

Note

Liquid phase oxidation of saturated nitrogen-containing heterocyclics over modified MCM-41 molecular sieves[†]

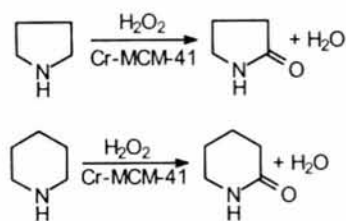
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Received 13 January 1999; accepted (revised) 15 June 1999

For the first time, the liquid phase oxidation reactions of saturated N-heterocyclics like piperidine and pyrrolidine to piperidone and pyrrolidone have been carried out over modified MCM-41 molecular sieves with 30-55% yield and >80% selectivity.

A number of liquid phase oxidation reactions over redox molecular sieves have been reported¹⁻³. We have carried out liquid phase oxidation of cyclohexene⁴, anthracene to 1,4-anthraquinone, stilbene to stilbene-oxide⁵, 2-picoly alcohol to pyridine-2-carboxaldehyde⁶ and 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone⁷ over redox/modified molecular sieves, in the presence of an oxidant like H₂O₂. In this note, we report the liquid phase oxidation of saturated N-heterocyclics like piperidine and pyrrolidine over modified MCM-41 molecular sieve in the presence of H₂O₂.



Results and Discussion

The liquid phase oxidation of piperidine and pyrrolidine was carried out over various modified MCM-41 mesoporous molecular sieves and the results are depicted in **Tables I** and **II**. The yields of piperidone were 27.5, 53.5, 30.2, 48.2 and 27.3 wt% at 34.4, 54.7, 39.3, 52.3 and 30.3 % conversions over Fe(ac)

Table I—Liquid phase oxidation of piperidine to piperidone over modified MCM-41 molecular sieves

{Catalyst wt.=1g; Reactant wt.=1g; Reactant : H₂O₂=1:4 molar; Solvent: Methanol (20 mL); Duration=20hr; ac=acetyl}

S. No.	Catalyst	Conversion of piperidine (%)	Yield (wt%)	
			Piperidone	Other products
1	Mn(ac)MCM-41	3.2	2.8	0.4
2	Co(ac)MCM-41	6.9	5.1	1.8
3	Ti(ac)MCM-41	6.2	5.6	0.6
4	TiMCM-41	7.3	6.8	0.5
5	VMCM-41	8.2	7.0	1.2
6	CoMCM-41	11.6	11.2	0.4
7	Fe(ac)Y	30.3	27.3	3.0
8	Fe(ac)MCM-41	34.4	27.5	6.9
9	Cu-MCM-41	27.9	27.7	0.2
10	Fe-MCM-41	39.3	30.2	9.1
11	Mn-MCM-41	44.8	44.4	0.4
12	Cr-MCM-41	52.3	48.2	4.1
13	Cr(ac)MCM-41	54.7	53.5	1.2

Table II—Liquid phase oxidation of pyrrolidine to pyrrolidone over modified MCM-41 molecular sieves

{Pyrrolidine=1g; Catalyst=1g; Pyrrolidine :H₂O₂=1:4 molar; Solvent: methanol (20 mL); Duration=20 hr}

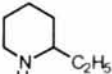
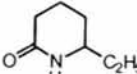
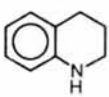
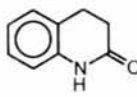
Sl. No	Catalyst	Conversion of pyrrolidine (%)	Yield (wt%)	
			Pyrrolidone	Other products
1	Co(ac)MCM-41	5.4	4.9	0.5
2	Fe(ac)MCM-41	6.8	5.7	1.1
3	Fe-MCM-41	8.4	6.1	2.3
4	Mn-MCM-41	7.3	6.3	1.0
5	Ti(ac)MCM-41	7.6	6.4	1.2
6	Co-MCM-41	8.7	7.7	1.0
7	Fe(ac)Y	8.0	7.8	0.2
8	Mn(ac)MCM-41	16.5	15.2	1.3
9	Cu-MCM-41	23.7	23.3	0.4
10	V-MCM-41	46.5	41.4	5.1
11	Cr-MCM-41	49.8	47.1	2.7
12	Cr(ac)MCM-41	54.8	53.5	1.3

MCM-41, Cr (ac) MCM-41, Fe-MCM-41, Cr-MCM-41 and Fe (ac) Y molecular sieves respectively (*cf* **Table I**).

There was no specific trend in the activity of the redox metal ions but redox potential is considered to be responsible for the activation of the reactant molecule and H₂O₂. In the liquid phase oxidation of pyrro-

[†] IICT Communication No.: 3972.

Table III—Liquid phase oxidation of various saturated *N*-heterocyclics over Cr modified MCM-41 molecular sieves [Reactant wt. = 1g, Catalyst wt.=1g, Reactant : 2 =1:4 molar, Duration 20 hr, Solvent: Methanol (20 ml), a= other products (corresponding diketones or aldehydes)]

Sl.No.	Substrate	Conversion (%)	Product	Product Yield (wt%)	Others
1		49.8		47.1	2.7
2		52.3		48.2	4.1
3		55.7		19.1	36.6 ^a
4		78.2		49.3	28.9 ^a
5		100		96.6	3.4

lidine, the yields of the pyrrolidone were 53.5, 15.2, 47.1 and 41.4 wt% at 54.8, 16.5, 49.8 and 46.5% conversions over Cr (ac) MCM-41, Mn (ac) MCM-41, Cr-MCM-41, and V-MCM-41 molecular sieves respectively and the results are given in **Table II**. We have also studied the effect of various solvents and oxidants and redox molecular sieves like VSAPO, etc.,

The stoichiometric equations for the reaction may be written as follows :

The results of the liquid phase oxidation of various saturated nitrogen-containing heterocyclics over Cr-MCM-41 are given in **Table III**. The conversions and yields are in the range of 50-100 % and 20-97 % respectively. In general, we have developed a methodology for the oxidation of saturated cyclic amines to amides over redox molecular sieves. The work is being extended to other heterocyclics. These processes can be commercially useful and eco-friendly.

Experimental Section

MCM-41 was prepared according to the literature procedure⁸ and the catalysts were highly crystalline. The typical molar gel mixture composition in the preparation of Cr (M^{n+}) MCM-41 was as follows: 0.5 Cr_2O_3 : 31.01 SiO_2 : 0.5 Al_2O_3 : 2.2 (surfactant)₂O : 3.16 (TEA)₂O : 1.89 Na_2O : 615-820 H_2O . The tem-

plate and surfactant were removed by calcining at 500°C for 12 hr and represented as Cr-MCM-41. Cr (ac) MCM-41 was prepared by refluxing above Cr-MCM-41 in acetic anhydride in methanol for 5 hr. The catalysts have been characterized by XRD, IR and Sorption techniques. IR spectra showed a peak at 960 cm^{-1} corresponding tetrahedral M^{n+3} (transition metal ion). The reaction was carried out taking 20 ml of methanol as a solvent, 1g of reactant and 1g of the catalyst in a round bottom flask. H_2O_2 was used as an oxidant and the molar ratio of reactant: H_2O_2 was 1:4. The reaction mixture was refluxed for 20 hr. The product was analyzed by gas chromatography using FID and 5% SE-30 column and confirmed by mass spectra, GC-Mass and NMR.

Acknowledgment

We are thankful to Department of Science and Technology, New Delhi, for financial support. KVVBSRM is thankful to the CSIR, New Delhi, for Research Associateship.

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