Selective oxidation on chromia-pillared zirconium phosphate and phenylphosphonate

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Chromia-pillared zirconium phosphate and zirconium phenylphosphonate were prepared by an indirect intercalation method. The pillared materials have surface area in the range of 316–462 m^2/g and narrow pore size distributions with $\geqslant$70% mesoporosity. They are efficient catalysts for selective oxidation of aromatics, alkanes, cycloalkanes, cycloalkenes and alcohols using 30% H_2O_2 as the oxidant with catalytic activities much higher than CrAPOs and CrMCM-41.

Keywords: chromia-pillared zirconium phosphates and phenylphosphonate, surface area, porosity, thermal stability, selective oxidation

1. Introduction

Selective oxidation of organic compounds was traditionally carried out with stoichiometric amount of Cr^{6+} reagents [1]. The main disadvantages of the reaction are the difficulty in regenerating the oxidant and the generation of a large amount of toxic effluents. Recently, heterogeneous catalysts such as Cr-PILC [2], CrAPO-5 [3], CrAPO-11 [4] and CrMCM-41 [5] have been reported to be active for selective oxidation of various organic compounds using *tert*-butylhydroperoxide, hydrogen peroxide or O_2 as oxidants.

Metal-oxide-pillared layered metal(IV) phosphates are a new type of catalytic materials having high surface area, large pore volume, uniform mesoporosity and high thermal stability. In comparison with MCM-type materials, the pillared phosphates are more versatile in framework chemical variety and composition, which are indeed of importance to catalysis. Hence much attention has been focused on the study of the preparation, characterization, sorption and catalytic properties of these materials. Chromia-pillared α-zirconium phosphate (α-ZrP) and α-tin phosphate (α-SnP) with BET surface area of 250–330 and 380–445 m^2/g, respectively, have been prepared [6–8]. IR spectra of the chromia-pillared phosphates after adsorption of pyridine show that both Lewis and Brønsted acid sites are present [9]. The activity and selectivity of the pillared phosphates in the decomposition reaction of isopropanol in helium or air reveal that these catalysts possess acid and redox active sites [9]. However, in the previous literature selective oxidation of various organic compounds on chromia-pillared zirconium phosphate and zirconium phenylphosphonate using hydrogen peroxide as the oxidant has not been investigated.

In this work, chromia-pillared α-zirconium phosphate and phosphonate were prepared by an indirect intercalation method [10], in which preswelling of the layered substance by ethylamine was performed prior to the intercalation of the pillaring species. The pillared materials are well characterized and for the first time their catalytic performance in selective oxidation of various organic compounds with 30% H_2O_2 was investigated.

2. Experimental

α-$Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP) was prepared following the procedures in literature [11]. 1 g of α-ZrP was mixed with 100 ml of 0.1 mol/l ethylamine solution. After aging for 24 h at ambient temperature, a freshly prepared solution containing 15 mmol $Cr(OAc)_3$ was added slowly. Then the mixed solution was diluted to a total volume of 400 ml, and refluxed for 72 h. The precipitate was filtered, washed thoroughly and dried at 60 °C. The pillared materials obtained were designated as CZP.

$Zr(PO_4H)_{2-n}(PO_3Ph)_n$ (ZrPP) with $n = 0.4$, 0.6 and 1.0 were prepared as reported elsewhere [12]. The typical synthesis procedure was as follows: Solution A with F^-/Zr^{4+} mole ratio of 12 was obtained by adding 2.5 g $ZrOCl_2{\cdot}8H_2O$ to HF solution. Solution B containing 10 ml 85% H_3PO_4 and 1.25n g H_2PO_3Ph ($n = 0.4, 0.6, 1.0$) was mixed with solution A. The total volume of the mixed solution was 150 ml. The mixed solution was then refluxed at 100 °C for 24 h with vigorous stirring. The product obtained was $Zr(PO_4H)_{2-n}(PO_3Ph)_n$ (ZrPP). Chromia-pillared phenylphosphonates were prepared by the same method as the chromia-pillared α-ZrP. The products were designated as CZPP-n.

XRD patterns were obtained on a Rigaku D/MAX-IIA diffractometer using Cu Kα radiation at 40 kV and 20 mA.

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TG/DTG analysis was carried out on a Rigaku Thermoflex instrument in flowing air or N_2 from ambient temperature to 800 °C at a heating rate of 10 °C/min. N_2 isotherms were measured on a Micromeritics ASAP-2000 instrument. The surface area and micropore volume were calculated by the BET and α_s-plot methods [13], and the pore size distribution by the Cranston–Inkley method [14]. The amount of chromium in the samples was analyzed by a colorimetric method using a Shimadzu UV-240 spectrometer.

Oxidation reactions were carried out in a thermostated flask equipped with a condenser and a magnetic stirrer. Typically, 0.2 g catalyst, 2 ml reactant, 14 ml acetone and 5 ml 30% H_2O_2 were added into the flask. The reaction was continued at 55 °C for a certain period of time, and then the reaction products were analyzed by a gas chromatograph.

3. Results and discussion

The chromium contents of the pillared materials are given in table 1. The chromium uptakes of CrZPP are obviously smaller than that of CrZP, and increasing the number of n will decrease the uptake of Cr, because the substitution of the large phenylphosphonate groups not only reduces the number of exchangeable OH groups on the sheets but also obstructs the intercalation of Cr to a same extent.

Results of TG/DTG analysis of CZP and CZPP-1.0 in flowing air and N_2 are shown in figure 1. There are two peaks on the DTG profile of CZP in air. The first peak at 76 °C corresponds to dehydration of the pillared material, and the second peak at 281 °C corresponds to elimination of organic residues in the material [7]. In N_2, the two peaks shift to 90 and 442 °C, respectively. There are two additional peaks on the DTG profiles of CZPP-1.0, which correspond to elimination of ethylamine residue and benzene rings on the sheets. The temperatures of these two additional peaks are 360 and 420 °C in air, and they shift to 454 and 575 °C in N_2.

XRD patterns of the pillared materials were recorded after heating in air on N_2 at elevated temperatures for 3 h. Figure 2 depicts the changes in the diffraction patterns of CZP and CZPP samples after heating, and the d-spacings of the samples heated under different conditions are given in table 1. The pillared structure of CZP is still distinguishable when heating up to 300 °C in air and up to 400 °C in N_2, but its d-spacing decreases from 3.40 to 2.10 and 1.88 nm, respectively. The thermal stability of the CZPP samples depends on the amount of phenylphosphonate groups on the sheets. CZPP-1.0 with the greatest value of n is the most stable among all the samples. In our previous work [15], it has been observed that the phenyl groups in the interlayer region of zirconia pillared phenylphosphonate may act as stabilizers. On the one hand, their presence reduces the number of P–OH groups and, on the other hand, shields the P–OH groups from interaction with the pillars, thus restricting the spreading of the oxide pillars and the col-

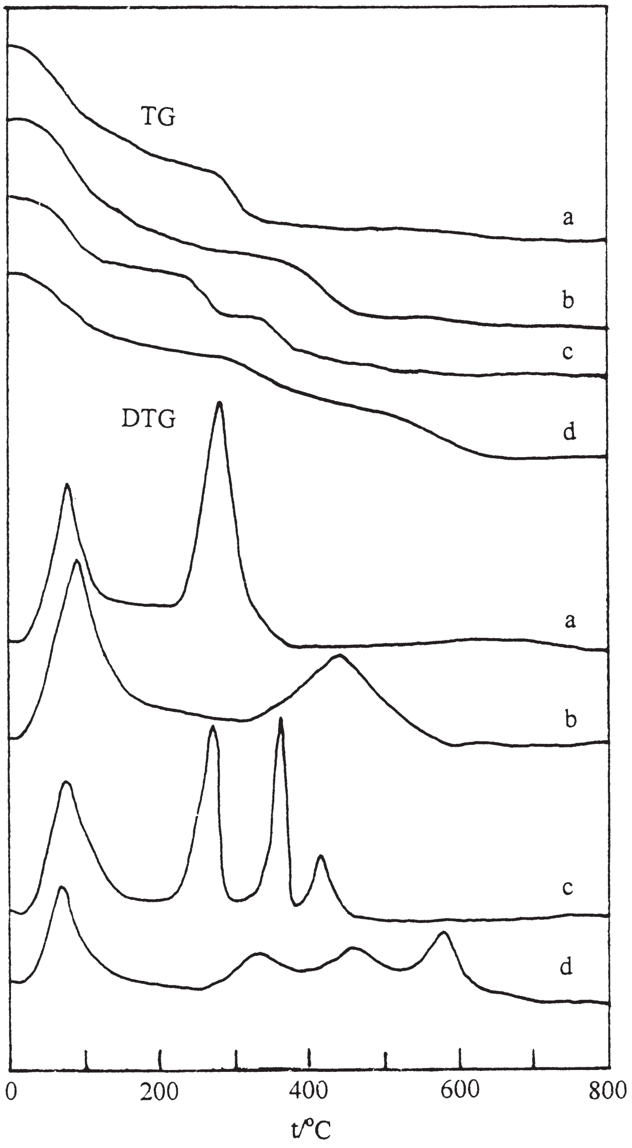

Figure 1. TG/DTG profiles of the samples. (a) CZP (air); (b) CZP (N_2); (c) CZPP-1.0 (air); (d) CZPP-1.0 (N_2).

Table 1
Composition and properties of the samples.

Sample	Cr uptake (mg/g ZP, ZPP)	d_{002} (nm)			
		Uncalcined	250 °C (air)	300 °C (air)	400 °C (N_2)
CZP	576	3.40	2.21	2.10	1.88
CZPP-0.4	464	2.76	2.60	–	–
CZPP-0.6	384	2.85	2.60	–	–
CZPP-1.0	291	3.05	2.76	2.76	2.76

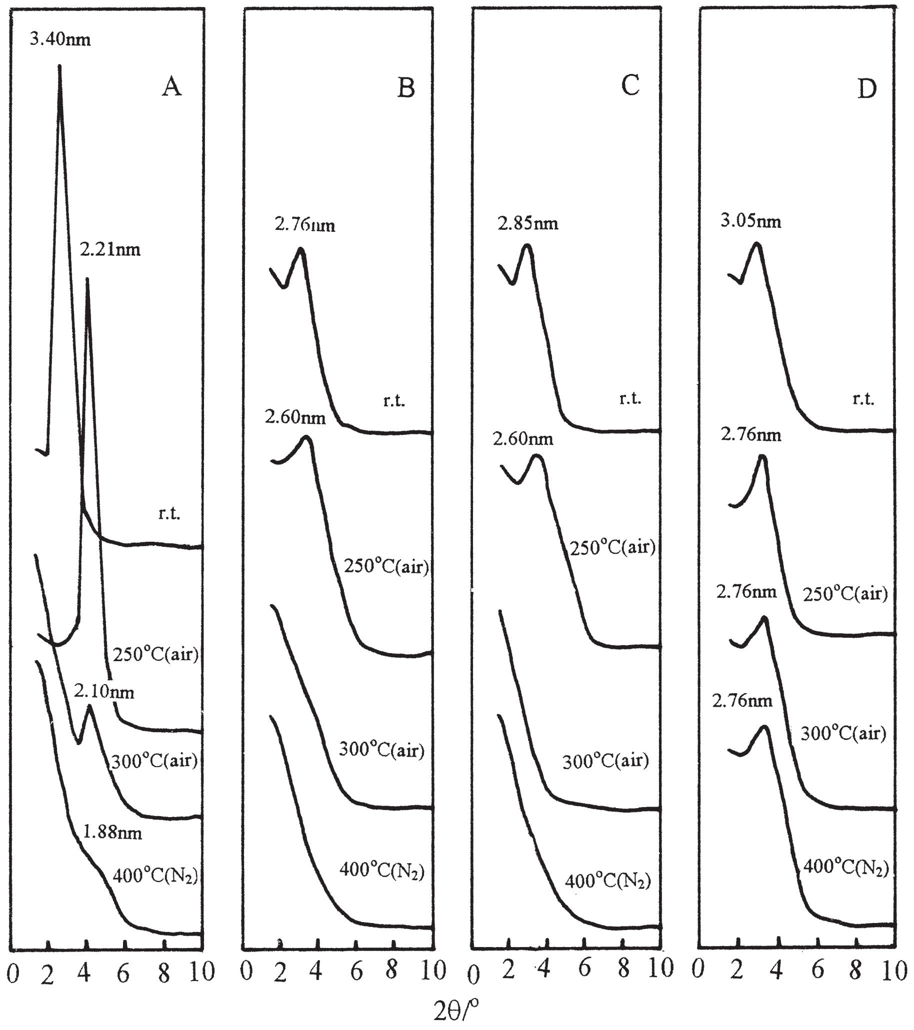

Figure 2. XRD patterns of pillared materials heated under different conditions. (A) CZP; (B) CZPP-0.4; (C) CZPP-0.6; (D) CZPP-1.0.

Table 2
Textural properties of the samples calcined under different conditions.

Sample	Condition	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
CZP	250 °C (air)	427	0.259	0.080
	400 °C (N_2)	428	0.266	0.076
CZPP-0.4	250 °C (air)	411	0.302	0.035
	400 °C (N_2)	462	0.312	0.040
CZPP-0.6	250 °C (air)	403	0.299	0.027
	400 °C (N_2)	414	0.283	0.030
CZPP-1.0	250 °C (air)	382	0.269	0.028
	400 °C (N_2)	316	0.208	0.028

lapse of the pillared structure upon heating. Therefore, in consideration of thermal stability of the pillared materials, α-ZrPP with an adequate amount of phenylphosphonate groups is probably a better starting material to use than α-ZrP.

The textural properties of CZP and CZPP samples calcined in air and N_2 are summarized in table 2, and the typical pore size distribution curves of CZP and CZPP-1.0 are shown in figure 3. The surface areas of the pillared materials are all in the range of 316–462 m^2/g. They are predominantly mesoporous with $\leqslant$30% microporous contribution. The pore size distributions of the samples are quite narrow with a maximum diameter centered at ca. 2 nm.

Liquid-phase oxidation of benzene and cyclohexane with 30% H_2O_2 was carried out on the pillared materials. The results are listed in table 3 and compared with data on other types of Cr-containing porous materials available in literature. Benzene and cyclohexane are selectively oxidized on the catalysts to form phenol or cyclohexanone and cyclohexanol, respectively. The yields of the oxygenated products on most of the catalysts are much higher than those on CrAlPO-11 and CrMCM-41. Furthermore, their catalytic activities decrease slightly after recycling three times. This shows that the chromium-pillared phosphates are a promising new type of selective oxidation catalysts.

It can be seen from table 3 that the catalytic activities of most of the catalysts calcined at 250 °C in air are higher than those of the catalysts calcined at 400 °C in N_2, and CZPP-0.6 and CZPP-1.0 are more active than

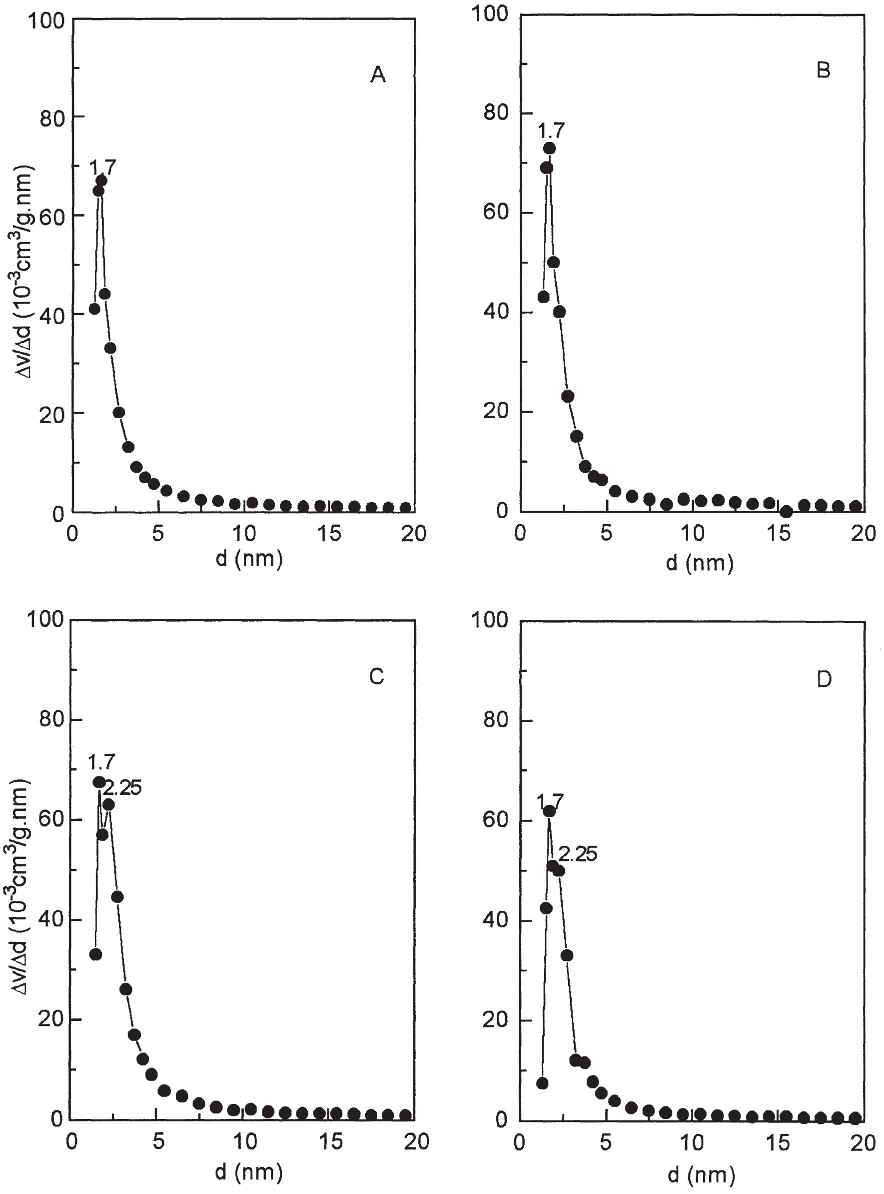

Figure 3. Pore size distribution of the samples. (A) CZP (air); (B) CZP (N_2); (C) CZPP-1.0 (air); (D) CZPP-1.0 (N_2).

Table 3

Catalytic oxidation of benzene and cyclohexane with 30% H_2O_2.

Catalyst	Treatment	Benzene			Cyclohexane		
		Time (h)	Conversion (%)	Product (% yield)	Time (h)	Conversion (%)	Product (% yield)
CZP	250 °C (air)	12	34.1	Phenol (27.9)	6	51.7	Cyclohexanol (38.6) + cyclohexanone (13.1)
CZP	400 °C (N_2)	12	21.9	Phenol (16.4)	6	46.5	Cyclohexanol (38.7) + cyclohexanone (7.8)
CZPP-0.4	250 °C (air)	12	37.9	Phenol (30.6)	6	46.5	Cyclohexanol (34.2) + cyclohexanone (12.3)
CZPP-0.4	400 °C (N_2)	12	29.8	Phenol (22.5)	6	23.1	Cyclohexanol (15.8) + cyclohexanone (7.3)
CZPP-0.6	250 °C (air)	12	58.6	Phenol (46.8)	6	49.1	Cyclohexanol (38.5) + cyclohexanone (10.6)
CZPP-0.6	400 °C (N_2)	12	14.5	Phenol (11.1)	6	19.4	Cyclohexanol (11.8) + cyclohexanone (7.6)
CZPP-1.0	250 °C (air)	12	40.3	Phenol (31.8)	6	56.5	Cyclohexanol (41.9) + cyclohexanone (14.6)
CZPP-1.0[a]	250 °C (air)	–	–	–	6	52.6	Cyclohexanol (40.6) + cyclohexanone (12.0)
CZPP-1.0	400 °C (N_2)	12	37.3	Phenol (29.7)	6	57.2	Cyclohexanol (40.2) + cyclohexanone (17.0)
CZPP-1.0[a]	400 °C (N_2)	–	–	–	6	53.1	Cyclohexanol (39.1) + cyclohexanone (14.0)
CrAPO-11 [4]	–	12	8.0	Phenol (8.0)	–	–	–
CrMCM-41 [5]	–	12	7.8	Phenol (7.6)	12	25	Cyclohexanol (10) + cyclohexanone (15)

[a] Recycled three times.

Table 4
Catalytic oxidation of other organic compounds with 30% H_2O_2.

Catalyst	Reactant	Time (h)	Conversion (%)	Product (% yield)
CZP	Toluene	12	100	Benzoic acid (92.1)
CZPP-0.6	Toluene	12	100	Benzoic acid (93.4)
CZPP-1.0	Toluene	12	100	Benzoic acid (90.7)
CrMCM-41 [5]	Toluene	20	50	Benzoic acid (45)
CrAlPO-11 [4]	Toluene	12	7.7	Cresol (7.2)
CZP	Ethylbenzene	6	100	Acetophenone (100)
CZPP-0.6	Ethylbenzene	6	100	Acetophenone (100)
CZPP-1.0	Ethylbenzene	6	100	Acetophenone (100)
CrMCM-41 [5]	Ethylbenzene	12	88	Acetophenone (85)
CZP	Cyclohexene	6	61.8	Cyclohexanone (10.9) + cyclohexene oxide (50.9)
CZPP-0.6	Cyclohexene	6	77.5	Cyclohexanone (13.2) + cyclohexene oxide (64.3)
CZPP-1.0	Cyclohexene	6	65.6	Cyclohexanone (13.1) + cyclohexene oxide (52.5)
CZP	n-heptane	6	51.2	2-heptanone (37.1) + 3-heptanone (14.1)
CZPP-0.6	n-heptane	6	45.4	2-heptanone (25.7) + 3-heptanone (19.7)
CZPP-1.0	n-heptane	6	48.5	2-heptanone (32.9) + 3-heptanone (15.6)
CrMCM-41 [5]	n-heptane	12	20	2-heptanone (10) + 3-heptanone (8)
CZP	n-butanol	12	88	n-butyraldehyde (88)
CZPP-0.6	n-butanol	12	89	n-butyraldehyde (89)
CZPP-1.0	n-butanol	12	90	n-butyraldehyde (90)

Table 5
Amounts of Cr leaching from different catalysts after the oxidation of cyclohexane.

Catalyst	Treatment	Leaching Cr of catalysts (mg)		
		Recycled once	Recycled twice	Recycled three times
CZP	250 °C (air)	3.12	–	–
CZP	400 °C (N_2)	0.32	–	–
CZPP-0.6	250 °C (air)	2.28	–	–
CZPP-0.6	400 °C (N_2)	0.16	–	–
CZPP-1.0	250 °C (air)	1.64	0.57	0.24
CZPP-1.0	400 °C (N_2)	0.20	0.20	0.20

CZPP-0.4. The oxidation of toluene, ethylbenzene, cyclohexene, n-heptane and n-butanol with 30% H_2O_2 as the oxidant was carried out on CZP, CZPP-0.6 and CZPP-1.0 calcined at 250 °C in air. The results are summarized in table 4. For these reactions, the pillared materials again exhibit very high catalytic activity and selectivity. The alkylaromatics oxidize on the catalysts more readily than benzene. Toluene and ethylbenzene are selectively oxidized on the catalysts to form benzoic acid and acetophenone, respectively, with excellent yields. Butanol is oxidized to butyraldehyde in high yield as well. Heptane and cyclohexane are oxidized in moderate yields to form ketones and a mixture of ketone and epoxide, respectively.

The leaching of Cr during the oxidation reaction is also investigated, and the results are listed in table 5. The leaching of Cr can be negligible for those N_2-treated catalysts, since after oxidation of cyclohexane the Cr contents in the liquids being separated from catalysts are very low. But for those air-treated catalysts, the values are nearly ten times higher than those of the N_2-treated ones. This may be caused by the high oxidation state of Cr in the air-treated catalysts. But the contents of Cr leaching from the air-treated catalysts decrease rapidly with increasing the recycle times. This can be attributed to the reduction of the high oxidation state Cr during the reaction. The filtrate containing the leaching Cr is also used in the oxidation reaction, but no catalytic activity is detected.

After oxidation of cyclohexane the surface area and pore volume of air-treated CZPP-1.0 catalysts are 243 m^2/g and 0.184 cm^3/g, respectively, which are much lower than those before the reaction, suggesting that the leaching of Cr damages the pore structure of air-treated CZPP-1.0 catalyst. In contrast, after the reaction the surface area and pore volume of the N_2-treated CZPP-1.0 catalyst are 326 m^2/g and 0.209 cm^2/g, respectively, which are unchanged in comparison with those before the reaction, indicating that the N_2-treated catalyst is more stable than the air-treated one during the oxidation reaction. XRD spectra (figure 4) also show that N_2-treated catalysts are more stable than the air-treated one during the reaction since they remain better pillared layer structure.

Therefore, it can be concluded that the oxochromium species in CZP and CZPP catalysts are also active for selective oxidation of a wide variety of organic compounds as

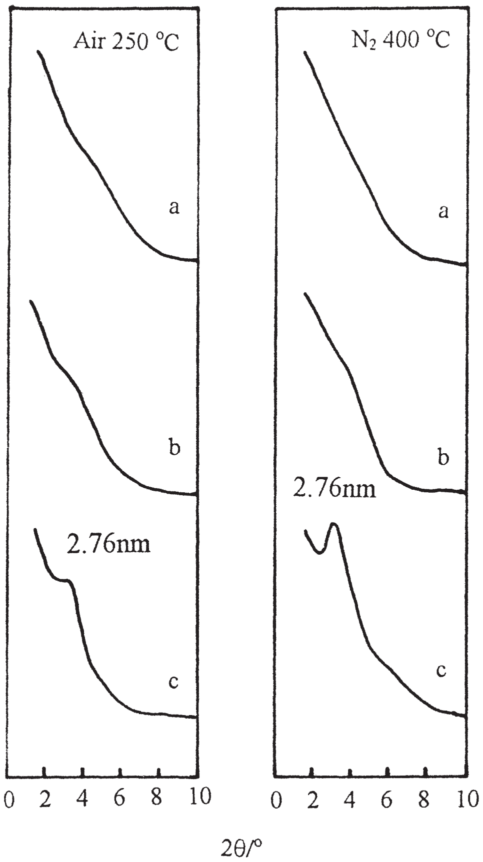

Figure 4. XRD patterns of catalysts after the oxidation of cyclohexane. (a) CZP; (b) CZP-0.6; (c) CZP-1.0.

the framework chromium species in AlPOs and MCM-41 molecular sieves, and the high Cr content and the mesoporous structure of the pillared materials are probably responsible for their high catalytic activities for the oxidation reactions.

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