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Catalysis Today 117 (2006) 279–283
CATALYSIS TODAY
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Liquid phase oxidation of cyclohexane over transition metal incorporated amorphous 3D-mesoporous silicates M-TUD-1 (M = Ti, Fe, Co and Cr)

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Abstract

Redox metals such as Ti, Co, Fe and Cr are incorporated into the framework of TUD-1 (a three-dimensional mesoporous silicate) and characterized by means of XRD, UV–vis and N_2 sorption measurements. The catalytic activity of these materials (M-TUD-1) was tested in the liquid phase oxidation of cyclohexane with *tert*-butylhydroperoxide (TBHP) as oxidant. Cr- and Co-TUD-1 showed excellent performance in the oxidation of cyclohexane, Cr-TUD-1 being highly selective to cyclohexanone. Leaching of Cr is estimated as 13% during this reaction. In contrast to this it was also proven that the reaction is truly heterogeneous with Co-TUD-1.

Keywords: Cyclohexane; Oxidation; Mesoporous materials; TUD-1

1. Introduction

More than 20% of all industrial organic materials are obtained by catalytic oxidation. Current processes tend to be energy intensive, to have low conversion efficiencies and they are prone to over-oxidation. Moreover, they often generate environmentally hazardous waste and by-products. In the oxidation of alkanes, the low selectivity for the desired product is due to the fact that the products are more reactive than the inert C–H bonds in the alkanes. One such industrial process is the cyclohexane oxidation in which no heterogeneous or soluble (cobalt) catalysts are applied, molecular oxygen and temperatures above 150 °C are employed industrially to give a cyclohexane conversion of ~3% with selectivity to cyclohexanol and cyclohexanone of 78% [1]. The drawbacks of the above-mentioned process are the poor conversion of cyclohexane (about 4%) and a selectivity for cyclohexanone and cyclohexane (K-A-oil) of just about 70–85% depending on the conversion of cyclohexane. To better the above-mentioned industrial process, various authors [2–11] developed new catalyst systems for the oxidation of cyclohexane, which work under milder conditions compared to the industrial process. Also they aim at improved selectivities for the desired products (cyclohexanone and cyclohexanol). A noteworthy development in this regard are the results by Thomas et al. in that their catalyst, FeAlPO-31, allowed for a clean, solvent-free one step process, albeit with a significant co-production of adipic acid [12].

In this paper we studied the solvent-free cyclohexane oxidation under milder conditions (70 °C) utilizing TBHP as oxidant. As catalyst carrier we employed TUD-1. Recently this new mesoporous silicate family, has been reported [13]. Its surfactant-free one-pot synthesis procedure makes TUD-1 an environmentally friendly as well as a cost-effective material. Its three-dimensional silicate network, sponge-like structure with a highly tuneable surface area, high substrate accessibility and thermal stability give it the advantages over other microporous and mesoporous materials. These advantages of TUD-1 combined with the properties of redox metals are expected to show high activity in the oxidation of alkanes such as

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doi:10.1016/j.cattod.2006.05.031

cyclohexane. Various redox metals (M = Ti, Co, Cr, and Fe) were incorporated with a tetrahedral coordination into the silica matrix of TUD-1 avoiding M–O–M bond formation. These M-TUD-1 materials were studied as catalysts for the oxidation of cyclohexane under liquid phase conditions with TBHP acting both as radical initiator as well as the oxidant.

2. Experimental

2.1. Synthesis of 3D mesoporous metallosilicates (M-TUD-1) and characterization

Metal incorporated mesoporous materials, M-TUD-1 (M = Ti, Co and Fe) with Si/M ratio of 100, were synthesized in an one-pot surfactant-free procedure based on the sol–gel technique using triethanolamine (TEA) as template and tetraethyl ammonium hydroxide (TEAOH) as base [14–17]. In general, M-TUD-1 can be synthesized according to the molar ratio SiO_2:0.01 MO_x:0.5 TEAOH:1 TEA:11 H_2O. A mixture with appropriate amounts of TEA (97%, ACROS) and deionized water was added drop-wise into a mixture of tetraethyl orthosilicate (98%, ACROS) and solutions of the respective metal salt ($Ti(BuO)_4$, $FeNO_3 \cdot 9H_2O$ and $CoSO_4 \cdot 2H_2O$ in 5 ml deionized water) while stirring. Once the addition was complete and the reaction mixture stirred for a further 5 min, the appropriate amount of TEAOH (35%, Aldrich) was added. Then the mixture was aged at room temperature for 24 h, dried at 98 °C for 24 h, followed by a hydrothermal treatment at 180 °C for 8 h. Finally these materials were calcined at 600 °C for 10 h at a ramp of 1° C/min. The synthesis and characterization of Cr-TUD-1 has been described elsewhere [18].

These materials were characterized by XRD, nitrogen sorption, diffuse reflectance UV–vis and elemental analysis. X-ray powder diffraction (XRD) patterns were recorded using Cu Kα radiation on a Philips PW 1840 diffractometer equipped with a graphite monochromator. The samples were scanned over the range of 0.1–80° 2θ with steps of 0.02°. Nitrogen sorption isotherms were recorded on a Quantachrome Autosorb-6B at 77 K. Samples were previously evacuated at 623 K for 16 h and the BJH model was used to calculate mesoporosity. Diffuse reflectance UV–vis spectra were recorded using a CaryWin 300 spectrometer with $BaSO_4$ as reference. Samples were ground carefully, heated overnight at 180 °C, and then scanned from 190 to 800 nm. Elemental analyses were carried out by using instrumental neutron activation analysis (INNA) on the "Hoger Onderwijs Reactor" nuclear reactor with a thermal power of 2 MW and maximum neutron reflux of 2.10 m^{-2} s^{-1}.

2.2. Oxidation of cyclohexane with TBHP

For the oxidation of cyclohexane with TBHP as oxidant, a stock solution of TBHP in cyclohexane is used, which had been prepared by extraction of commercial TBHP (Aldrich, 70% in water) into an equal volume of cyclohexane. Phase separation was promoted by saturation of the aqueous layer with solid NaCl. The organic layer was dried over $MgSO_4$, filtered and stored at 4 °C.

In a typical experiment, M-TUD-1 containing 0.1 mmol active metal (pre-treated at 180 °C prior to the reaction) was added to 20 ml of a mixture of cyclohexane (65 mol%), TBHP (35 mol%) and 0.1 g chlorobenzene (internal standard). The round bottom glass flask with the reaction mixture containing the catalyst was then immersed in a thermostated oil bath at 70 °C. The gas phase above the reaction mixture was filled with nitrogen and a gas burette was attached. The course of the reaction was followed by analyzing the liquid samples on a GC.

2.3. GC analysis

The reaction samples were analyzed using a GC (Agilent 6890 gas chromatograph) equipped with a split inlet (200 °C, split ratio 10.0) and using a Sil 5 CB capillary column

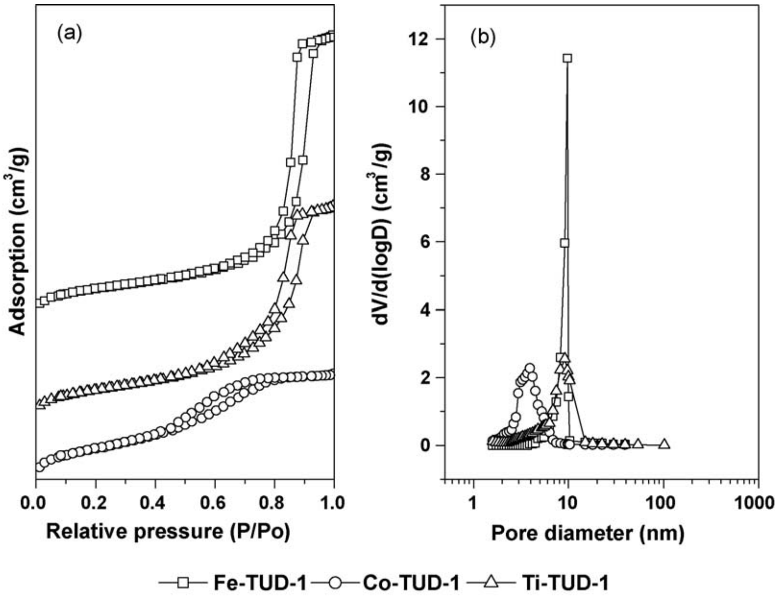

Fig. 1. (a) Nitrogen sorption isotherms of M-TUD-1 samples. (b) The pore size distribution of M-TUD-1 samples.

Table 1
Physical characteristics of M-TUD-1

Sample	Si/M ratio		Active site[a]	S_{BET}[b] (m^2/g)	V_{meso}[c] (cm^3/g)	D_{meso}[d] (nm)	Colour after calcination
	Synthesis mixture	After calcination[e]					
TUD-1	∞	∞	–	655	1.71	2.2	White
Ti-TUD-1	100	112	Ti^{4+}	864	0.78	3.7	White
Cr-TUD-1[f]	100	130	Cr^{6+}	565	1.54	8.4	Yellow
Co-TUD-1	100	108	Co^{2+}	619	0.73	4	Dirty violet
Fe-TUD-1	100	113	Fe^{3+}	568	1.82	15.9	White

[a] UV–vis.
[b] Specific surface area.
[c] Mesopore volume.
[d] Mesopore diameter.
[e] As obtained from INNA.
[f] Full characterisation in Ref. [18].

(50 m × 0.53 mm i.d.; constant flow of carrier gas N_2 4.0 ml/min) coupled to FID detector. The concentration of carboxylic acid side-products was determined from GC analysis by converting them into their respective methyl ester as described earlier [15,16,19].

3. Results and discussion

3.1. Catalyst characterization

The pore structure parameters of the M-TUD-1 samples were calculated by using Barrett–Joyner–Halenda (BJH) formula for the adsorption branch of N_2 adsorption–desorption isotherms (Fig. 1). All M-TUD-1 samples showed type IV adsorption isotherms indicating their meso-structured character, with a narrow pore size distribution. Elemental analysis shows that the Si/M ratio of the calcined samples is very close to that used in the synthesis gel. The results are summarized in Table 1.

XRD patterns for all M-TUD-1 samples showed (Fig. 2) a single intensive peak at 0.1–2.5° 2θ, indicating a meso-structured nature of these materials. Moreover, XRD patterns also showed that there are no detectable M-oxide phases and/or other bulky metal oxide phases. High-resolution TEM images of these materials showed a sponge-like 3D structure similar to all silica TUD-1 mesoporous material [13,16]. UV–vis spectra of different M-TUD-1 samples are shown in Fig. 3. The Ti-TUD-1 spectrum showed an absorption band centering at 220 nm which is attributed to the charge–transfer transition associated with an isolated Ti(IV) framework site in tetrahedral coordination [20,21] with no distorted tetrahedral environment or octahedral coordination sphere. The spectrum of Fe-TUD-1 exhibits a peak around 260 nm, this band is assigned to the charge–transfer between the Fe and O atoms of Fe–O–Si in the framework, indicating the presence of isolated, tetrahedrally coordinated Fe(III) species [22]. The spectrum of Co-TUD-1

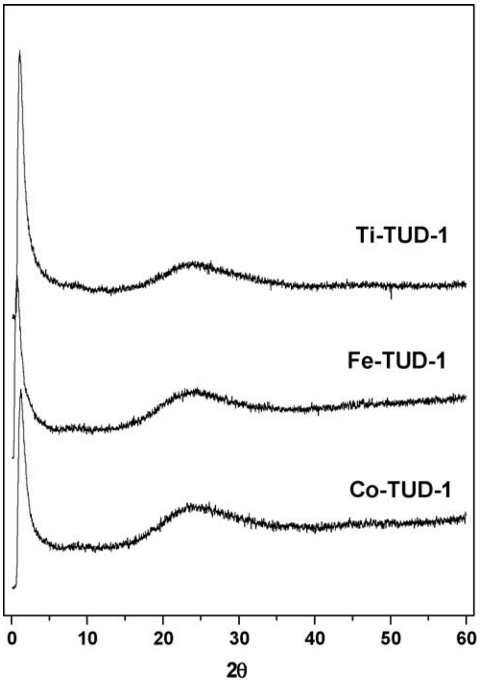

Fig. 2. XRD pattern of M-TUD-1.

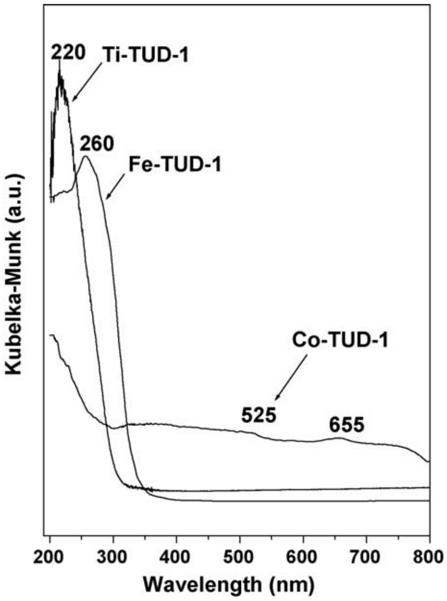

Fig. 3. UV–vis spectra of M-TUD-1.

exhibit two peaks around 525 and 654 nm, both absorption bands can be assigned to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition of divalent cobalt ions (Co^{2+}) in tetrahedral co-ordination [23,24]. All the above characterizations clearly indicate that the metals are incorporated into the silica network of TUD-1 as isolated M atoms.

3.2. Catalytic activity of M-TUD-1 in the oxidation of cyclohexane

The main products observed during the oxidation of cyclohexane with TBHP under solventless conditions were cyclohexanol (A), cyclohexanone (K), cyclohexyl hydroperoxide (CHHP) and some minor products such as cyclohexylformate and cyclohexyltertbutylper-ether. These products are grouped as mono-oxygenated products. The acids identified include mainly adipic acid along with some small quantities caproic acid, glutaric acid, succinic acid and valeric acid. Hydroxyacids such as 6-hydroxycaproic acid and 6-hydroxyvaleric acid were identified only at higher conversion levels.

In the liquid phase cyclohexane oxidation, at 70 °C, with TBHP as oxidant both the conversion of cyclohexane (Fig. 4a) and TBHP (Fig. 4b) was catalysed by all M-TUD-1 catalysts. Cr-TUD-1 is an outstanding catalyst performing significantly better than the other M-TUD-1 under study. It decomposes TBHP much faster than other M-TUD-1 and hence effects the conversion of cyclohexane. Nevertheless, a plot of conversion of cyclohexane versus selectivity for mono-oxygenated products (Fig. 4c) displays a different trend. Even though the decomposition of TBHP was slow with Co-TUD-1, both Co- and Cr-TUD-1 performed equally well, exhibiting high activity with very high selectivity to mono-oxygenated products even at excellent conversion levels of 5–8%. When comparing M-TUD-1 at a low conversion of cyclohexane (~2%), all these catalysts behave differently. The selectivity for mono-oxygenated products dropped sharply for Ti and Fe-TUD-1 whereas Co-TUD-1 showed a very slow decrease even at higher conversion levels of cyclohexane (as compared with Cr-TUD-1). As expected Cr-TUD-1 produces more cyclohexanone than cyclohexanol (Fig. 4d), whereas Co-TUD-1 produced initially more of the alcohol, which is then slowly oxidized to the ketone and the K/A ratio improves.

To address the issue of leaching, hot filtration studies were performed with the two most promising catalysts: Cr- and Co-TUD-1 (Fig. 5). After 1 h of the reaction, the reaction mixture was filtered hot (at around 50 °C), and the reaction was continued with the filtrate in the absence of any solid catalyst. In addition, these filtrates were subjected to AAS analysis after the reaction. As compared to Co-TUD-1, a high catalytic activity of cyclohexane oxidation was observed in the filtrate from Cr-TUD-1. This may be due to the almost near complete conversion of TBHP (92%) after 1 h with sufficient amount of radicals being present in the filtrate to continue the reaction. Another possibility may be that a part of chromium leached from the framework into the solution under the reaction conditions. The leaching of chromium was confirmed by AAS analysis which revealed a leaching of 13%. In the filtrate of Co-TUD-1, however, the conversion of TBHP (not shown) almost stopped and the rate of cyclohexane oxidation slowed down. Residual reactivity is most likely due to the radicals still present in the reaction mixture but not to any active metal. Indeed, AAS analysis of the filtrate revealed the absence of any cobalt in the filtrate (below detection limits). These studies confirm that the Co-TUD-1 catalysed reaction is truly heterogeneous. Although these first studies do not yet concern the aerobic oxidation of cyclohexane, the fact that Co-TUD-1 is efficient at low

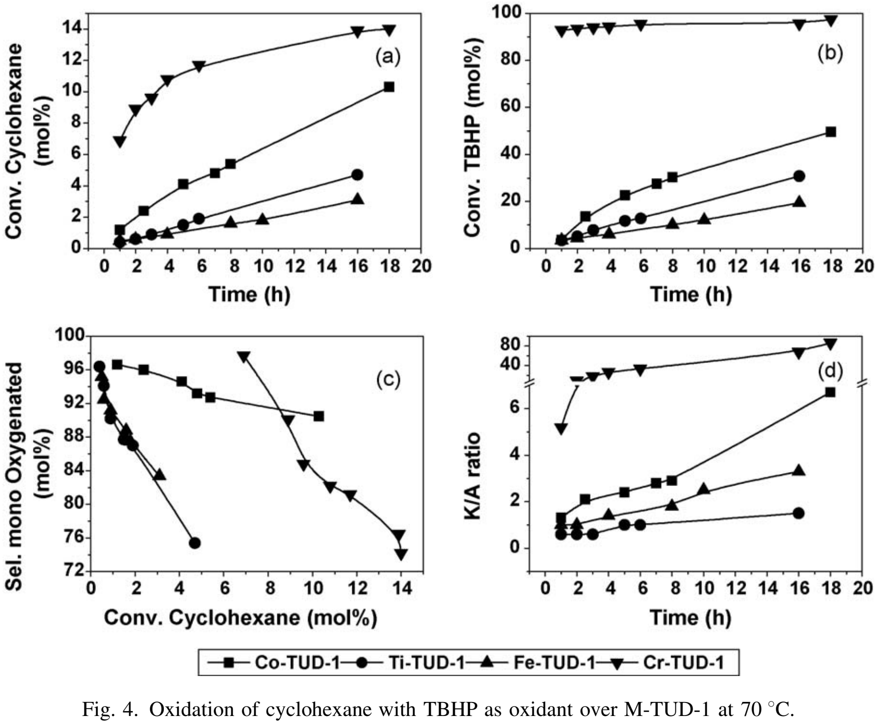

Fig. 4. Oxidation of cyclohexane with TBHP as oxidant over M-TUD-1 at 70 °C.

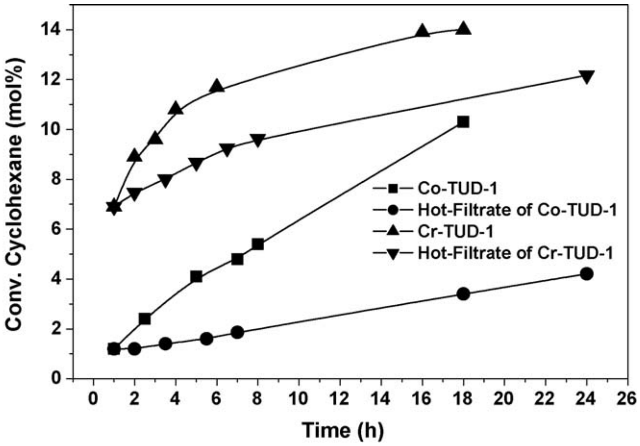

Fig. 5. Comparison of cyclohexane conversion over Co- and Cr-TUD-1 and after hot filtration.

temperatures and solvent-free conditions, indicates that it might compete with the catalysts that have been described to date, such as the metal AlPO's that are used at 100–130 °C.

4. Conclusions

Novel TUD-1 variants with the metals Ti, Fe, Co or Cr incorporated into the framework were synthesized. The various characterization techniques proved that the metals are indeed isolated and incorporated into the framework of the TUD-1 silicate network. All these M-TUD-1's are active in the liquid phase oxidation of cyclohexane with TBHP as oxidant. A conversion close to 3% was achieved with 85% selectivity to mono oxygenated products over Fe and Ti-TUD-1. Cr- and Co-TUD-1 were particularly active in the oxidation of cyclohexane with TBHP. Above 90% selectivity towards mono oxygenated products was achieved at conversion levels as high as 8–10%. The leaching of chromium makes Co-TUD-1 the most promising catalyst amongst the studied M-TUD-1's for the oxidation of cyclohexane.

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