Catalysis Letters 55 (1998) 15–23

Redox solid catalysts for the selective oxidation of cyclohexane in air

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Received 29 May 1998; accepted 6 August 1998

The selective oxidation of cyclohexane to cyclohexanol, cyclohexanone and adipic acid using molecular oxygen as the oxidant and at moderate temperatures (403 K) has been investigated over four different cobalt-containing aluminophosphate (AlPO) molecular sieves. There is a correlation between catalytic activity and the fraction of (framework) Co(II) ions that is first oxidised to Co(III) in air. CoAlPO-36 (pore aperture 6.5 × 7.5 Å) exhibits significant activity for the oxidation of cyclohexane in contrast to CoAlPO-18, which, although it has the highest fraction of oxidisable cobalt, does not show any activity chiefly because of its smaller pores.

Keywords: CoAlPO catalysts, cyclohexane oxidation, molecular oxygen, shape-selectivity, EXAFS, redox

1. Introduction

Selective oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (the so-called K-A oil) under mild conditions is of considerable importance in the production of Nylon-6 and Nylon-6-6. For this reaction several distinct types of catalysts both homogeneous and heterogeneous have been developed. Thus, cobalt naphthenate [1], Co(III) acetate both in its free [2] and immobilised [3] state and the so-called GIF catalysts developed by Barton et al. [4] are well known examples of the homogeneous kind. Interesting examples of the heterogeneous kind include redox molecular sieves [5], encapsulated (i.e., “ship-in-bottle”) Ru(II), Co(II), Cu(II), Fe(II) phthalocyanines [6] and porphyrins [7] as well as Co(III) acetate trimer anchored to a mesoporous silica [3]. Almost without exception, however, these catalysts entail the use of sacrificial co-reductants and stoichiometric amounts of hydroperoxide (typically tertiary butyl hydroperoxide, TBHP, or its cumene analogue).

Recent investigations [8–10] in this laboratory have uncovered a number of shape-selective, redox, molecular sieve catalysts which effect conversion of alkanes in air. These are mainly aluminophosphates (AlPO’s) in which Co(II) ions have replaced a few atom percent of the Al(III) ions of the open framework. Such solids are exceptionally good solid acid catalysts [11–14] when operated under conditions that maintain the cobalt in its 2+ oxidation state and thereby have, for every Co atom in the framework, a loosely bound proton at a nearby oxygen (figure 1). But when the cobalt is in the Co(III) state, which is the case [11,12] when the catalyst is operated in air or oxygen at moderate temperatures, we have discovered that the solid is an effective selective oxidation catalyst for a variety of hydrocarbons [8–10]. Others have also reported [15–17] upon the merits of the CoAlPO redox molecular sieves as selective oxidation catalysts for hydrocarbons in general, and for cyclohexane [18–20] in particular.

The last named studies of the CoAlPO catalysts for cyclohexane oxidation [18–20] have entailed two approaches: one uses acetic acid as a solvent, the other does not, but each involves moderate pressure (ca. 15 bar) and rather low temperatures (ca. 150 °C). Unfortunately, the first of these leads to considerable leaching of cobalt from the framework [18] whereas the second, although it also suffers some leaching of the cobalt, has been demonstrated not to involve the leached cobalt as the active catalyst.

A variety of microporous aluminophosphate structures with different pore dimensions can be chosen to introduce the required shape selectivity, and Co(II) ions may be readily be substituted into many of them. Although, in all the cases, cobalt ions are present in a high-spin state with tetrahedral environment, two factors dominate their use as useful catalysts: (a) the stability of the particular microporous structure [12] and (b) the fraction of cobalt that can undergo redox {Co(II) to Co(III)} reaction [11] in the framework.

Here we describe a systematic catalytic study of cyclohexane oxidation in air at moderate temperature and pressure using four different CoAlPO’s – CoAlPO-5, CoAlPO-36, CoAlPO-11 and CoAlPO-18 (figure 2) – which differ in the pore dimensions and the fraction of oxidisable cobalt centres. This set enables us to relate structure and catalytic performance. Our results show that CoAlPO-36 is superior to the other three catalysts.

2. Experimental

Oxidation of cyclohexane was carried out employing a high-pressure catalytic reactor (Cambridge Reactor Design)

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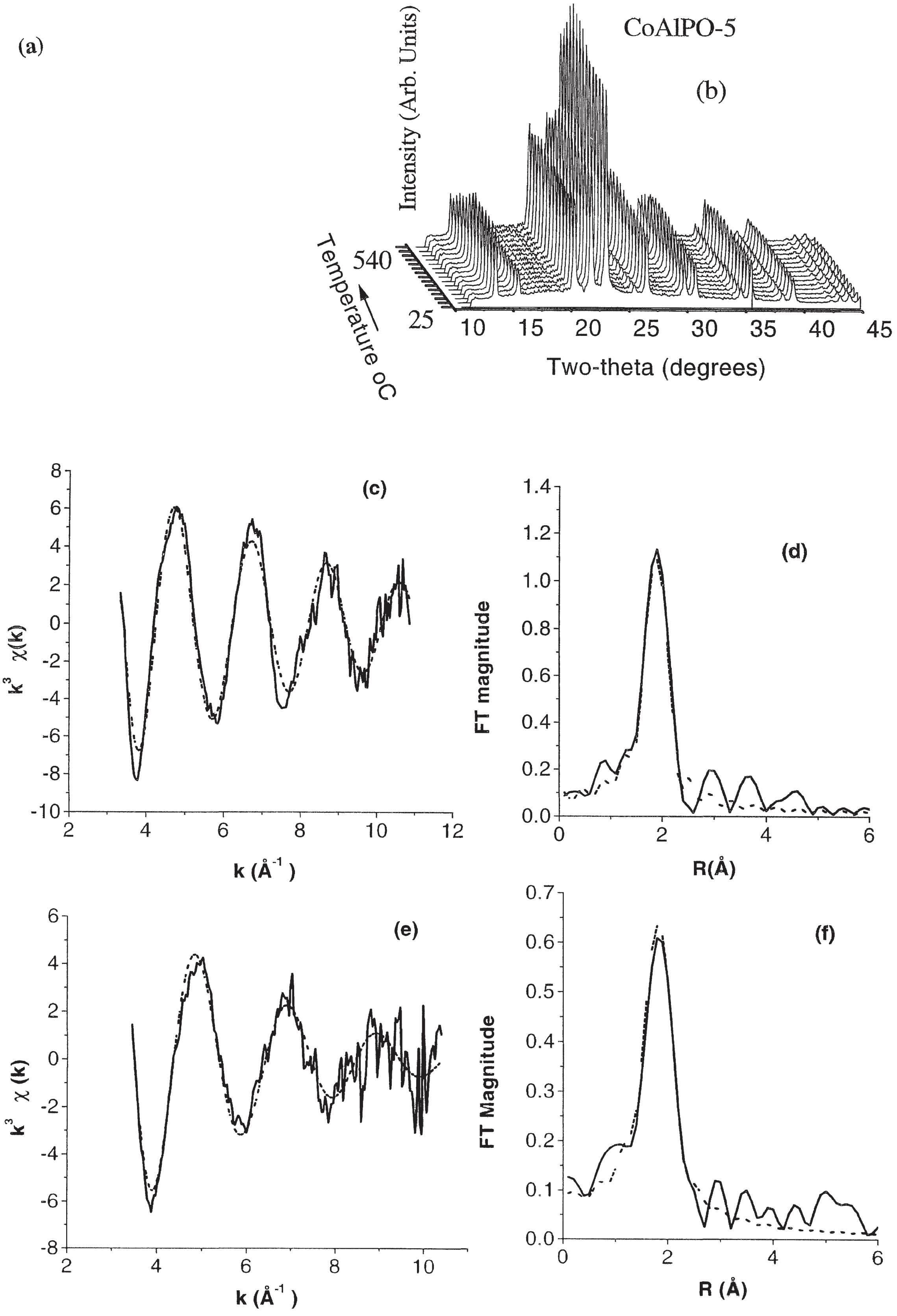

Figure 1. (a) Computer graphic representation of the AlPO-5 structure. (b) XRD patterns of CoAlPO-5 catalyst recorded *in situ* during calcination in O_2 using combined XRD/XAS. The corresponding Co K-edge EXAFS data recorded at RT and after calcination at 550 °C are shown in (c) and (e) along with the associated FT's in (d) and (f), respectively. Solid line: experimental data; dashed curve: calculated data using parameters listed in table 1.

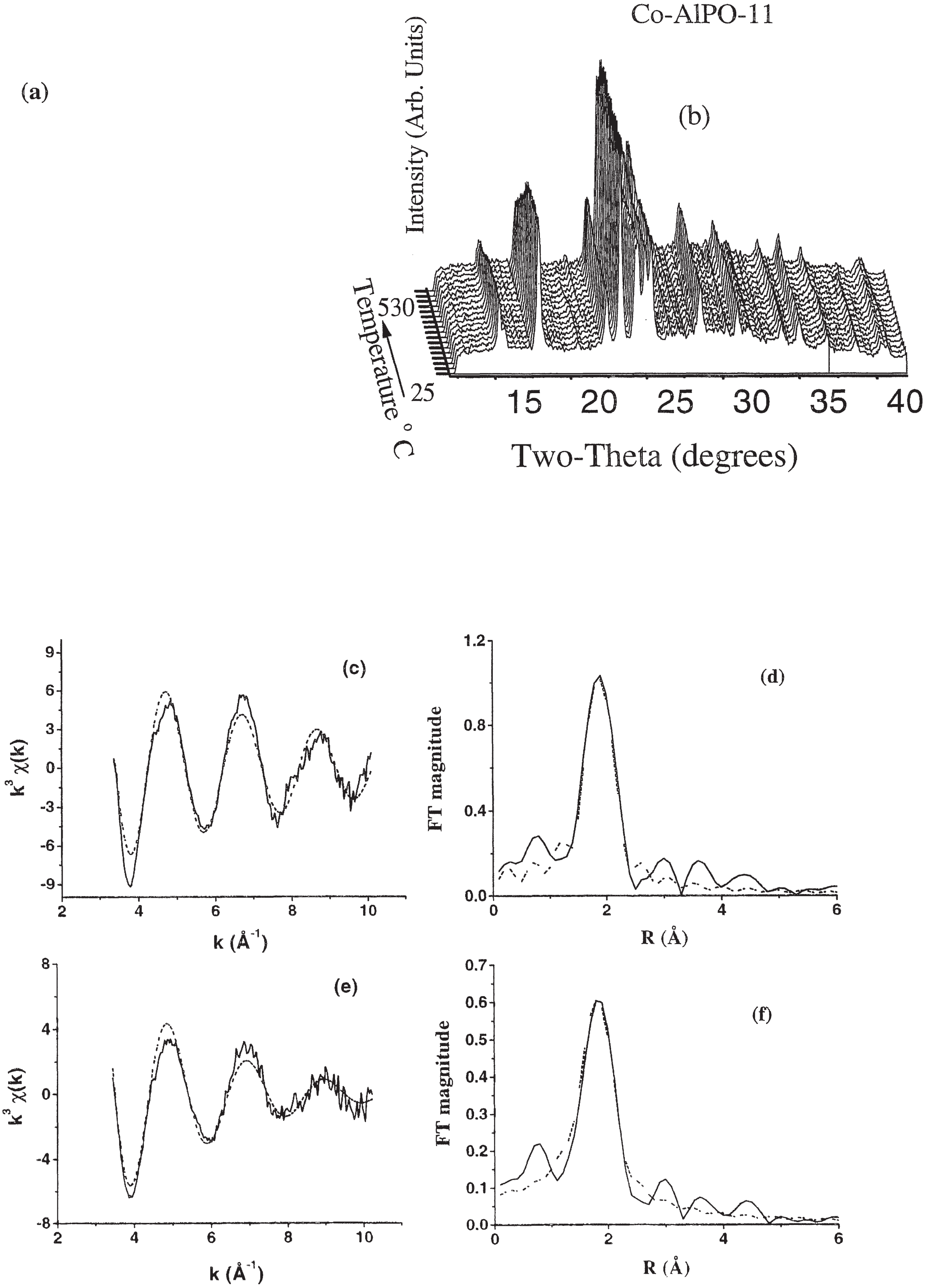

Figure 2. (a) Computer graphic representation of the AlPO-11 structure. (b) XRD patterns of CoAlPO-11 catalyst recorded *in situ* during calcination in O_2 using combined XRD/XAS. The corresponding Co K-edge EXAFS data recorded at RT and after calcination at 550 °C are shown in (c) and (e) along with the associated FT's in (d) and (f), respectively. Solid line: experimental data; dashed curve: calculated data using parameters listed in table 1.

and the products were analysed by gas chromatography (Varian model 3400). The catalysts used for this purpose were CoAlPO-5, CoAlPO-11, CoAlPO-36 and CoAlPO-18 prepared using a well established procedure [11,14,21] and the cobalt content in all the catalysts were $Co/P = 0.04$. The as-prepared materials were initially characterised by

Table 1
Local structural details around cobalt determined from the EXAFS data.

Catalyst	Average Co–O distance (Å)		
	As-prepared	Calcined	Fraction of Co(III)[a]
CoAlPO-5	1.94	1.91	0.25
CoAlPO-11	1.93	1.90	0.3
CoAlPO-36	1.93	1.86	0.5
CoAlPO-18	1.93	1.82	1.0

[a] See [11] for details.

X-ray powder diffraction using a Siemens D500 diffractometer. The catalysts were calcined in oxygen at 550 °C to remove occluded organic template molecule, prior to use for the oxidation of cyclohexane.

In a typical reaction 500 mg of the calcined CoAlPO catalyst was introduced into the Parr reactor, cyclohexane (ca. 50 g) and 1,2-dichlorobenzene (internal standard) were added and this mixture was continuously stirred. Dry air was pressurised (ca. 15 bar) into the reaction vessel (which was subsequently sealed) and heated to ca. 130 °C. Samples for analysis were withdrawn at regular intervals (without perturbing the pressure) to follow the kinetics. In one batch, the sample was extracted on cooling the reactor after 24 h, so as to minimise the loss of reactants and to achieve complete mass balance of the product. (Note that with the present facility it is not possible to analyse gaseous products.) The amounts of cyclohexyl hydroperoxide (CHHP) and the acids formed (which were esterified using $BF_3 + CH_3OH$ and analysed as methyl esters) were determined using a well established procedure [6]. In addition, the solid catalysts were thoroughly washed with methanol to remove any trapped residual reaction products and the extract was also analysed. The products formed in all the above mentioned cases were normalised with respect to their response factors (using a calibration curve obtained by injecting known volumes of standard compounds) and the internal standard.

In situ experiments of the catalysts studied here were carried out using combined XRD/XAS to monitor the integrity of the microporous structure as well as to determine the local structural changes around cobalt. These experiments were performed at station 9.3 of the Daresbury Synchrotron Radiation Source which operates at 2 GeV with a typical current of 130–250 mA (because of the low concentration of cobalt, $Co/P = 0.04$, X-ray diffraction studies could not provide any structural information about the substituted cobalt centres). Station 9.3 is equipped with Si(220) double-crystal monochromator and ion chambers for measuring incident (I_0) and transmitted (I_t) beam intensities. In a typical experiment, 40 mg of the catalyst was calcined using an *in situ* cell, described elsewhere [22], at ca. 550 °C in O_2 flow. The combined XRD/XAS measurements were recorded during the course of ramping the temperature (5 °C/min) and at the final temperature. The XRD patterns were collected at a wavelength of 1.64719 Å, below the Co K-edge. Each XRD pattern was measured for 180 s and each XAS one for 380 s. The dead time associated with the measurement is ca. 40 s giving rise to a total cycle time of 10 min. The data were analysed using the suite of programs, namely, EXCALIB, EXBROOK and EXCURV92 available at the Daresbury laboratory.

In situ IR measurements were carried out using a Perkin-Elmer 1725X spectrometer. In a typical experiment the sample was pressed into a disc and the sample was calcined in oxygen at 550 °C and evacuated at 200 °C before performing the IR measurement at room temperature. This calcined sample was reduced in H_2/N_2 (10% H_2) flow at 375 °C and once again the cell was evacuated before measurements were made at room temperature.

3. Results and discussion

X-ray diffraction (XRD) patterns of the four as-prepared, templated forms showed that there are no impurities (such as other microporous or dense phases) present in these catalysts. Our combined XRD/XAS studies (for details, see [12]) of all the catalysts performed during calcination (under operating conditions) showed good thermal stability of the microporous structure (see figures 1–4).

Evidence for the state of the Co(II) ions in the framework is primarily derived from the X-ray absorption spectroscopy and a detailed analysis of the EXAFS data reveals that, in the as-prepared form, they are tetrahedrally co-ordinated (see table 1 and figures 1–4, where the best fits to the EXAFS data are shown). However, upon calcination, EXAFS analysis shows different average Co–O distances, implying that the amount of oxidisable cobalt present in these systems varies from one to another; we have shown [11] previously how to estimate the fraction of oxidisable cobalt. The trend in the fraction (x) of Co(III) present in the four catalysts studied here is CoAlPO-18 > CoAlPO-36 > CoAlPO-11 > CoAlPO-5. When these materials are reduced in hydrogen the resulting average Co–O distance falls in the range of 1.90–1.95 Å.

Further evidence for the changes in oxidation state upon oxidation and subsequent reduction comes from the IR study where, upon calcination, there are only bands associated with the stretching frequency of terminal P–OH in the OH stretching region. Although for some of the catalysts only a fraction of Co(II) can be oxidised, there is no evidence for a bridging hydroxyl in the IR spectra of the calcined catalysts. This, we believe [11], is because of the formation of an oxygen ion vacancy where a pair of four-coordinated Co(II) centres and under-coordinated Co(II) centres result in the charge compensation without the need for protonated sites. Reduction in hydrogen results in the formation of a new OH band associated with Brønsted acid sites [11,12,23,24] and its intensity varies considerably among the four systems studied here. The cycle of oxidation and reduction can be performed several times without any loss of microporous structure and the acid sites can be regenerated many times over as shown in figure 5, for CoAlPO-36 as a typical example.

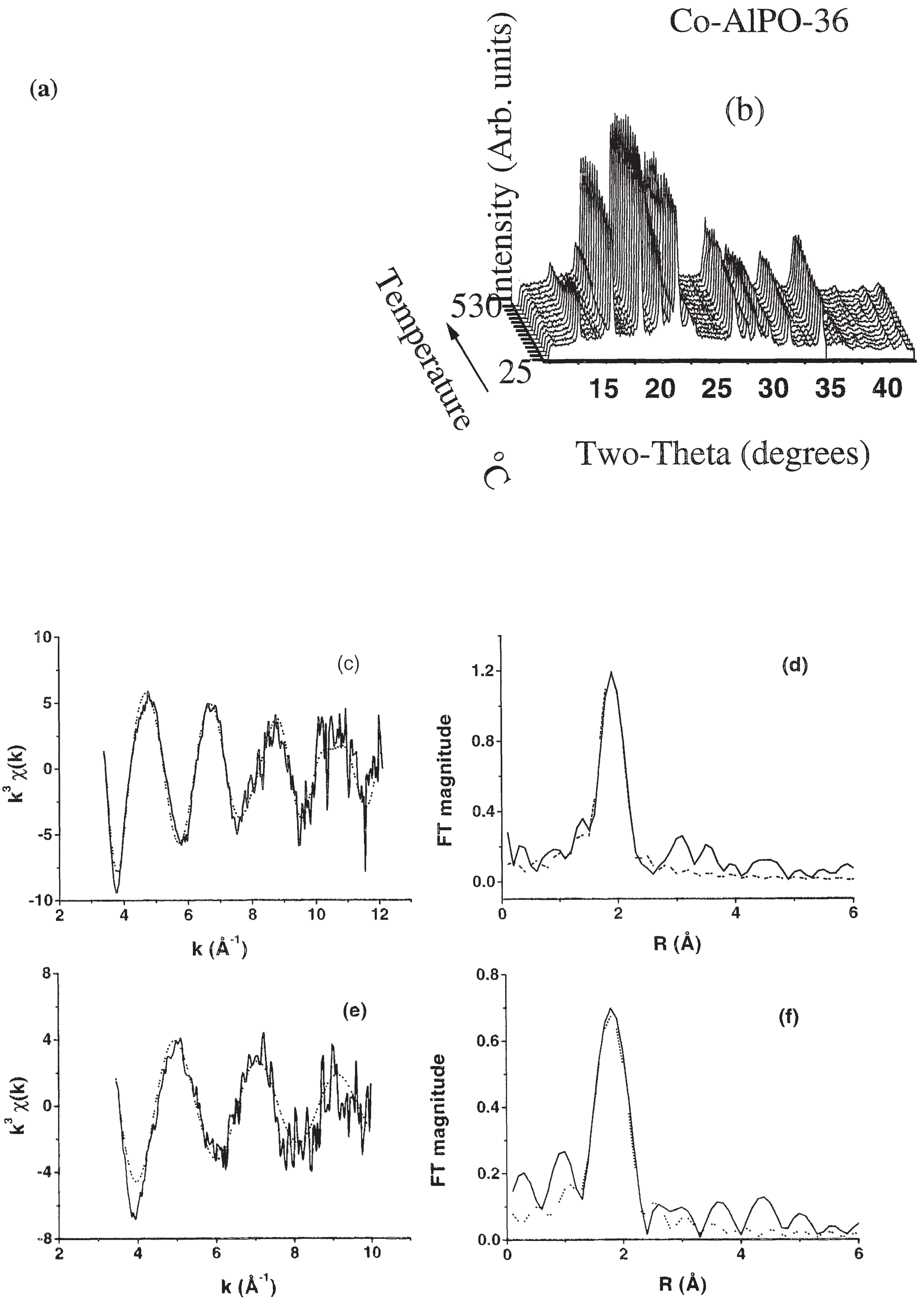

Figure 3. (a) Computer graphic representation of the AlPO-36 structure. (b) XRD patterns of CoAlPO-36 catalyst recorded *in situ* during calcination in O_2 using combined XRD/XAS. The corresponding Co K-edge EXAFS data recorded at RT and after calcination at 550 °C are shown in (c) and (e) along with the associated FT's in (d) and (f), respectively. Solid line: experimental data; dashed curve: calculated data using parameters listed in table 1.

The catalytic results (see table 2) show that CoAlPO-36 is indeed the most active catalyst compared to either CoAlPO-5 or CoAlPO-11. The performance of CoAlPO-11 is comparable to that reported by Jacobs et al. [20]; and CoAlPO-18 shows no activity. These results are not surprising in that CoAlPO-36 possesses not only the appro-

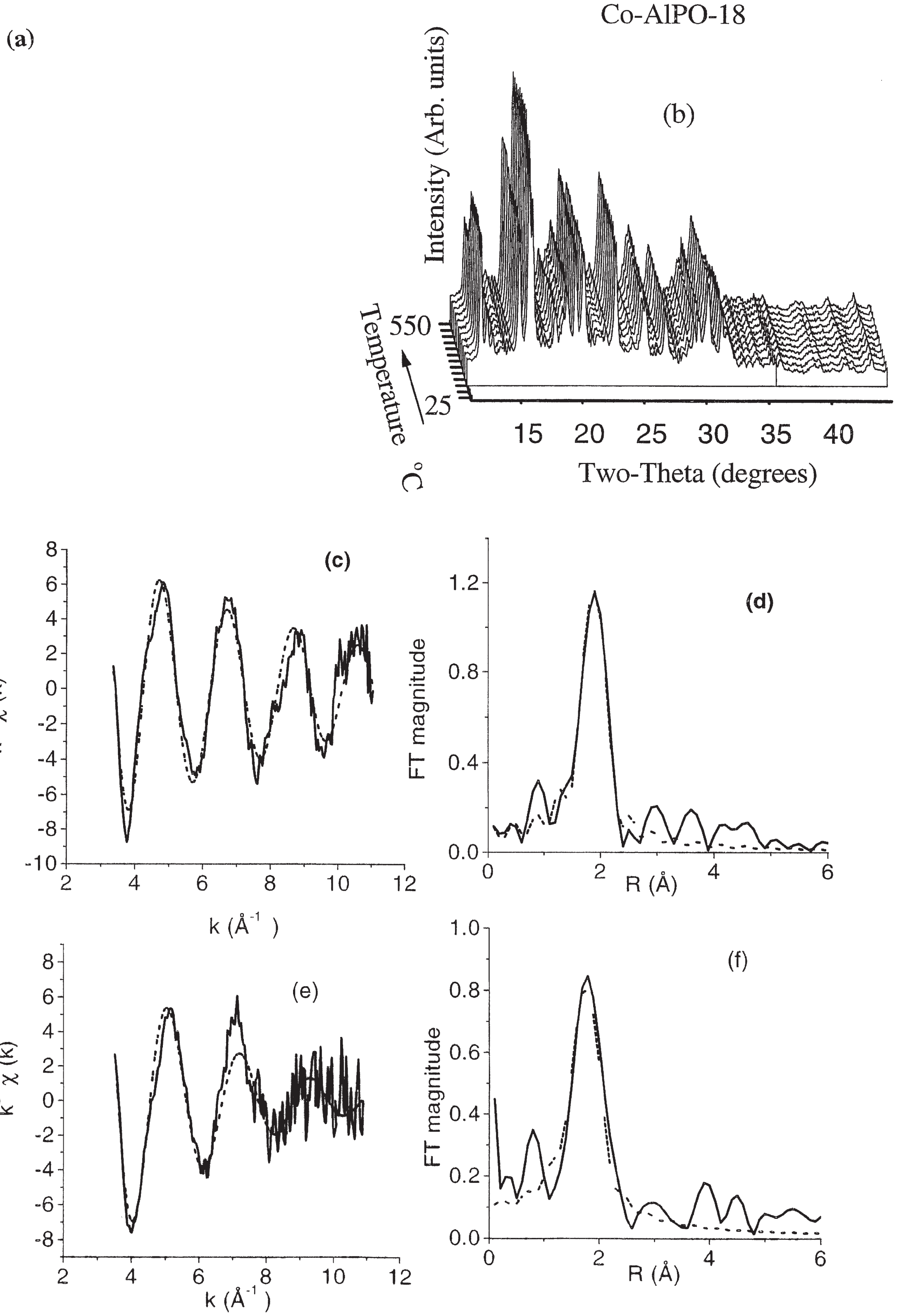

Figure 4. (a) Computer graphic representation of the AlPO-18 structure. (b) XRD patterns of CoAlPO-18 catalyst recorded *in situ* during calcination in O_2 using combined XRD/XAS. The corresponding Co K-edge EXAFS data recorded at RT and after calcination at 550 °C are shown in (c) and (e) along with the associated FT's in (d) and (f), respectively. Solid line: experimental data; dashed curve: calculated data using parameters listed in table 1.

priate pore dimension for cyclohexane to diffuse into the channels and react with the catalytically active centres, but also this catalyst has a higher fraction of oxidisable cobalt centres compared to CoAlPO-11 and CoAlPO-5. Although CoAlPO-18 has the highest fraction of all oxidisable cobalt centres, because of its smaller pore openings the cyclo-

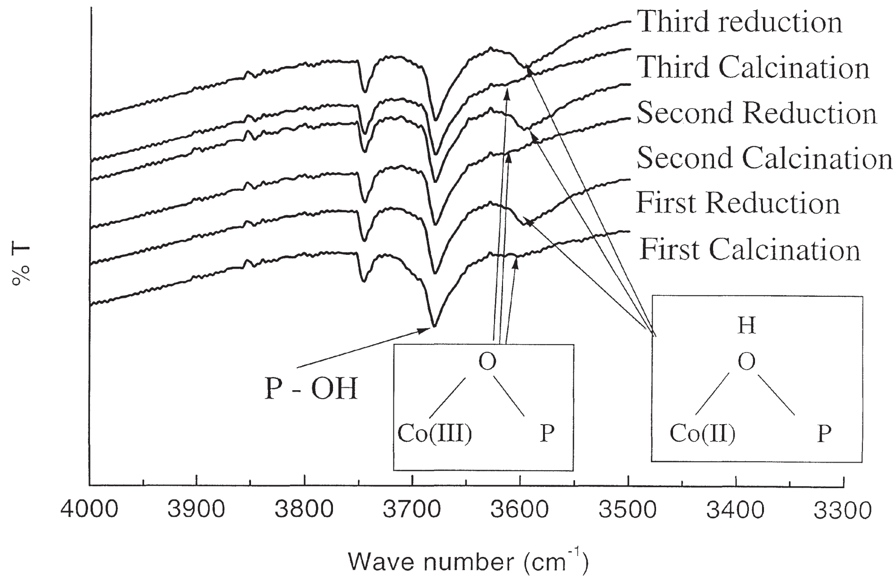

Figure 5. *In situ* IR spectra of calcined and reduced CoAlPO-36 catalysts. Also shown are the spectra of the CoAlPO-36 catalyst after re-calcination and re-reduction. For clarity only the OH stretching regions are shown.

Table 2
Oxidation of cyclohexane[a] in dry air (1.5 MPa).

Catalyst	Temp (K)	Time (h)	TON[b]	Conv. (mmol)	Product distribution (mol%)						
					cHHP[c]	-ol	-one	aa	ga	sa	others
CoAlPO-5	368	8	25.52	8.33	44.3	32.5	23.7	–	–	–	–
		16	28.76	10.12	14.5	47.7	36.0	–	–	–	1.9
	403	8	29.0	9.52	44.1	35.0	21.7	–	–	–	–
		16	33.36	11.31	14.8	26.4	54.3	–	–	–	4.8
CoAlPO-11	368	8	31.43	10.72	36.9	36.1	27.1	–	–	–	–
		16	42.26	14.30	8.3	37.0	50.3	–	–	–	4.5
	403	8	47.17	16.07	24.2	28.6	44.7	–	–	–	2.6
		16	56.12	19.05	7.2	25.2	62.6	–	–	–	5.3
CoAlPO-18	368	16	0	–	–	–	–	–	–	–	–
	403	16	0	–	–	–	–	–	–	–	–
CoAlPO-36[d]	368	8	84.23	28.57	–	64.5	31.9	2.7	–	–	1.1
		16	106.93	36.31	–	30.9	61.1	5.4	–	–	2.4
	403	8	126.15	42.86	–	51.2	41.0	6.3	–	–	1.7
		16	166.37	56.55	–	33.5	49.7	12.9	–	–	4.2

[a] Cyclohexane = 49.5 g; catalyst = 0.5 g; pressure (air) = 1.5 MPa.

[b] TON = turnover number = moles of cyclohexane converted per mole of cobalt in the catalyst.

[c] cHHP = cyclohexyl hydroperoxide; -ol = cyclohexanol; -one = cyclohexanone; aa = adipic acid; ga = glutaric acid; sa = succinic acid; others = small amounts of valeraldehyde, valeric acid in the liquid mixture and probably CO_2, CO, water and traces of lower olefins/hydrocarbons in the gas phase.

[d] After each reaction the catalyst was filtered off, washed thoroughly with methanol and calcined at 550 °C for 12 h. It was then recycled three times without significant loss in catalytic activity. In a separate experiment, when TBHP (tertiary butyl hydroperoxide) was added as an initiator (5% mole of cyclohexane), the initial induction period of 2 h was reduced to 45 min.

hexane molecule does not gain access to its interior active sites and no catalytic activity ensues.

Detailed studies of the kinetics of the oxidation of cyclohexane using the CoAlPO-36 as the catalyst are summarised in figure 7. After the initial induction period (120 min), cyclohexanol and cyclohexanone were the major products at low conversion levels and residence times. When the reaction is continued beyond 8 h, significant amounts of adipic acid start to appear in the product mixture. On further continuation, cyclohexanol is oxidised to cyclohexanone which is in turn converted to adipic acid. In one set of two identical experiments, the solid catalyst (CoAlPO-36) was filtered from the reaction mixture after a reaction time of 8 h. While the conversion of cyclohexane continued in the presence of the solid catalyst, there was no further conversion when the catalyst was removed from the reaction system. This indicates that the oxidation of cyclohexane by free or dissolved cobalt ions (leached out from the aluminophosphate framework) is negligible. This conclusion was independently confirmed by the analysis of the reaction

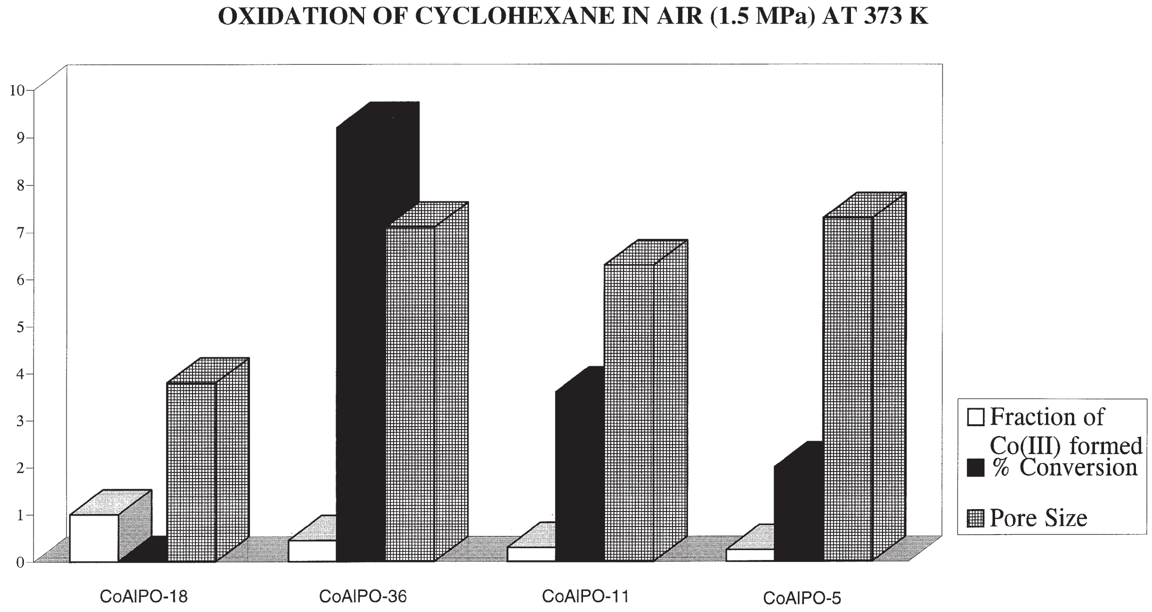

Figure 6. Bar chart representation of the fraction of oxidised cobalt, pore dimension and catalytic activity of CoAlPO-5, CoAlPO-11, CoAlPO-36 and CoAlPO-18 catalysts.

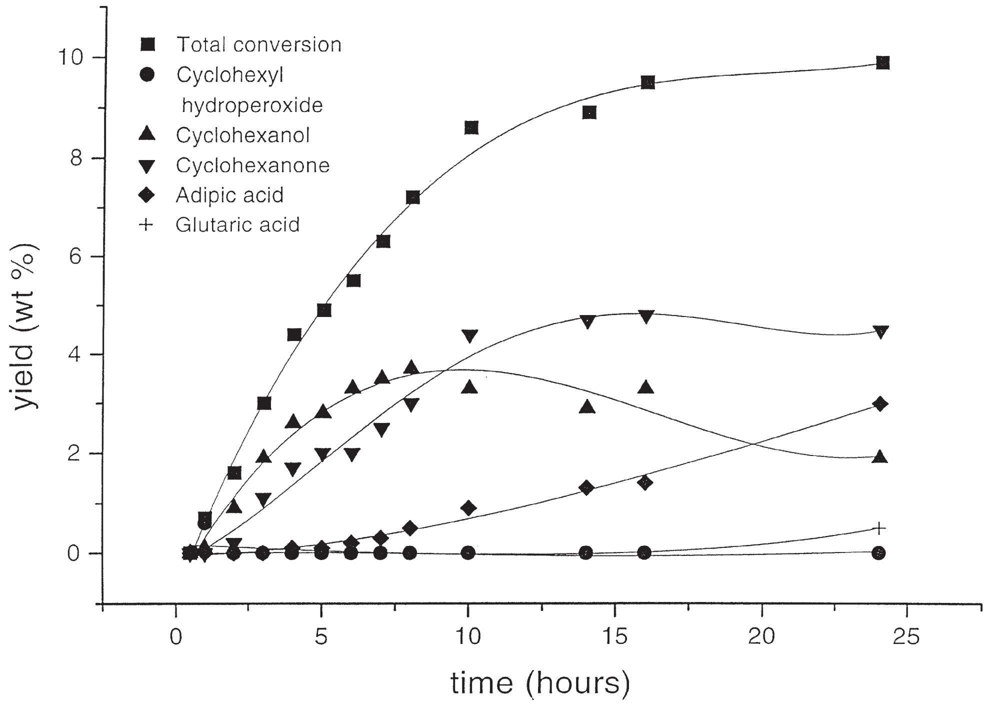

Figure 7. Typical kinetics plot for the oxidation of cyclohexane using CoAlPO-36 as the catalyst, at 403 K, under experimental conditions given in table 2.

products for cobalt (ICP, atomic absorption spectroscopy). In addition, if such leached-out cobalt is responsible for the catalytic reaction, we should have observed some catalytic activity with CoAlPO-18, but there is none. There was no decrease in activity when the CoAlPO-36 catalyst was re-used, at least twice, after washing thoroughly with methanol and calcined in air at 550 °C.

In summary, framework-substituted cobalt is responsible for the catalytic activity, and there is a correlation between the degree of activity and the amount of oxidisable cobalt in the framework.

Acknowledgement

We thank EPSRC for financial support (rolling grant to JMT) and synchrotron beam time and CCLRC for the facilities. RR thanks the Royal Commission for the Exhibition of 1851 for a Research Fellowship.

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