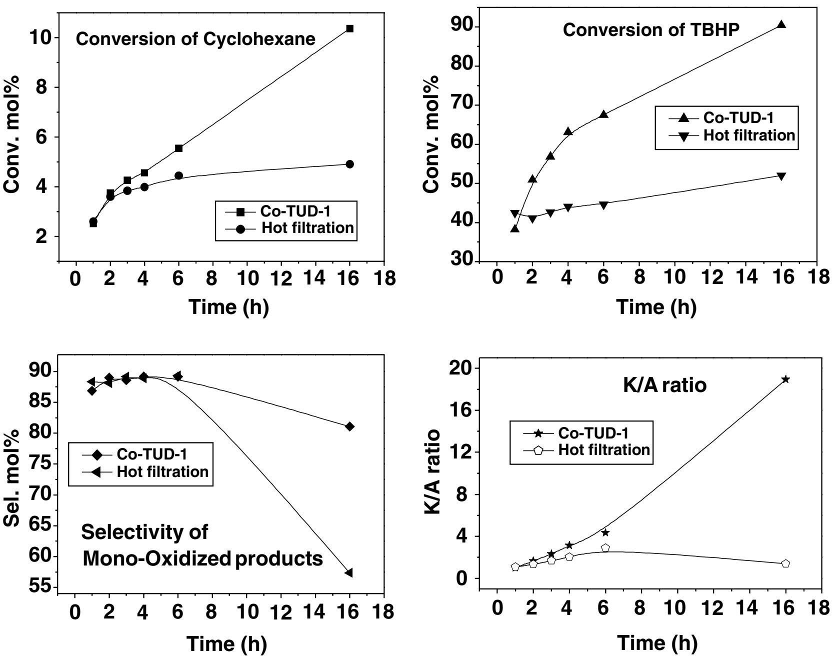

Figure 3. Comparison of results of oxidation of cyclohexane over Co-TUD-1 and hot filtration studies at 70 °C.

consistent with all the cobalt added into the initial synthesis mixture being incorporated into the final product, indicating that this is a very efficient synthesis method.

The cyclohexane oxidation results at 70 °C over Co-TUD-1 are shown in figure 3. It can be observed that both the conversion of cyclohexane and TBHP increased with time. A large amount of oxygen was evolved as compared to the conversion of cyclohexane. This suggests that not all the oxygen released by the conversion of TBHP (figure 4) is utilized directly for the alkane oxidation. The ketone to alcohol ratio was 1 after 1 h of reaction and it increased with time suggesting that part of cyclohexanol was converted to cyclohexanone. A maximum selectivity to mono-oxygenated products (89.1%) with a conversion 5.54% was obtained

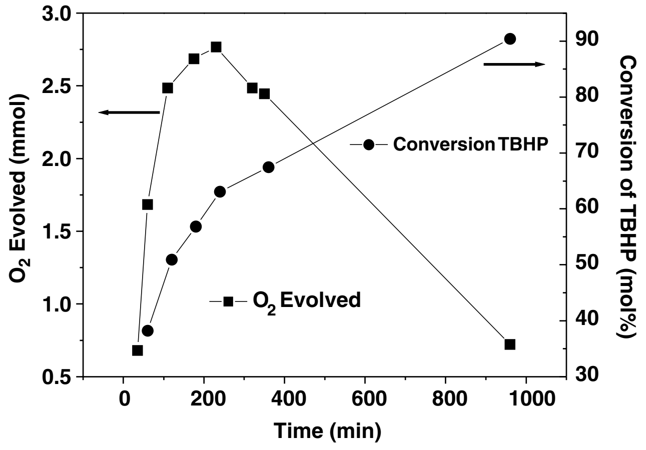

Figure 4. Oxygen evolved (mmol) and the conversion of TBHP during the course of study at 70 °C for the oxidation of cyclohexane over Co-TUD-1.

Table 1
Comparison of recycled Co-TUD-1 in cyclohexane oxidation with TBHP at 70 °C for 6 h

Time (h)	Conv. cyclohexane (mol%)	Conv. TBHP (mol%)	Sel. mono (mol%)	K/A ratio
1	2.52	38.23	86.86	1.03
*	1.37	53.19	86.67	1.48
2	3.75	50.91	88.96	1.67
*	2.06	59.74	87.86	1.82
3	4.26	56.83	88.55	2.32
*	2.68	64.27	86.73	2.33
4	4.56	63.07	89.17	3.14
*	3.13	67.92	88.09	3.00
6	5.54	67.45	89.15	4.35
*	4.19	75.18	88.74	5.76

* Recycled catalyst.

after 6 h of reaction. The mono-oxygenated products include, cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, cyclohexyltertbutyl ether and cyclohexyl formate. After 16 h of reaction, a high K/A ratio of 19 was obtained with a conversion of 10.4% of cyclohexane and the selectivity of mono-oxygenated product still being around 80%. The heterogeneity of the reaction was examined by the methodology suggested by Sheldon *et al.* [14], in which the products of the reaction were filtered hot and the reaction was continued with the filtrate without any solid catalyst. It was observed that after hot-filtration (1 hr) the conversion of cyclohexane slowed down significantly while the conversion of TBHP stopped almost completely (i.e. a change of 2% points from 42% over a period of 6 hs, cf. figure 3). This is consistent with the radical chain oxidation slowly coming to an end and with only negligible cobalt (that could decompose the TBHP quickly) being present in the filtrate. Thus, the TBHP is predominantly thermally decomposed. After 16 h, the K/A ratio dropped back to 1.4 with 57.3% selectivity to mono-oxygenated products, clearly showing over-oxidation due to unmodified/uncontrolled radical chains still being present and the cumulative effect of thermal TBHP decomposition inducing further radical chains.

These results are consistent with negligible leaching of cobalt and the conversion rate due to homogeneous catalysis being comparatively low. Therefore, it may be concluded that it is the cobalt in the TUD-1 that is active in the oxidation of cyclohexane under these mild conditions.

To address the issue of recycling, the catalyst was removed by filtration after 16 h of reaction, dried at 180 °C and reused. A comparison of the new and recycled catalyst over a period of 6 h is shown in table 1. It can be observed that there is a slight decrease in the conversion of cyclohexane as well as a higher TBHP conversion when using the recycled catalyst. This might be explained by the possible decrease in the isolated cobalt species that are active for the conversion of cyclohexane and by the parallel increase of cobalt clusters more efficient in TBHP decomposition. Nevertheless, the reused catalyst showed comparable selectivity to mono-oxygenated products and K/A ratio.

4. Conclusions

A new catalytic material, cobalt incorporated in TUD-1 silica matrix denoted as Co-TUD-1, was synthesized, characterized and shown to be active in the catalytic oxidation of cyclohexane with TBHP as oxidant. The activity increased with time and the catalyst could be recycled. It was also demonstrated that the reaction was heterogeneous.

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