Jointly published by
Akadémiai Kiadó, Budapest
and Springer, Dordrecht

React.Kinet.Catal.Lett.
Vol. 85, No. 1, 37-44
(2005)

RKCL4628

PILLARED CLAYS AS EFFICIENT CATALYSTS FOR CYCLOHEXANOL OXIDATION

Kurian Manju and Sankaran Sugunan[*]
Department of Applied Chemistry,
Cochin University of Science and Technology, Kochi-22, India

Received June 2, 2004
Accepted July 27, 2004

Abstract

Iron, aluminium and mixed iron aluminium pillared clays were prepared by partial hydrolysis method and doped with 10% V and Mo. The samples were characterized by XRD, FTIR and surface area and pore volume measurements. Oxidation of cyclohexanol with hydrogen peroxide was done as probe reaction to test catalytic activity. Iron pillared systems exhibited maximum activity. The effects of various reaction variables on the reaction were studied.

Keywords: Pillared clays, catalysis, cyclohexanol, oxidation, cyclohexanone

---

INTRODUCTION

Pillared clays constitute one of the widely studied families among the new group of microporous materials developed by molecular engineering. These solids also known as crosslinked clays or pillar interlayered clays (PILCs) are obtained by exchanging the interlayered cations of layered clays with bulky inorganic polyoxocations, followed by calcination. The intercalated polycations increase the basal spacing of the clays and upon heating, are converted to metal oxide clusters by dehydration and dehydroxylation. As a result, a two-dimensional porous network is generated. The maintenance of a well-defined porous network up to relatively high temperatures along with the presence of acid sites immediately suggest potential catalytic applications for these solids [1-4].

---

*Corresponding author. E-mail: ssg@cusat.ac.in

0133-1736/2005/US$ 20.00.

Many interesting results have been obtained for processes of significant practical importance; hydroxylation of phenol by Cu-doped Al_2O_3-PILCs [5], selective catalytic reduction of NO with NH_3 over V_2O_5 doped TiO_2 PILCs [6] and selective catalytic reduction of NO by ethylene in presence of O_2 by Cu-doped TiO_2 PILCs [7].

In this paper, we report the oxidation of cyclohexanol with hydrogen peroxide over V and Mo doped Al, Fe and Fe-Al mixed pillared clays. The results obtained for various catalysts and the effect of reaction variables on catalyst performance is also included. The catalysts were characterised by X-ray diffraction, FTIR spectroscopy, surface area and pore volume measurements.

EXPERIMENTAL

The pillared clays were prepared by partial hydrolysis method. 0.1 M solution of the corresponding nitrate was hydrolyzed by dropwise addition of 0.3 M Na_2CO_3 solution under vigorous stirring. The pillaring solution was aged for 24 h, added to previously swollen clay and stirred for 25 hours [OH/M ratio of 2 and M/clay ratio of 20 mmol/g clay]. The clay after exchange was washed several times, dried in air oven at 110°C and calcined for 6 h at 450°C. Calculated amounts (10 wt.%) of ammonium salt of V and Mo was added and refluxed under stirring using acetone as solvent. Acetone was dried off at room temperature, dried at 80°C and calcined at 300°C overnight. The catalyst samples prepared are denoted as M/PM PILC where M is incorporated transition metal and PM is pillaring metal.

Surface area and pore volume measurements were done in a Micromeritics Gemini 2360 analyser. XRD profiles were recorded with a Rigaku D Max C X-ray diffractometer using Cu-Kα radiation (λ = 1.5406 Å) by powder XRD method. FTIR spectra were recorded in a Shimadzu spectrophotometer (DR 8001) using KBr pellet method. The reactions were carried out in a closed 50 mL glass reactor fitted with a reflux condenser. In a typical run, appropriate amounts of cyclohexanol, solvent, H_2O_2 (30%) and catalyst were allowed to react at specified temperatures under magnetic stirring. Reaction mixture was withdrawn periodically and analysed using Chemito 8610 GC equipped with Carbowax column and FID. The conversion (%) is the total amount of cyclohexanol transformed into products.

RESULTS AND DISCUSSION

Surface area and pore volume measurements

Table 1

Surface area and pore volume measurements

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)
Fe PILC	179.6	0.1503
V/Fe PILC	53.7	0.0493
Mo/Fe PILC	46.8	0.0396
Fe-Al PILC	128.9	0.1113
V/Fe-Al PILC	43.3	0.0371
Mo/Fe-Al PILC	37.2	0.0312
Al PILC	113.4	0.0912
V/Al PILC	39.6	0.0323
Mo/Al PILC	29.8	0.0249

Table 1 shows the BET surface area and pore volume of the prepared samples. Pillaring increased the surface area of the parent clay significantly. Iron pillared samples exhibited maximum surface area. Incorporation of transition metals was found to have a diminishing effect on the surface area of the samples. This is indicative of the accumulation of the incorporated metals in the pores of the pillared clay structure. Pore volume measurements also support this observation.

X-ray diffraction

The d spacing of the (001) plane in the parent clay increased drastically as a result of treatment with the pillaring solution followed by subsequent calcination. Thus XRD profile was indicative of effective pillaring (Fig. 1). The d spacing obtained for the different pillars are given in Table 2. Fe pillaring was the most effective in propping apart the clay layers. After doping with the transition metals, the basal spacing remains the same.

Table 2

Basal spacing for pillared clays

Catalyst	Basal spacing (Å)
Fe PILC	19.2
Fe-Al PILC	17.7
Al PILC	17.9

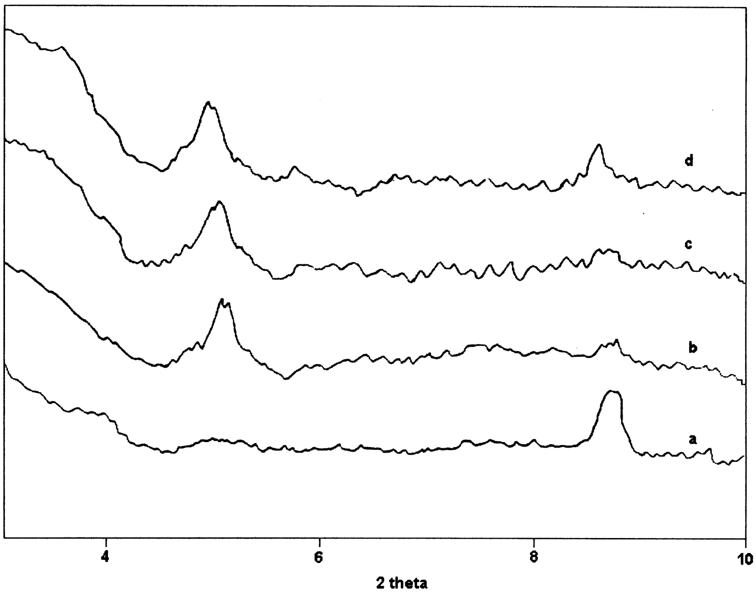

Fig. 1. XRD patterns of the pillared systems
a) montmorillonite; b) Al PILC; c) Fe PILC; d) Fe-Al PILC

FTIR spectroscopy

Figure 2 shows the FTIR spectrum of the parent, pillared and transition metal doped montmorillonites. The parent montmorillonite showed two bands on the OH stretching region; a band at 3740 cm^{-1} attributable to silanol groups of the external layer and a broader band at 3650 cm^{-1} due to Al_2OH group of the octahedral layer. In the pillared samples, the intensity of the band at 3740 cm^{-1} increased with respect to the other. This can be interpreted as an effect of pillaring. The IR spectra in the fingerprint region were characterised by absorptions at 1200-1000 cm^{-1} (asymmetric stretching vibrations of SiO_2 tetrahedra), a doublet around 800 cm^{-1} (stretching vibrations of Al^{IV} tetrahedra) and absorptions at 526-471 cm^{-1} (bending Si-O vibrations). The framework vibrations contain information about the structural characteristics of the material and their preservation after thermal treatments can be considered as a proof of the structural stability on pillaring.

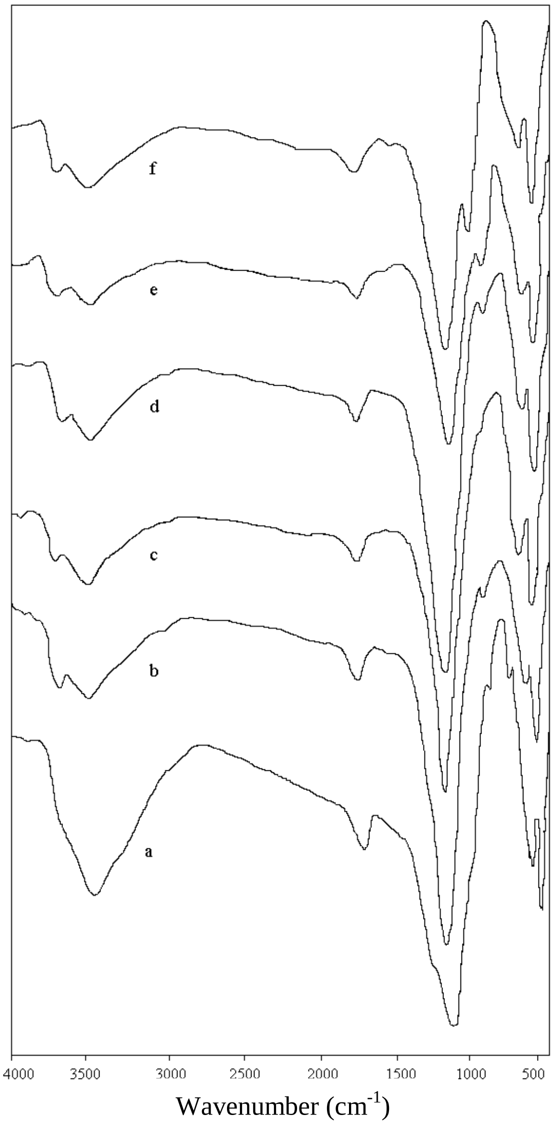

Fig. 2. FTIR spectra of pillared and transition metal doped pillared clays
a) montmorillonite; b) Al PILC; c) Fe PILC; d) Fe-Al PILC; e) V/ Fe PILC; f) Mo/Fe PILC

Catalytic activity of various systems

The catalytic activities of the systems prepared were tested for the oxidation of cyclohexanol (Table 3). V-doped pillared clays clearly show high activity towards cyclohexanol oxidation. The data in Table 4 also show that the reaction was much faster, when the catalyst contained iron. The oxidation activity is least for Al pillared clays as expected.

Table 3

Catalytic activity of various samples towards cyclohexanol oxidation

Catalyst	Conversion (%)
FePILC	10.58
V/FePILC	23.08
Mo/FePILC	15.45
Fe-AlPILC	4.58
V/Fe-AlPILC	14.90
Mo/Fe-AlPILC	7.31
AlPILC	4.59
V/AlPILC	15.79
Mo/AlPILC	7.07

Effect of reaction variables

The reaction was studied extensively using V/Fe PILC as reference (Table 4). A gradual increase in reaction rate was observed with increase in temperature up to 80°C after which, the activity decreases. The suppression of reaction at higher temperatures can be attributed to decomposition of hydrogen peroxide [8]. A linear increase in reaction rate with time was observed up to 90 min after which, the rate drops. The decrease in reaction rate at longer reaction time can be attributed to poisoning of surface sites by product [9]. Alcohol oxidations are sensitive to nature of solvent [10]. Acetonitrile was found to be the best solvent for cyclohexanol oxidation over pillared clays. With other solvents, catalytic activity was proportional to polarity of solvent. Increase in surface sites explains the increase in rate with catalyst concentration. After an optimum value, the rate levels off indicating that only a small amount of catalyst is needed. As the amount of hydrogen peroxide increases, steady increase in reaction rate was observed. After the optimum equivolume ratio, the reaction attains a steady state. This can be attributed to self decomposition of the oxidant at higher concentrations.

Table 4

Effect of reaction variables

Reaction variable	Conversion (%)
Temperature (°C)	
60	7.06
70	18.2
80	23.08
90	12.7
Time (min)	
30	14.11
60	17.87
90	23.08
120	17.48
Solvent	
Acetonitrile	23.08
Water	18.93
Dioxan	10.3
Acetone	14.15
Catalyst (g)	
0.5	15.29
0.75	17.19
1.0	23.08
1.25	23.15
Hydrogen peroxide (mL)	
1	3.57
3	8.22
5	23.08
7	22.82

CONCLUSIONS

Exchange of montmorillonite with partially hydrolyzed solutions of Fe and Al followed by calcination produced stable pillared clays. X-ray diffraction patterns and FTIR spectra indicated effective pillaring. Iron pillared catalysts were effective for the oxidation of cyclohexanol. A systematic study of the reaction variables showed that the reaction had an optimum temperature, time, solvent, peroxide to cyclohexanol ratio and catalyst concentration.

Acknowledgements. Our thanks are due to Dr. Winny Varghese, Principal and Dr. K.B Sherly, Department of Chemistry, M.A College, Kothamangalam, for providing facilities for part of this work. K. Manju thanks CSIR, New Delhi for the award of a Junior Research Fellowship.

REFERENCES

1. T.J. Pinnavia: *Science.*, **220,** (1983).
2. F. Figueras: *Catal. Rev. Sci. Eng.*, **30**, 457 (1988).
3. J.T. Kloprogge: *J. Por. Mat.*, **5**, 5 (1998).
4. A. Gil, L.M. Gandia, M.A. Vicente: *Catal. Rev. Sci. Eng.*, **42,** 145 (2000).
5. K. Bahranowski, M. Gazior, A. Kielski, J. Podobinski, E.M. Serwicka, L.A. Vastikian, K. Wodnicka: *Clays. Clay Min.*, **46,** 98 (1998).
6. R.T. Yang, R.Q. Long: *Appl. Catal. B.*, **24,** 13 (2000).
7. R.T. Yang, N. Tharappiwattananon, R.Q. *Long: Appl. Catal. B.*, **19**, 289 (1998).
8. R. Yu, F. Xiao, D. Wang, G. Pang, S. Feng, S. Qiu, R. Xu: *Catal. Lett.*, **49**, 49 (1997).
9. C.B. Lui, Z. Zhang, X.G. Yang, Y. Wu: *J. Chem. Soc. Commun.*, 1019 (1996).
10. R. Neumann, M. Levin-Elad: *Appl. Catal. A.*, **85**, 1122 (1995).