

Novel efficient synthesis of glycol monoethers over a niobium-containing MCM-41 mesoporous molecular sieve

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Letter

A niobium-containing MCM-41 mesoporous molecular sieve was synthesized by the hydrolysis of tetraethylorthosilicate and niobium pentachloride, using cetylpyridinium bromide as template in acidic medium, and was found to be highly active in the direct conversion of cyclohexene into *trans*-2-alkoxycyclohexanol at mild temperature in the presence of H_2O_2 and alcohol.

trans-2-Methoxycyclohexanol and other cyclic glycol monoethers play an important role in the synthesis of the antibacterial trinem¹ since the cyclohexane ring constitutes a central structural moiety in a number of naturally occurring biologically active molecules and chiral auxiliaries;² thus there has been increasing interest in the synthesis of 2-substituted cyclohexane-1-ols.^{3–4} These are traditionally synthesized by alcoholysis of cyclohexene oxide using protic acids, Lewis acids or biocatalysts in the presence of alcohol.^{2–6} Therefore, it is very interesting to find new efficient catalyst to directly synthesize glycol monoethers from cyclohexene. The breakthrough discovery of silica-based mesoporous molecular sieves (M41S), including the hexagonal MCM-41,^{7,8} offered new opportunities for creating highly dispersed and more accessible catalytic sites by incorporating transition metal ions into the silica-based frameworks.^{9–13} Niobium compounds and materials have shown great promise in heterogeneous catalysis within the past decade; they have been used in processes involving active acidic centers as well as redox characters,¹⁴ depending on the composition and structure of the catalysts. Ziolk and Nowak¹⁵ reported the synthesis of Nb-MCM-41 under hydrothermal conditions using niobium oxalate as niobium precursor, and they focused on gas-solid catalytic reactions for the decomposition of isopropanol and hydrosulfurization of methanol. Here, we report the synthesis of Nb-MCM-41 using conventional niobium pentachloride as the niobium precursor at mild temperature in acidic media; it was found that this catalyst was highly active in the direct conversion of cyclohexene into *trans*-2-alkoxycyclohexanol.

The powder X-ray diffraction pattern (Rigaku, D/Max-2400, Cu-K α radiation; $\lambda = 0.15418$ nm) of the calcined sample is depicted and indexed in Fig. 1; it was consistent with the previously reported^{8–9} spectrum of MCM-41 silica. Fig. 2 shows the Raman spectra (Nicolet, Raman 910) of Nb-MCM-41 and crystalline Nb_2O_5 [Shanghai, 99.9% Nb_2O_5]. The absence of intense peaks at *ca.* 996, 889, 681, 630, 549, 477, 263, and 134 cm^{-1} in the spectrum of Nb-MCM-41 indicates that the Nb might be highly dispersed in the silica-based framework structure. This result was also supported by the diffuse reflectance (DR) spectra of Nb-MCM-41 and Nb_2O_5 crystals in the UV-Vis region. In the DR UV-Vis spectrum of the calcined Nb-MCM-41 sample, there was no absorption band corresponding to the crystalline Nb_2O_5 . The chemical analysis using ICP atom emission spectroscopy (ARL 3520) showed the Nb content in

the Nb-MCM-41 was 1.43 mass%. The BJH pore size and BET surface area (Micromeritics ASAP 2010 sorptometer) of the calcined Nb-MCM-41 were 2.6 nm and $1086\text{ m}^2\text{ g}^{-1}$, respectively.

The oxidation of cyclohexene was carried out in alcohol using H_2O_2 as the oxidant and Nb-MCM-41, Si-MCM-41, or $\text{Nb}_2\text{O}_5\text{-SiO}_2$ as the catalyst. Here Si-MCM-41 was a pure silica sample synthesized by the method described above but leaving out the niobium ion precursor, and $\text{Nb}_2\text{O}_5\text{-SiO}_2$ was prepared using the same procedure adopted for Nb-MCM-41 except that no template was added. Table 1 lists the catalytic reaction results over the different types of catalysts. It is seen that Nb-MCM-41 is a by far superior catalyst for this reaction

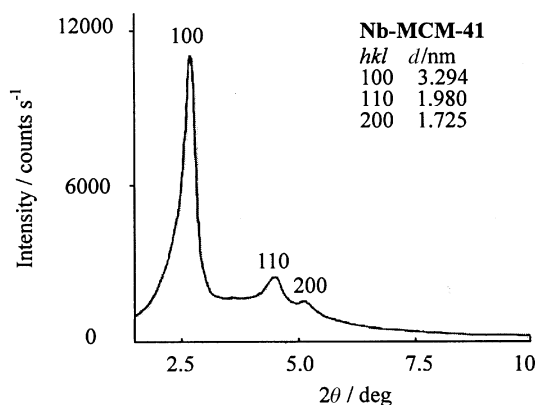


Fig. 1 Powder XRD pattern of the calcined Nb-MCM-41.

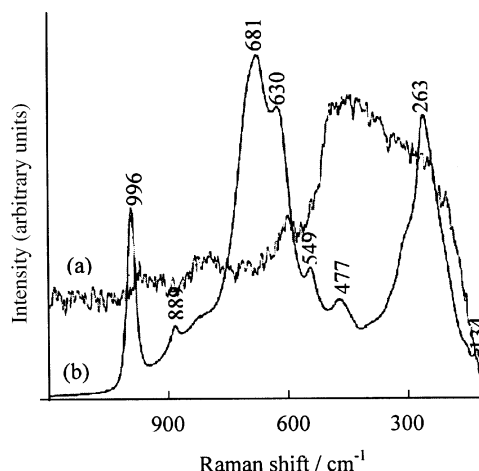


Fig. 2 Raman spectra of (a) Nb-MCM-41 and (b) crystalline Nb_2O_5 .

Table 1 Activity of Nb-MCM-41 and related materials for the oxy functionalization of cyclohexene^a

Catalyst	Conversion (%)		Selectivity (%) ^b	
	H ₂ O ₂	C ₆ H ₁₀	Glycolether	Glycol
Nb-MCM-41	98.5	84.7	92.3	4.0
Nb ₂ O ₅ -SiO ₂	97.0	28.1	90.1	3.8
Si-MCM-41	95.8	—	—	—
None	95.3	—	—	—

^a Reaction conditions: catalyst, 0.2 g; cyclohexene, 1.6 g (0.0194 mol); H₂O₂ (30% wt), 2.2 g (0.0194 mol); substrate : solvent, 1 : 30 (v/v); temperature, 333 K; reaction time, 5.5 h. ^b Selectivity is calculated on the basis of consumed cyclohexene.

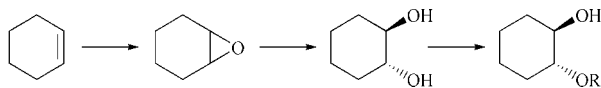
as compared to the others. The activity of Nb-MCM-41 was about 3 times of that of Nb₂O₅-SiO₂; these data indicate that the highly dispersed Nb in the silica-based mesoporous molecular sieve might play an important role in promoting the reaction.

Table 2 shows the effect of reaction media on cyclohexene conversion and product selectivity. The reaction carried out in acetone gave low cyclohexene conversion but high glycol selectivity, however, in both methanol and ethanol, high cyclohexene conversion, glycolether selectivity but poor glycol selectivity were observed. Such a product distribution is attributed to an effect of the reaction media. Scheme 1 shows the possible reaction mechanism. Epoxide might be first formed through epoxidation of the substrate. In the presence of alcohol and water coming from the hydrogen peroxide solution, the epoxide intermediate is subsequently opened to generate the glycol. Etherization of the glycol leads to the formation of the glycol monoethers. It is interesting to note that epoxide was not detected by GC-MS; the reason might be the

Table 2 Effect of reaction media on the catalytic activity of Nb-MCM-41^a

Solvent	Conversion (%)	Selectivity (%) ^b	
	Cyclohexene	Glycolether	Glycol ^c
Acetone	21.3	0	89.3
Methanol	84.7	92.3 ^d	4.0
Ethanol	85.1	81.4 ^e	4.3

^a Reaction conditions: as in Table 1. ^b Selectivity is calculated on the basis of consumed cyclohexane. ^c *trans*-Cyclohexane-1,2-diol. ^d *trans*-2-Methoxycyclohexanol. ^e *trans*-2-Ethoxycyclohexanol.

**Scheme 1**

reason that epoxide is very unstable in the test reaction system.

In conclusion, Nb-MCM-41 has been shown to be an effective catalyst in the oxidation of cyclohexene using hydrogen peroxide as oxidant in methanol or ethanol media; high substrate conversion and product selectivity were obtained. Systematic investigations toward understanding the mechanism of this catalytic reaction are still in progress.

Experimental

Nb-MCM-41 was prepared from tetraethylorthosilicate [Aldrich, 98% Si(OEt)₄, TEOS] as the silica source and an aqueous HCl solution of niobium pentachloride [Fluka, 99.9% NbCl₅] served as the niobium ion precursor with cetylpyridinium bromide [Aldrich, 98% C₁₆H₃₃NC₅H₅Br · H₂O, CPBr] as template. In a typical synthesis, the appropriate amount of CPBr was dissolved in aqueous HCl solution with magnetic stirring at 323 K. Under vigorous stirring, the determined amount of TEOS and niobium ion precursor was added dropwise. The final composition of the reaction mixture was 1 TEOS : 0.3 CPBr : 0.02 NbCl₅ : 6 HCl : 60 H₂O. After the resulting gel had aged at 323 K under gentle stirring for 22 h, the solid product was recovered by centrifugation, washed with distilled water and air-dried. The calcination of the Nb-MCM-41 was carried out in air at *ca.* 533 K for 1.5 h, then 873 K for 5 h.

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