Catal Lett (2009) 129:222–227
DOI 10.1007/s10562-008-9796-7

Co-doped Attapulgite Catalyzed Solvent-free Oxidation of Cyclohexane Using Molecular Oxygen

Yan Zhang · Zhen Li · Wei Sun · Chungu Xia

Received: 17 October 2008 / Accepted: 19 November 2008 / Published online: 4 December 2008

Abstract A series of Co-AT (attapulgite) catalysts were prepared by wetness impregnation method. Detailed characterization indicated that there indeed exists interaction between Co and the support AT, leading to the formation of spinel of $CoAl_2O_4$ and $CoFe_2O_4$. Al and Fe species of AT promote the formation of $CoFe_2O_4$ spinel with much lower temperature (400 °C). The catalytic behavior was investigated by the liquid-phase solvent-free oxidation of cyclohexane and Co-AT-1 shown better activity than $CoFe_2O_4$ and Co_3O_4, which was likely due to a cooperation effect between $CoFe_2O_4$ and Co_3O_4.

Keywords Attapulgite · Co catalyst · Molecular oxygen · Cyclohexane oxidation

1 Introduction

There is growing interests in studying interactions between metal and support during the past few years. It is well-known that the specific interaction may appreciably affect the surface properties of catalyst, and hence their reactivity. For example, the migration of metal ions into the alumina matrix is a common phenomenon in metal supported catalysts and which can lead to form Metal-Al compound such as $CoAl_2O_4$. The solid–solid interactions between ferric oxide and transition metal oxides or carbonates produce the corresponding ferrites such as $CoFe_2O_4$ [1, 2]. Gabal et al. [3] indicated CoO can react with α-Fe_2O_3 to form $CoFe_2O_4$ at 1,000 °C. Radwan et al. [4] revealed solid–solid interaction between Fe_2O_3 and Co_3O_4 takes place at temperatures higher than 700 °C to produce $CoFe_2O_4$. $CoAl_2O_4$ has been applied in some catalytic reaction [5–7]. Nevertheless, most of the reports have been focused on the magnetic behavior of $CoFe_2O_4$ nanoparticles [8]. Up to now, there is no report on cyclohexane oxidation using catalysts as stated above (including $CoAl_2O_4$, Co_3O_4 and $CoFe_2O_4$).

In our previous study, $CoFe_2O_4$ was formed on the surface of HAP-γ-Fe_2O_3 by solid–solid interaction between Fe_2O_3 and Co_3O_4. A cooperation interaction between these two oxides ($CoFe_2O_4$ and Co_3O_4) made the catalyst highly active [9]. In this work, we report on a novel class of cobalt-substituted AT catalysts synthesized by a simple impregnation method and their catalytic activity in the oxidation of cyclohexane with oxygen in the absence of any solvents or co-reductants. The results indicated that there existed metal-support interaction, which led to the formation of Co_3O_4 and two spinels $CoAl_2O_4$ and $CoFe_2O_4$. Co-AT-1 shows higher activity than both of $CoFe_2O_4$ and Co_3O_4, while the latter show higher activity than that of $CoAl_2O_4$. The results indicated that $CoAl_2O_4$ could not be the active component and the excellent catalytic activity was due to a cooperation effect between $CoFe_2O_4$ and Co_3O_4.

Y. Zhang · Z. Li · W. Sun · C. Xia (✉)
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, 730000 Lanzhou, People's Republic of China
e-mail: cgxia@lzb.ac.cn

Y. Zhang
Graduate School of the Chinese Academy of Sciences, 100049 Beijing, People's Republic of China
e-mail: zyanyan1980@gmail.com

2 Experimental

2.1 Materials and Equipments

Cyclohexane was distilled before use. AT was used without further purification. Oxygen with a purity of 99.99% was commercially available. Other reagents were of analytical grade and were used as received.

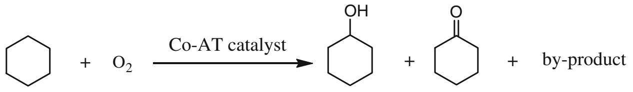
XRD was carried out on a PANalytical X'pert Pro Diffractometer. XPS was performed on a VG ESCALAB 210 spectrometer and all binding energies were calibrated using the C2p peak at 285.0 eV as a reference. FT-IR spectra were measured on a Nexus 870 FT-IR spectrophotometer. Temperature-programmed reduction (TPR) technique was applied to characterize the reduction behavior and the interaction between active phase and support of catalysts. Inductively coupled plasma-emission spectroscopy (ICP) was measured on an IRIS ER/S spectrophotometer.

2.2 Catalysts Preparation

At room temperature, AT powder (1.0 g) was treated with 10 mL of $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution with different metal content for 24 h, followed by filtration and washed thoroughly with distilled water, dried at 120 °C for 8 h, then heated in air at 500 °C for 2 h. The resulted materials are identified as Co-AT-1 to Co-AT-5 according to their metal content (the corresponding metal contents of Co-AT-1 to Co-AT-5 determined by inductively coupled plasma-emission spectroscopy (ICP) are 0.44, 0.57, 2.82, 4.01 and 17.14%, respectively). For comparison, the precursor of Co-AT-1 was calcined at 300 and 400 °C, respectively. Co_3O_4 was prepared by thermal decomposition of basic cobalt carbonate at 300 °C as reference material [10]. $CoAl_2O_4$ was obtained by heat-treating the polymeric precursors in air at 500 °C for 2 h [11] and $CoFe_2O_4$ was obtained by wet chemical method (co-precipitation) along with heat treatment at 600 °C for 10 h [12].

2.3 Oxidation of Cyclohexane

Liquid-phase oxidation of cyclohexane was carried out in a 30 mL stainless steel autoclave equipped with a magnetic stirrer and an automatic temperature controller. In a typical reaction, 50 mg catalyst and 4.0 mL (37.1 mmol) cyclohexane were charged into the reactor. The autoclave was flushed three times with O_2 and pressurized to the desired pressure, then heated to the desired temperature with stirring. After the reaction, the autoclave was cooled to room temperature and slowly depressurized. The reaction products were identified by HP 6890/5973 GC/MS and quantified by Agilent 6820 gas chromatograph. The main by-products of the reaction were dicyclohexyl adipate, heptanal, acids (including succinic acid, glutaric acid and adipic acid) (Scheme 1).



Scheme 1 Oxidation of cyclohexane

3 Results and Discussion

3.1 Catalyst Characterization

Information on the phase constitution of Co-AT samples can be obtained from a combination of the powder X-ray diffraction and X-ray photoelectron spectroscopy, respectively. Figure 1a shows the powder X-ray diffraction patterns of AT and Co-AT samples. In comparison with AT, a slight decrease of crystallinity in the Co-AT samples is observed, indicating that Co could enter into the framework of AT or interact with Al and Fe species of AT. Durand et al. [13] illuminate the differentiation between the spinel phases Co_3O_4 and $CoAl_2O_4$. The peak of the spinel phase at $2\theta = 18.9°$, characteristic of Co_3O_4 [14], is present in the five diffraction diagrams. Four diffraction peaks at 31.3, 36.9, 44.4 and 59° detected in Co-AT-5 are ascribed to a mixture of crystallized $CoAl_2O_4$ (formed due to the interaction between Co and Al) and Co_3O_4 [6, 13, 15, 16].

For all catalysts (Co-AT-1 to Co-AT-5), a new extra-framework Co-crystalline phase ascribed to $CoFe_2O_4$ is found at $2\theta = 17.7°$ [14], revealed that Co_3O_4 could interact directly with Fe species possessed by AT to form $CoFe_2O_4$ at 500 °C. The peak intensity firstly increase and then decrease with increasing the Co content from 0.44 to 17.14%, meaning that the formation of $CoFe_2O_4$ phase competed with that of $CoAl_2O_4$ and Co_3O_4 phase.

In order to study the temperature effect on the formation of $CoFe_2O_4$ phase, we selected Co-AT-1 as a typical example and compared the samples precalcined at 300, 400 and 500 °C (the framework of AT could be destroyed if the calcined exceed 500 °C), respectively, together with the carrier AT. The Co-AT-1 sample calcined at 400 °C exhibits a similar behavior to that at 500 °C and both exhibit the characteristic lines of $CoFe_2O_4$ (Fig. 1b), which is absent at 300 °C, indicating the inability of formation of cobalt ferrite. All these suggested that $CoFe_2O_4$ phase could be formed at temperature higher than 400 °C, and the formation temperature is much lower than the previous reported value [3, 4]. Moreover, $CoFe_2O_4$ phase is

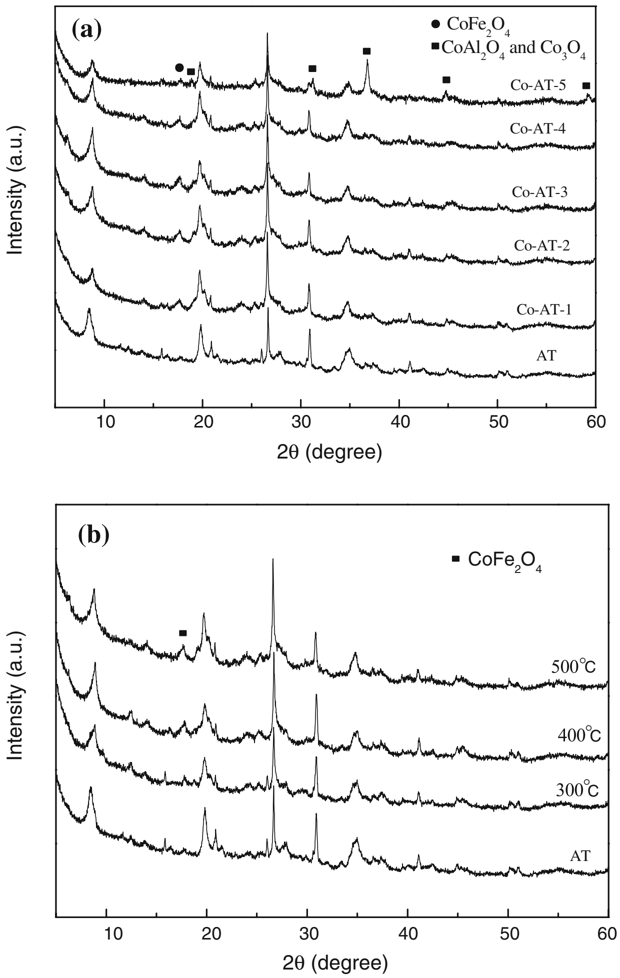


Fig. 1 XRD patterns of the **a** AT and Co-containing AT and **b** Co-AT-1 heat treated at different temperatures for 2 h in air

generated directly due to the interaction between Co_3O_4 and Fe species of AT, other than due to the interaction between either CoO and α-Fe_2O_3 or Co_3O_4 and Fe_2O_3. Radwan et al. [4] reported that addition of aluminum nitrate stimulating the solid–solid interactions between Fe_2O_3 and Co_3O_4 could produce cobalt-ferric compound. Therefore the low formation temperature could be explained by the fact that Al species of AT promote the interaction between Co_3O_4 with Fe species of AT, leading to form $CoFe_2O_4$.

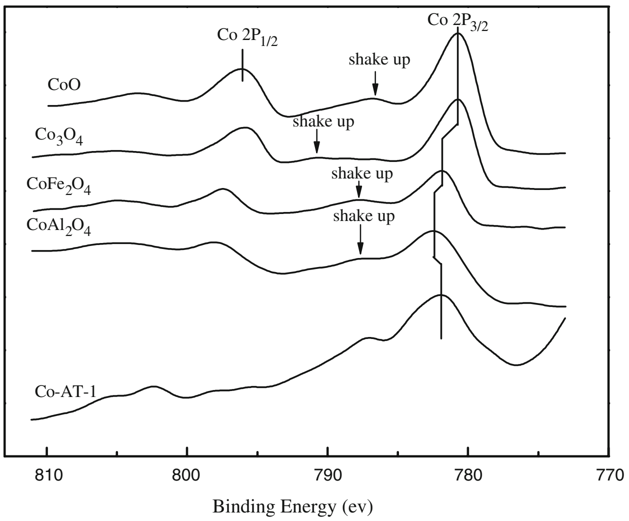


Fig. 2 Co 2p XP spectra of Co-AT-1

To be able to exactly interpret the XPS spectra of the calcined supported catalysts Co-AT-1, the XPS of the pure Co_3O_4 [17], CoO [18], $CoAl_2O_4$ [17] and $CoFe_2O_4$ [18] are taken. Co 2p core level spectra of nanoparticles are displayed in Fig. 2. The Co binding energies in CoO (Eb(Co $2p_{3/2}$) = 780.0 eV, Eb(Co $2p_{1/2}$) = 795.9 eV), and in Co_3O_4 (Eb(Co $2p_{3/2}$) = 780.2 eV, Eb(Co $2p_{1/2}$) = 795.5 eV) are lower than that in the calcined catalyst, while the spinell $CoAl_2O_4$ (Eb(Co $2p_{3/2}$) = 781.5 eV, Eb(Co $2p_{1/2}$) = 797.2 eV) and $CoFe_2O_4$ (Eb(Co $2p_{3/2}$) = 781.9 eV, Eb(Co $2p_{1/2}$) = 798.3 eV) shows significantly comparable binding energies. Moreover, the main peak (Co $2p_{3/2}$) of pure $CoAl_2O_4$ and $CoFe_2O_4$ exhibit shoulder at their high binding energy side which can be exclusively ascribed to the shake-up process of Co^{2+} compound in the high spin state, while that of Co_3O_4 is remarkably weak because the low-spin Co^{3+} ion does not show shake-up process. It is found that there is strong shake-up satellite observed in Co-AT-1. However, the intensity of the shake-up signals in Co_3O_4 is remarkably reduced in comparison to CoO in agreement with the Co^{3+}/Co^{2+} ratio of 2:1 in Co_3O_4. The Fe binding energies in Co-AT-1 (Eb(Fe $2p_{3/2}$) = 712.6 ev) is in good agreement with the binding energy of $CoFe_2O_4$ (Eb(Fe $2p_{3/2}$) = 712.3 ev) [18]. Therefore the XP spectra of Co-AT-1 point to a preferred presence of Co_3O_4, $CoAl_2O_4$ and $CoFe_2O_4$.

The surface atomic composition of the Co-AT catalysts, derived from XPS data, is listed in Table 1. The concentration of surface Fe atoms decrease gradually with increasing Co content and is indicative of a migration of Fe into AT framework. The concentration of surface O and Al atoms, however, show an opposite trend compared with that of Fe atoms, confirming that the formation of Co_3O_4

Table 1 Surface atomic concentration of Co-AT catalysts derived from XPS

Sample	Surface atomic concentration (%)			
	Co	Fe	O	Al
Co-AT-1	1.509	3.713	63.513	5.257
Co-AT-2	1.625	3.020	62.501	5.369
Co-AT-3	2.306	2.935	63.962	5.654
Co-AT-4	2.472	2.198	65.179	5.680
Co-AT-5	3.172	2.074	65.268	5.727

Table 2 Characterization of AT and Co-AT materials by N_2 adsorption–desorption isotherm

Catalyst	AT	Co-AT-1	Co-AT-2	Co-AT-3	Co-AT-4	Co-AT-5
BET surface area (m^2/g)	82.63	67.77	61.34	57.63	48.73	35.61
Pore volume (cm^3/g)	0.203	0.116	0.109	0.145	0.149	0.097
Pore diameter (Å)	98	69	71	101	122	78

and $CoAl_2O_4$ phase is easier in the sequence of Co-AT-5 > Co-AT-4 > Co-AT-3 > Co-AT-2 > Co-AT-1. The results indicated that higher cobalt content facilitate the formation of Co_3O_4 and $CoAl_2O_4$ rather than that of $CoFe_2O_4$.

N_2 sorption data for all the Co-AT samples are compiled in Table 2. A decrease of the BET surface areas is observed with increase of Co content. However, an interesting observation is that the Pore volume and Pore diameter (except Co-AT-5) increase with increasing Co content. For the Co-AT system, the increase of Pore volume and Pore diameter may be attributed to high dispersion of cobalt nano-oxides and the special interaction between Co_3O_4 and Al or Fe species of AT, however, crystallinity Co nano-oxides existed on the surface of Co-AT-5 lead to decline of specific surface area, Pore volume and Pore diameter.

X-ray diffraction and photoelectron spectroscopy yielded information on the properties of the supported Co catalysts. However, they do not give information on the reduced and the oxidation state of cobalt species of catalyst, which can be investigated by means of temperature-programmed reduction (TPR). The TPR profile of the oxidation state of Co-AT-1 is shown in Fig. 3, which shows a large range of temperatures of reduction, is indicative of the presence of different cobalt species. Reduction peaks centered at 543, 647, 738, 810, 945 and 1,046, 1,089 K are observed. The low temperature peak (543 K) is typically assigned to the reduction of Co_3O_4 phase ($Co_3O_4 \rightarrow Co^0$) on the surface of the catalysts [19], whereas the peaks at 810, 945 and 1,046 K could be attributed to the reduction of surface Co^{2+} to Co metal [20, 21], the shoulder at 738 K could be traced to the reduction of Co^{3+} [21]. The broad peak centered at 647 K could be assigned to the reduction of $CoFe_2O_4$ [22]. The peak centered at 1,089 K at higher temperature, ascribed to the reduction to Co metal of surface Co^{2+} with a high number of O–Al ligands, is similar to a $CoAl_2O_4$ phase [23], whereas the temperature is not high enough to observe the complete reduction of $CoAl_2O_4$ due to the limited conditions.

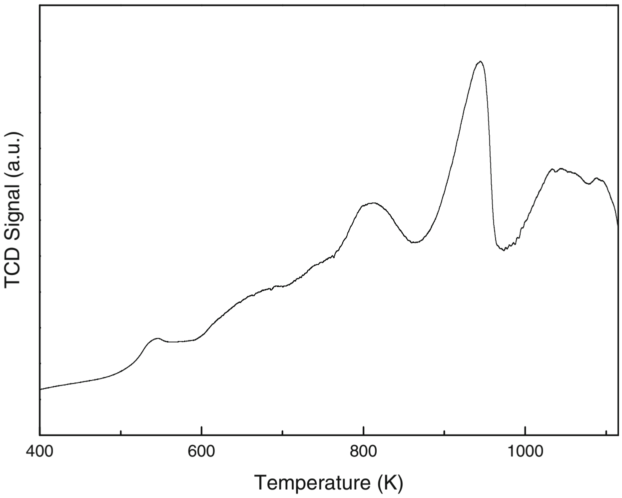


Fig. 3 TPR profile of Co-AT-1

All of the above mentioned clearly shown that there were three phase, $CoAl_2O_4$, Co_3O_4 and $CoFe_2O_4$, in cobalt-substituted AT system. Al species of AT promote the direct interaction of Co_3O_4 with Fe species of AT, leading to formation $CoFe_2O_4$ at relatively low temperature.

3.2 Co-AT Catalyzed Cyclohexane Oxidation

In order to study the effect of phase composition of catalyst on catalytic behavior, the oxidation of cyclohexane was carried out in the presence of various M-AT catalysts with reaction proceeded at 150 °C for 5 h without any initiator and solvent. The parent AT gave only 4.4% conversion (Table 3, entry 1) and $CoAl_2O_4$ showed catalytic activity as low as that of the homogenous result, indicating that parent AT and $CoAl_2O_4$ do not be the active component of the catalyst (entries 2, 3). Co_3O_4 and $CoFe_2O_4$ exhibited better catalytic activity than that of $CoAl_2O_4$ (entries 4, 5), could be the active component. It was found that Co-AT-1 (12.3% conversion) showed much higher activity than either Co_3O_4 or $CoFe_2O_4$ (entry 6). A reasonable explanation was that there could be cooperative activation between Co_3O_4 and $CoFe_2O_4$. In order to validate the hypothesis, the physical mixture of Co_3O_4 and $CoFe_2O_4$ was used as catalyst in the control experiments (entry 6), which showed activity, though slightly fall, comparable to that of the corresponding Co-AT-1, which indicated that there existed cooperativity between $CoFe_2O_4$ and Co_3O_4.

It was reported that the highest conversion and selectivity for cyclohexanone obtained with CoAlSi-NHG-400 for liquid-phase oxidation of cyclohexane was 6 and 49%, respectively [24]. Vanadia-niobia-silica catalysts was said to give only 15% conversion at high temperature (500 °C) [25].

Table 3 The effect of cobalt contents in the catalyst on the conversion and selectivity[a]

Entry	Catalyst	Conversion (%)	TON	Selectivity (%)	
				Cyclohexanone	Total[c]
1	Carrier	4.4	–	54.4	83.9
2	$Co(NO_3)_2$[d]	5.2	–	64.0	78.7
3	$CoAl_2O_4$[e]	5.8	–	72.3	89.6
4	Co_3O_4[f]	8.8	–	62.7	92.7
5	$CoFe_2O_4$[g]	10.2	–	66.2	92.2
6	$Co_3O_4 + CoFe_2O_4$[h]	11.1	–	65.0	92.4
7	Co-AT-1	12.3	1,221	60	94.1
8	Co-AT-2	12.4	950	68.4	92.4
9	Co-AT-3	13.3	207	63.0	91.3
10	Co-AT-4	14.6	159	65.6	90.7
11	Co-AT-5	15.0	38	64.7	87.8

[a] Reaction condition: catalyst 50.0 mg, cyclohexane 4.0 ml, 1.2 MPa successive O_2, 150 °C

[b] Moles of substrate converted per mole of metal (Co) in the catalyst

[c] Total selectivity, the selectivity of cyclohexanone add the selectivity for cyclohexanol

[d] $Co(NO_3)_2$ as a homogeneous catalyst

[e] Pure $CoAl_2O_4$ reference material [18], 5.0 mg

[f] Pure Co_3O_4 reference material [19], 5.0 mg

[g] Pure $CoFe_2O_4$ reference material [20], 5.0 mg

[h] The physical Co_3O_4 and $CoFe_2O_4$ (together 5.0 mg)

Although Au nanoparticles in MCM-41 applied to oxidation of cyclohexane by O_2 at 150 °C could achieve higher conversion (19%), the reaction time was as long as 6 h and unfortunately conversion was decreased to below 10% after four recycles [26]. The Co-AT reported here were efficient catalysts for liquid-phase oxidation of cyclohexane considering that the conversion was still higher than 9% after four cycles with relatively low temperature and short reaction time. In addition, oxygen was the only oxidant and no other co-catalyst or solvent is added in the system.

Subsequently, we studied the effect of cobalt content on the reaction. It was found that cyclohexane conversion increases with increasing in cobalt content (entries 7–11), while the total selectivity decreases, due to the fact that high cobalt content favors the formation of ring oxidized products such as hexanoic acid and heptanal. For Co-AT-1 maximum turnover number of 1,221 was obtained. Considering both the turnover number and the total selectivity, Co-AT-1 is the optimum catalyst.

As to the recyclability of the catalyst, four reaction runs were carried out with Co-AT-1 as catalyst. After reaction the catalyst was recovered by filtration and then dried at 393 K for 8 h. The regenerated catalyst was directly used for the recycling study under similar conditions. The results obtained were shown in Fig. 4. The conversion and selectivity had minimal decreases owing to leaching of a small amount of loosely bound extra framework cobalt species in the matrix, which was further confirmed by loss of approximately 0.1 wt% cobalt indicated by cobalt analysis of the catalyst after first run. Note that in the subsequent cycles, the conversion decreased slightly and the total selectivity remained nearly constant. Since we noticed leaching of cobalt from calcined (fresh) Co-AT-1 catalyst, here we carried out filtrate experiment over recycled catalyst (catalyst collected after second run) to check further leaching of cobalt in recycled catalyst. It was worthy to mention that filtrate solution showed only 3.2% cyclohexene conversion, suggesting that the homogeneous part of the recycled catalyst makes negligible contribution to the total activity, as further evident by the cobalt analysis (ICP-AES) that only 0.02% cobalt was detected in the quenched solution.

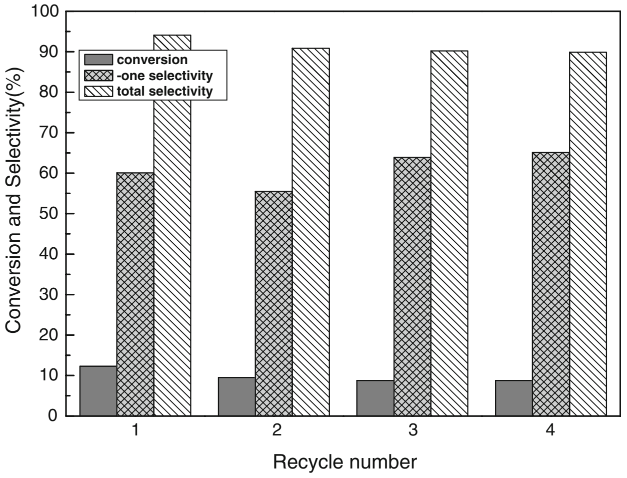


Fig. 4 Reuse of the catalyst. Conditions: catalyst 50.0 mg, cyclohexane, 4.0 ml, 1.2 MPa successive O_2, 4 h, 150 °C

4 Conclusions

In summary, three species, e.g., Co_3O_4, $CoAl_2O_4$ and $CoFe_2O_4$, are formed in the Co-AT catalysts, in which Al and Fe species of AT enhanced the formation of $CoAl_2O_4$ and $CoFe_2O_4$ at relatively low temperature. Co-AT exhibit high activity for the liquid-phase solvent-free oxidation of cyclohexane and the catalyst can be easily recovered and reused without obvious loss of conversion or selectivity. The high activity can be traced to a cooperation effect presented between Co_3O_4 and $CoFe_2O_4$.

Acknowledgments The authors are grateful to the National Natural Sciences Foundation of China (20373082, 20625308) for financial support.

References

1. El-Shobaky GA, Abdalla FHA, Fouad Zikry AA (1996) Thermochim Acta 289:81
2. El-Shobaky HG (2000) Thermochim Acta 343:145
3. Gabal MA, El-Bellihi AA, Ata-Allah SS (2003) Mater Chem Phys 81:84
4. Nagi RE, Hala G, El-Shobaky R (2000) Thermochim Acta 360:147
5. Liotta LF, Pantaleo G, Di Carlo G, Marcì G, Deganello G (2004) Appl Catal B Environ 52:1
6. Xiong HF, Zhang YH, Liew KY, Li JL (2005) J Mol Catal A Chem 231:145
7. Álvarez PM, Beltrán FJ, Pocostales JP, Masa FJ (2007) Appl Catal A Gen 72:322
8. de Vicente J, Delgado AV, Plaza RC, Duran JDG, Gonzalez-Caballero F (2000) Langmuir 16:7954
9. Zhang Y, Li Z, Sun W, Xia CG (2008) Catal Comm (In Press)
10. Radwan NRE, Mokhtar M, El-Shobaky GA (2003) Appl Catal A Gen 241:77
11. Maaz K, Mumtaz A, Hasanain SK, Ceylan A (2007) J Magn Magn Mater 308:289
12. Choa WS, Kakihana M (1999) J Alloy Compd 287:87
13. Ouahdi N, Guillemet S, Demai JJ, Durand B, Er Rakho L, Moussa R, Samdi A (2005) Mater Lett 59:334
14. Liu XM, Fua SY, Xiao HM, Huang CJ (2005) Physica B 370:14
15. Zhou LP, Xu J, Miao H, Wang F, Li XQ (2005) Appl Catal A Gen 292:223
16. Somjit BJ, Panpranet JJ, Goodwin JG (2001) J Catal 204:98
17. Zsodos Z, Guczi L (1992) J Phys Chem 99:9393
18. Thimmaiah S, Rajamathi M, Singh N, Bera P, Meldrum F, Chandrasekhard N, Seshadri R (2001) J Mater Chem 11:3215
19. Jacobs G, Das T, Zhang YQ, Li JL, Racoillet G, Davis BH (2002) Appl Catal A Gen 233:263
20. Yan JY, Kung MC, Sachtler WMH, Kung HH (1997) J Catal 172:178
21. Arnoldy P, Moulijn JA (1985) J Catal 93:38
22. Fino D, Russo N, Saracco G, Specchia V (2008) Powder Technol 180:74
23. Voß M, Borgmann D, Wedler G (2002) J Catal 212:10
24. Caetano BL, Rocha LA, Molina E, Rocha ZN, Ricci G, Calefi PS, de Lima OJ, Mello C, Nassar EJ, Ciuffi KJ (2006) Appl Catal A Gen 311:122
25. Resini C, Panizza M, Raccoli F, Fadda M, Carnasciali MM, Busca G, Lopez EF, Escribano VS (2003) Appl Catal A Gen 251:29
26. Lü GM, Jia D, Qian G, Qi YX, Wang XL, Suo JS (2005) Appl Catal A Gen 280:175