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Influence of Preparation Parameters on Characteristics of Zirconia-Pillared Clay using Ultrasonic Technique and its Catalytic Performance in Phenol Hydroxylation Reaction

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Abstract–Ultrasonication method was employed for preparation of zirconia-pillared montmorillonite (Zr-PILC) by using polyhydroxy zirconium cation. The influences of various preparation parameters such as pH, concentration of pillaring agent, aging period on physico-chemical properties of Zr-PILCs are reported. The characterization was done by using different characterizing tools such as powder X-ray diffraction (XRD), thermal analysis (TG/DTA), Fourier transform infrared spectroscopy (FTIR), X-ray photo-electron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF) and surface area measurements. Effective pillaring was obtained in the pH range 2.0-2.8 at reduced preparation time by using ultrasonication. Ultrasonication, especially at higher pH and concentration of pillaring agent with no aging after ultrasonic agitation of the clay slurry was found to increase zirconium content and specific BET surface area leaving no scope for remarkable increase in d001 spacing. The presence of -OH groups attached to Zr has been revealed by pyridine-adsorbed FTIR, TG/DTA and XPS techniques. The acidic character, ease of accessibility and good dispersion of active sites in Zr-PILC were found to be controlling factors for the challenging activity in hydroxylation reaction of phenol. Probably, this first report on the use of Zr-PILC in hydroxylation of phenol and its preparation by employing ultrasonication technique may attract great attention in the catalysis area of academic and industrial importance.

Key words: Montmorillonite, Ultrasonication, Zr- Pillared Clay, Hydroxylation of Phenol, Zr-PILC

INTRODUCTION

Pillared clays have now led to the development of new classes of selective heterogeneous catalysts [Molina et al., 1994; Bartley, 1988; Pinnavaia et al., 1985; Burch et al., 1986] for cracking, acid catalyzed and hydroisomerization reactions. Pillared clays intercalated with Al, Zr, Ga, Si, Fe, Cr, Ti oxides have been well documented [Zurita et al., 1996; Vaughan et al., 1979]. Two preparation methods have been reported in the open literature to obtain Zr-pillared clays: 1) ion exchange by aging suspension of clay in fresh $ZrOCl_2$ solution and 2) by refluxing $ZrOCl_2$ before and after addition to the clay suspension [Farfan-Torres et al., 1992]. The main drawback of these methods is the longer preparation time. Therefore, efforts were made to reduce the intercalation period by using a novel route, which comprises the use of ultrasonication (u.s.) technique for preparation of Zr-pillared clays.

Hydroxylation of phenol is one of the commercially important reactions for production of dihydroxybenzenes. TS-1 is one of the best-known heterogeneous catalysts [Notari et al., 1989] for hydroxylation of phenol to hydroquinone and catechol. Catalytic hydroxylation of phenol over various solid acids had been reported earlier [Allian et al., 1993]. It was thought interesting to investigate the catalytic activity of the Zr-PILC clay as a catalyst for the hydroxylation of phenol as the preparation method, and suitable candidature of Zr-PILC clay may prove a better eco-friendly and cost-effective process. In view of this, we are reporting for the first time the hydroxylation of phenol over Zr-PILC in the present communication.

While employing the ultrasonication technique, we also studied, and discussed in this paper, the influence of different preparation parameters such as pH, concentration of zirconium oxychloride and aging time after u.s. treatment, on the structural, textural and catalytic properties of Zr-pillared montmorillonite. The structural and textural properties of zirconia-pillared clays have been investigated by using XRD, FTIR spectra of adsorbed pyridine, XPS, low temperature N_2 adsorption and chemical analysis by XRF techniques. The catalytic activity of Zr-pillared clays in hydroxylation of phenol was evaluated under an identical set of experimental conditions.

EXPERIMENTAL

Na-montmorillonite (Kunipia-F, Kunimine Industrial Company) with structural formula $(Na_{0.35}K_{0.01}Ca_{0.02})(Si_{3.89}Al_{0.11})(Al_{1.60}Fe_{0.08}Mg_{0.32})O_{10}(OH)_2 \cdot nH_2O$ and a cation exchange capacity (CEC) 1.28 meq·g^{-1}, was used for zirconia pillaring. The clay was used without further purification, sieving or refining. The solid $ZrOCl_2 \cdot 8H_2O$ supplied by LOBA Chemie Pvt. Ltd. (99%), India, was used for preparing the pillaring agent and ZrO_2.

In a typical preparation procedure for obtaining Zr-pillared clay, 1.0 g of clay was added slowly to 133 ml of 0.06 M aqueous solution of $ZrOCl_2 \cdot 8H_2O$ having pH 2.0 with constant stirring. Then the mixture was immediately subjected to ultrasonication (Sheshin, Japan; operating frequency 50 kHz) for 20 min at ambient temperature. The aging after ultrasonication and/or use of 0.1 M Na_2CO_3

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Table 1. Preparation conditions and product characterization of zirconia-pillared clays

No.	Sample	Preparation parameters				Product characterization		
		Zr_4/clay (meq·g^{-1})	Conc. of $ZrOCl_2 \cdot 8H_2O$ (M)	Aging period after ultrasonication (h)	pH	% ZrO_2	d001 (nm)	BET surface area ($m^2 g^{-1}$)
1.	ZrP_a	1.6	0.10	0.0	2.8	19.57	1.70	272
2.	ZrP_b	1.6	0.06	0.0	2.8	16.39	1.70	244
3.	ZrP_c	1.6	0.06	4.0	2.8	14.75	2.00	230
4.	ZrP_d	1.6	0.06	4.0	2.0	13.00	1.60	214
5.	ZrO_2	-	-	-	3.0	100.00	-	-
6.	Clay	-	-	-	-	-	1.16	22

solution for adjusting the pH at appropriate stages were employed wherever required. The product was then separated by centrifuge and washed with distilled water till the effluent was free from chloride ions. The material was then air dried overnight at 333 K followed by the calcination at 723 K for 4 h. All calcined Zr-pillared clay samples were treated with 1 M ammonium acetate solution to remove alkali metal ions, if any, and then calcined again at 623 K in air for 4 h. Similarly, pure ZrO_2 was prepared by conventional precipitation technique using aqueous solution of $ZrOCl_2 \cdot 8H_2O$ and aqueous ammonia. The precipitate along with its mother liquor was subjected to the similar ultrasonic treatment. The precipitate was then filtered, washed and dried in air oven maintained at 383 K for 6 h. It was further calcined at 723 K for 4 h.

The zirconia content in the pillared clays was determined by using a wavelength dispersive X-ray fluorescence spectrometer, XRF model, Rigaku, 3070E. To average out the matrix effect of co-existing elements on the analysis of zirconium, standards for XRF were prepared by the addition of appropriate amounts of ZrO_2 (Aldrich, 99.99%) to the clay itself. A regression calibration curve made for zirconium was used for the quantitative estimation of zirconium in the pillared clay.

X-ray powder diffraction patterns of the clay and the calcined pillared samples were recorded by using an X-ray diffractometer (Rigaku, D-max III VC) with Ni filtered monochromatic CuKα radiation (1.5404 Å). Thermal behaviour of the clay and the pillared clay samples was compared by recording DTA/TG thermograms in air (Setaram TG/DTA, 92 model) at a heating rate of 10 K/min. The BET surface area of the samples was determined by N_2 adsorption at 77 K by using Omnisorp 100 CX (Coulter) equipment after degassing the sample at 423 K for 8 h. The FTIR measurements (Nicolet 60 SXB) were carried out by using a self-supported wafer. The samples were degassed at 673 K under reduced pressure (10^{-4} Torr) for 2 h prior to contacting with pyridine vapours for 5 min at 373 K. The IR spectra were recorded after degassing at 373, 473, 573 and 673 K for 1 h and were normalized to constant concentration 10 mg cm^{-2} of the samples. X-ray photoelectron spectra were recorded on V.G. Scientific (UK) ESCA 3000 by using Mg Kα (1253.6 eV) as the excitation source. The binding energies measured in the XPS analysis were corrected for specimen charging by referencing the C_{1s} level to 285.0 eV.

Phenol hydroxylation reaction was carried out in a 100 ml capacity, two-necked glass flask, fitted with a mechanical stirrer, condenser, feed pump and a septum. The temperature of the reaction vessel was maintained by using an oil bath. In a standard run, 1 g phenol, 10 g solvent and 0.1 g catalyst were placed in the reaction flask. Before H_2O_2 (30% aqueous solution) was added through the feed pump, the desired temperature of the flask was maintained. The catalytic activities were evaluated by the yield of catechol and hydroquinone periodically, removing aliquots of reactant mixture by using a microlitre syringe and analyzed by GC (HP 5880A) equipped with a capillary column (HP 1; 50 m×0.2 mm) and a flame ionization detector.

RESULTS AND DISCUSSION

The preparation parameters for four different pillared clays and pure ZrO_2 sample, their compositional and textural characteristics are summarized along with their designation in Table 1. For all samples, the ultrasonic agitation time (20 min) was kept constant and they were calcined at 723 K for 4 h in air.

Fig. 1 illustrates the powder XRD profiles of the calcined pillared clay samples and the original clay in the 2θ range, 3.0 to 8.5°. The XRD pattern of the original clay with d001 reflection shows basal spacing of 1.16 nm (profile 5). All calcined pillared clay samples have shown the d001 reflection for basal spacing at lower 2θ values in the range of 4.3-5.6°. The d001 values for each sample are presented in Table 1. The change in the position of 2θ seems to be associated with the preparation conditions. The change in the position of 2θ as a function of each preparation parameter is dis-

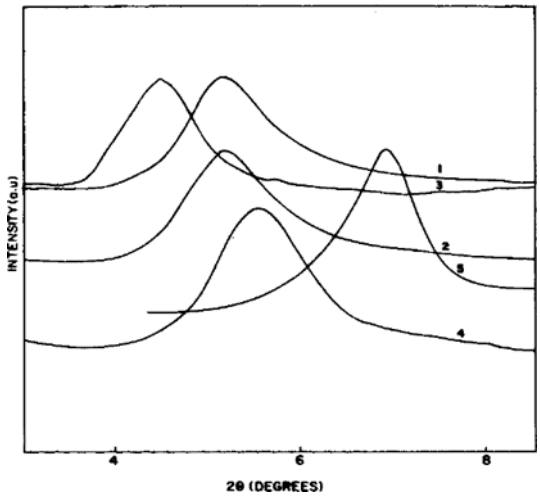

Fig. 1. XRD patterns of clay and pillared clays (1) ZrP_a, (2) ZrP_b, (3) ZrP_c, (4) ZrP_d and (5) clay.

cussed in the following appropriate section. The salient feature of this figure is the absence of the diffraction peak ~7° in all pillared clay samples attributed to the d001 reflection found in the original clay. This suggests that there is not any contribution due to unpillared portion in the product obtained. Mixed species containing zirconia-pillared clay and non-pillared clay were reported [Suzuki et al., 1991] as a result of conventional ion exchange of montmorillonite with CEC in the range of 0.51 to 0.66 meq·g^{-1}. Moreno et al. [Moreno et al., 1999] have reported heterogeneous pillaring in Zr-PILC prepared by conventional ion exchange. Thus, the ultrasonic technique provides a novel route to overcome the drawback of the conventional ion exchange method as far as successful pillaring to maximum extent leaving no possibility for the presence of nonpillared portion is concerned.

1. Influence of Preparation Parameters

Attempts were made to investigate the influence of various preparation parameters on the textural and compositional characteristics of the product by employing the ultrasonication technique.

1-1. Influence of pH

In order to examine the effect of pH on the product quality, ZrP_c and ZrP_d were prepared at different pH (2.8 and 2.0, respectively), keeping all other preparation conditions almost identical. The runs were also conducted at different pH viz. 1.8, 1.9 and 3.0. It was observed that below pH 2.0, the structure of the clay was found to be collapsed due to higher acidity. On the contrary, the clay structure was found to remain unaltered, but the precipitation of Zr hydroxide occurred from the pillaring solution at higher pH (>2.8). It is evident from Table 1 that ZrP_c has exhibited larger basal spacing (2.0 nm), increased BET surface area (230 m^2 g^{-1}) and high zirconia content (14.75%) as compared to ZrP_d. This may be attributed to the formation of bigger size polymer of the hydrolyzed species at higher pH due to the hydrolysis of the salt, thereby resulting in larger basal spacing and higher zirconia content as well. The optimum pH of the pillaring agent for successful pillaring was found to be in between 2.0 to 2.8.

1-2. Influence of Concentration of Pillaring Agent

In the earlier report [Bartley, 1988], the zirconyl chloride solution was used in the preparations in the range of 0.1 to 0.33 M without using ultrasonication. Since pH of the solution varies with the change in the concentration and hence influences the degree of polymerization to different extent, an attempt was made in the present studies to investigate the quality of the product as a function of concentration of solution keeping identical pH by using ultrasonic technique. The results obtained were totally different compared to that of the earlier report wherein ultrasonication and adjustment in pH was not employed. Keeping Zr_4/clay ratio, pH and ultrasonication period constant, ZrP_a and ZrP_b were obtained by using the concentration of pillaring agent 0.10 M and 0.06 M, respectively. It is interesting to note that the identical d001 basal spacing was obtained for both the samples ZrP_a and ZrP_b (refer Table 1). The incorporation of zirconia in the clay was also found to be increased with the increase in the concentration of the pillaring agent. This can be attributed partly to higher population of identical polyhydroxy-cationic species in 0.1 M solution than in 0.06 M solution. This is well reflected in an increase in BET surface area for ZrP_a (272 m^2 g^{-1}) as compared to that of ZrP_b (244 m^2 g^{-1}). Probably, instead of increasing pillar height, the increase in number of pillars might have resulted by the combined effect of increased concentration of the pillaring agent at the same pH level and the same ultrasonic treatment.

1-3. Influence of Aging after Ultrasonication

It is well established from the above studies that ultrasonic treatment during the preparation of Zr-pillared clay forms the basis of one of the key controlling parameters. Furthermore, the aging after this ultrasonic treatment was considered as yet another preparation parameter and studied systematically in the present studies. ZrP_c and ZrP_b were obtained by keeping all the preparation parameters constant except a parameter viz. aging after ultrasonication. ZrP_c and ZrP_b were prepared with and without aging, respectively. The basal spacing of d001 reflection for ZrP_b was found to be lower (1.7 nm) than that of ZrP_c (2.0 nm). Surprisingly, the zirconia content was found to decrease upon aging. In spite of having lower zirconia content, the increase in the basal spacing in case of ZrP_c suggested that aging seems to favour the degree of polymerization. Similar results were reported [Clearfield et al., 1956] while investigating the influence of temperature and they were correlated with the increased rate of hydrolysis at higher temperature. On the contrary, a diffuse and broad XRD profile of the pillared clays has been observed when subjected to an aging in the absence of ultrasonication [Toranzo et al., 1998] at lower pH condition. However, a well-defined d001 reflection was observed in the present studies. Thus, the unique feature of ultrasonication when coupled with post aging is the uniform distribution of polyhydroxy cations with higher degree of polymerization.

Even though all the above parameters were found to contribute significantly in governing the textural and compositional characteristics of the product, it is believed that all of them seem to have a substantial interplay between them.

The dimensions of Zr tetramer reported [Cool et al., 1998] are 0.89 nm in width and length and 0.58 nm in thickness. The possibility of condensation of tetramers is by two ways, either length/breadth wise or thicknesswise. Taking into account the 0.96 nm thickness of silicate layer of montmorillonite, the interlayer free space of Zr-pillared clays (ZrP_d, ZrP_a, ZrP_b) with 1.6 and 1.7 nm basal spacings were estimated to a value of 0.64 and 0.74 nm, respectively. The increase in interlayer space by 0.69±0.05 nm can be considered justifiable due to fixation of a single Zr tetramer lying flat. The interlayer free space of Zr-pillared clay (ZrP_c) with 2.0 nm basal spacing was estimated to be a value of 1.04 nm. The increase in interlayer space by 1.04 nm can be considered as a close agreement with the fixation of either double layer flat lying Zr tetramers or a single layer of Zr tetramer standing normal to the silicate layer. However, the influence of preparation parameters such as aging after the ultrasonication and higher pH condition are believed to be operative in fixation of double layer flat lying Zr tetramers in ZrP_c.

ZrP_c sample was selected as a representative sample for further characterization by TG/DTA, FTIR spectra of adsorbed pyridine and XPS studies.

2. Thermal Behaviour by TG/DTA

The thermal analysis results of ZrP_c and clay are presented in Fig. 2A and 2B, respectively. The DTA and TG curves of ZrP_c have revealed the three stages of weight loss due to dehydration-dehydroxylation processes.

(1) Room temperature - 531 K: A weight loss of 17.23% was ob-

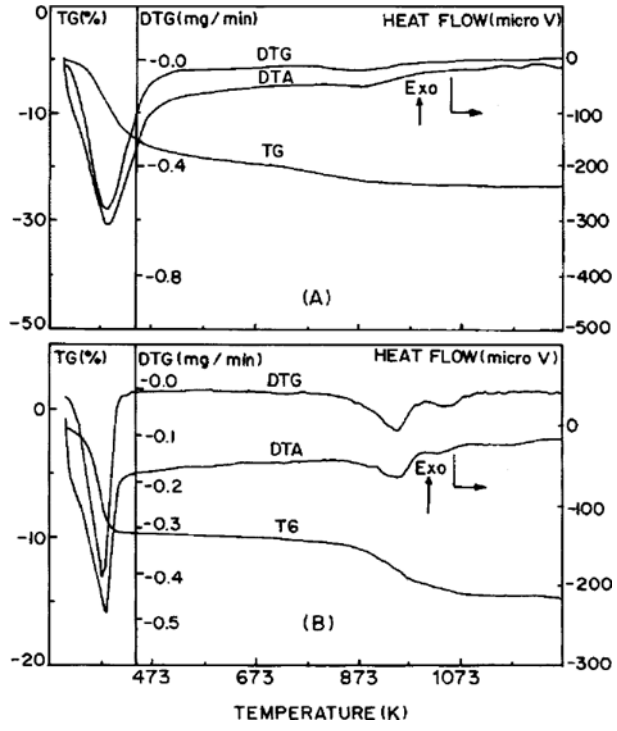

Fig. 2. Thermograms of (A) ZrP_c and (B) clay.

served in this stage which can be attributed [Pinnavaia et al., 1984] to the dehydration of water molecules loosely adsorbed in the interlayer spaces and on the external surface. The DTA profile has exhibited a broad endotherm, the minima of which was found to appear at 390 K. When compared with the clay, the dehydration process was found to complete at higher temperature.

(2) 531-832 K: In the next stage, a weight loss of 3.45% was observed which can be attributed to dehydration of water molecules strongly associated with hydroxy-zirconium cations and dehydroxylation of hydroxy-zirconium. Fig. 2B illustrates that no weight loss has occurred up to 819 K in clay sample as there is no contribution due to hydroxy-zirconium cations.

(3) 832-983 K: In the third stage, the weight loss observed was 2.07%. This can be attributed to the decomposition of the silicate structure by dehydroxylation [Burch et al., 1986]. The clay has shown structure collapse at ~793 K, whereas pillaring has shown enhanced thermal stability up to 832 K.

2. Nature of Acid Sites by FTIR Spectra of Adsorbed Pyridine

The infrared spectra of pyridine adsorbed on the clay and pillared clay (ZrP_c) after evacuation at 373, 473, 573 and 673 K (curves 1, 2, 3, 4 respectively) are shown in Fig. 3A and 3B, respectively. The spectrum of the clay has exhibited a very weak band at ~1,550 cm^{-1} characteristic of pyridinium ion due to Bronsted acid sites arising from hydration spheres of cations and hydroxyl groups at the edges [Lambert et al., 1997]. The band at ~1,550 cm^{-1} in the spectrum of ZrP_c is strong even after degassing at 673 K. This indicates strong acidic character of the Bronsted acid sites in the pillared clay. These may arise from the hydroxyl groups attached to Zr and the structural hydroxyl groups in the pillared clay [Farfan-Torres et al., 1992). It is reported that during the calcination process, ion exchanged Zr polyhydroxy-cation is converted to hydrated ZrO_2 pillars [Farfan-Torres et al., 1992] and hydroxyl groups attached to Al/Mg are formed [Cool et al., 1998]. However, according to Cool et al. [Cool et al., 1998] aluminol and magnesol groups do not possess strong Bronsted acid character. Therefore, it may be inferred that the strong Bronsted acidity observed may be associated with the hydroxyl groups in hydrated zirconia. The 1,450 cm^{-1} band due to pyridine co-ordinately bound to Lewis acid sites [Morterra et al., 1990] of the clay is very weak. This may arise due to terminal Al ions in the clay. This band in the pillared clay is very strong indicating the presence of Lewis acid sites due to zirconia pillars. However, the effect of temperature on the intensity of this band is quite pronounced, suggesting the weaker nature of the Lewis acid sites when compared to the Bronsted acid sites.

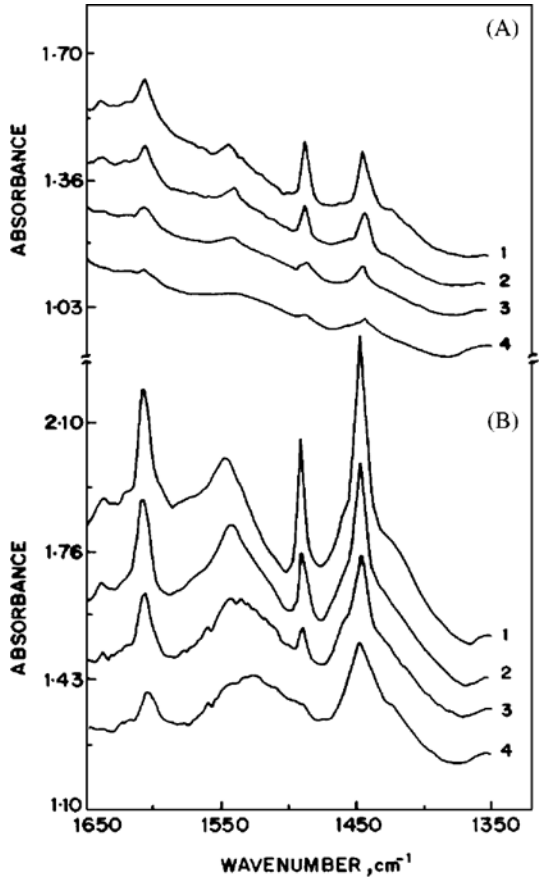

Fig. 3. FTIR spectra of pyridine adsorbed on (A) clay and (B) ZrP_c heated at different temperatures: (1) 373 K, (2) 473 K, (3) 573 K and (4) 673 K.

3. Environment of Zirconium by XPS Studies

Fig. 4 depicts the XPS spectra of O_{1s} and Zr_{3d} levels in ZrO_2 (curves A, A', respectively) and Zr-pillared clay sample, ZrP_c (curves B, B', respectively) The binding energy values of these levels were found useful to obtain the information on the environment of zirconium in ZrP_c. As evident from Fig. 4A, ZrO_2 has exhibited a single symmetric peak of O_{1s} at 530.3 eV. The deconvoluted spectra of O_{1s} level of ZrP_c (Fig. 4B) show two distinct peaks. A main peak which has appeared at 532.8 eV can be attributed [Borade et al., 1990] to silicate lattice oxygen. Another peak appeared at 529.7 eV in ZrP_c which may not be associated with the extra lattice oxidic zirconium species alone. The XPS spectra of Zr_{3d} level of both the

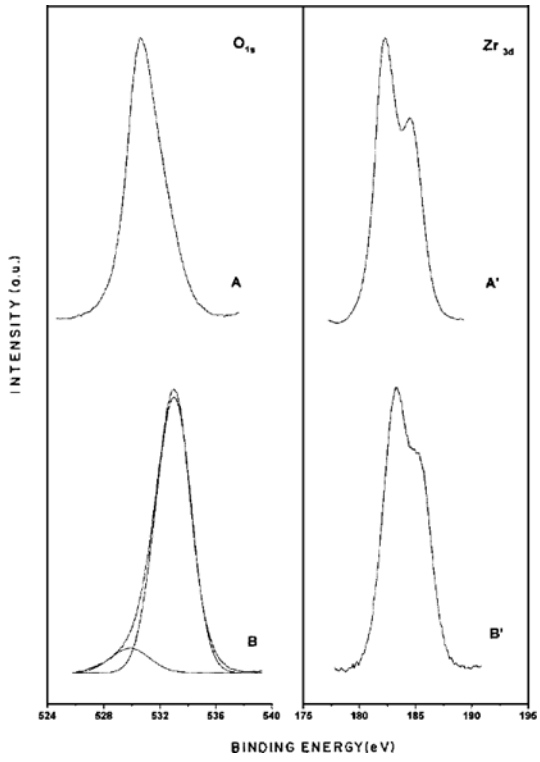

Fig. 4. XPS spectra of O_{1S} levels of (A) ZrO_2, (B) ZrP_c and of Zr_{3d} levels of (A') ZrO_2, (B') ZrP_c samples.

samples have shown a similar pattern except the difference of 0.8 eV in the B.E. of Zr_{3d} levels in ZrP_c as compared to ZrO_2. This indicates that the environment of zirconium in ZrP_c is not exactly the same as the environment of zirconium in ZrO_2. The binding energy (183 eV) of $Zr_{3d}^{5/2}$ level in ZrP_c was found in close agreement with B.E. (182.7 eV) of Zr attached to -OH groups [Wagner et al., 1978]. Therefore, it can be concluded that the surface of ZrP_c is enriched in hydroxy zirconium species. The thermal analysis data and results on pyridine adsorbed FTIR also partly support the findings in relation to presence of -OH groups attached to Zr.

4. Selective Oxidation of Phenol

Selective oxidation efficiency of Zr-pillared clays obtained by employing ultrasonication was evaluated in hydroxylation of phenol reaction that is one of the commercially important reactions. The better catalytic performance by introducing Zr in the pillar configuration in the clay may prove a potential catalyst as far as cost effectiveness and healthy environmental protection are concerned. The Zr-pillared clay samples, ZrO_2 prepared by using u.s. technique and clay samples were tested for hydroxylation of phenol reaction. The results obtained are summarized in Table 2. It is clearly evident from the tabulated data that introducing Zr in the pillar configuration in the clay enhances not only phenol conversion, H_2O_2 selectivity but also the contribution of catechol in the product. The original clay and pure ZrO_2 prepared by using u.s. technique followed by calcination at the same temperature as the Zr-pillared clays, have exhibited very poor catalytic activity. These results indicated the demand of large space, which forms one of the basic necessities for phenol hydroxylation reaction. In addition, the increased acidic character in the Zr-pillared clays was found to favor the phenol hydroxylation process. Furthermore, both the zirconia content and specific BET surface area have found a remarkable influence on the yield (conversion X fraction in product) of catechol. ZrP_a sample has not only shown highest catechol yield but also higher phenol conversion and H_2O_2 selectivity in the present studies. It is surprising to note that, the turnover number in all the Zr-pillared clays was found nearly constant, suggesting the identical active site density. Thus, it seems that the increase in the zirconium content alone does not necessarily increase the active sites of required strength in a given surface area and hence may perform differently under identical set of experimental conditions. Moreover, the initiation of phenol hydroxylation reaction has been reported [Germin et al., 1996] as a result of an electrophilic aromatic substitution catalysed by the acid function of the catalyst.

ZrP_a sample has shown higher catechol yield, phenol conver-

Table 2. Hydroxylation of phenol[a] over clay and zirconia-pillared clays

No.	Catalyst	%ZrO_2 incorporated	TON*	Phenol conversion[b] wt%	H_2O_2 selectivity[c] mole %	% Product distribution		
						CAT[e]	HQ	PBQ[f]
1.	ZrP_a	19.57	10.0	45.2	40.3	49.1	47.1	3.8
2.	ZrP_b	16.39	9.3	35.2	32.3	51.0	42.4	6.6
3.	ZrP_c	14.75	10.6	35.8	31.1	54.3	44.6	1.1
4.	ZrP_d	13.00	10.5	31.3	25.6	51.1	36.6	12.3
5.	ZrO_2	100.00	0.0	0.1	0.2	0.0	100.0	0.0
7.	Clay	-	-	1.0	1.6	15.3	84.8	-

[a]Reaction conditions: Catalyst=0.1 g; phenol/H_2O_2 (mole)=3.0; H_2O_2=30% aqueous solution; Temp.=353 K; Solvent=water (10 g); Reaction time=12 h

*Turn over number=moles of phenol converted per mole of Zr atom

[b]Phenol converted for formation of dihydroxy benzenes (DHB) and quinones (HQ)

[c]H_2O_2 Selectivity $= \frac{H_2O_2 \text{(moles) consumed in formation of DHB and quinones}}{\text{Total } H_2O_2 \text{(moles) added}} \times 100$

[e]Catechol

[f]p-benzoquinone

sion and also H_2O_2 selectivity as compared to ZrP_c. As discussed earlier, if it is assumed that there exists an arrangement of fitting a single and double flat lying Zr tetramers into the interlayer space in ZrP_a and ZrP_c respectively, it is logical to conclude that flat lying single Zr tetramer in between silicate layers enhances catechol yield, phenol conversion and H_2O_2 selectivity as well. Studies on zirconium containing mesoporous silicas have also reported [Tuel et al., 1996] that the dispersion of Zr atoms is a necessary condition for the oxidation reactions in liquid phase. Similarly, isomorphous substitution of Si^{4+} by Zr^{4+} in pentasil framework has been reported [Dongare et al., 1991] to be active for hydroxylation of aromatics, whereas total inactivity has been exhibited by pure ZrO_2 under the same set of experimental conditions. Thus, it can be believed that Zr-pillared clay prepared by using ultrasonic technique with no aging may be operative in the uniform dispersion of flat lying single Zr tetramer in between silicate layers at high pH and high concentration of pillaring agent conditions. The controlled calcination of such clays resulting in acidic sites with a strength required for hydroxylation of phenol may prove a potential catalyst.

CONCLUSION

Zr-PILC with uniform large interlayer basal spacings (1.6-2.0 nm) was successfully prepared with reduced preparation time by ultrasonication. The ultrasonic technique was found to provide a novel route to overcoming the drawback of the conventional ion exchange method as far as successful pillaring to maximum extent leaving no possibility for the presence of nonpillared portion in the product is concerned. The optimum pH of the pillaring agent for successful pillaring was found to be in range of 2.0-2.8. The increase in BET surface area and zirconia content is favored at higher pH irrespective of aging after u.s. treatment. However, without being subjected to aging after u.s., the change in the concentration of pillaring agent solution has not shown a considerable change in the d001 spacing in spite of yielding increased zirconia content and BET surface area. Zirconia pillars were found to introduce both the Bronsted and Lewis acid sites in Zr-pillared clays. However, the strength of former is found to be higher than that of the latter. Hydroxyl groups attached to Zr form the basis of enhanced Bronsted acidity. XPS data showed that the surface of the pillared clays is enriched with hydroxy zirconium species.

Zr-PILC efficiently catalyzes the hydroxylation of phenol to catechol and hydroquinone with H_2O_2. Higher Zr content and flat lying single Zr tetramer in between silicate layers enhances catechol yield, phenol conversion and H_2O_2 selectivity as well due to better utilization of H_2O_2 and higher conversion level. Thus Zr-PILC may prove a potential candidate catalyzing oxidation of phenol from the viewpoint of cost effectiveness and healthy environmental protection.

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