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## RESEARCH ARTICLE

### HYDROGENATION WITH RUTHENIUM NANO PARTICLES SUPPORTED ON MCM-48

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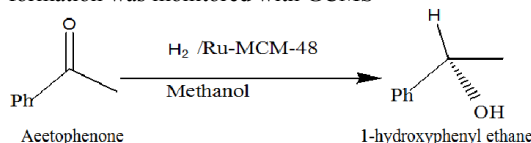
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#### ABSTRACT

MCM-48 was synthesized by hydrothermal method using tetraethylorthosilicate (TEOS) and N-Cetyl-N,N,N-trimethylammoniumbromide (CTAB) as the template in a Teflon lined stainless steel autoclave at 433 K for 60 hours. The prepared MCM-48 was characterized by taking IR, XRD, SEM, EDX and Surface Area Analysis. The XRD pattern shows well ordered MCM-48 structure. The particle size was determined from the SEM image. Ruthenium nano particle were prepared by stirring Ruthenium chloride (0.0185g) and polyvinylpyrrolidone (PVP) (0.4162g) in ethylene glycol (75mL) at 573 K. An UV of the Ru-nano sols confirms formation of nano particles. Ru-MCM-48 was then synthesized by post synthesized impregnation method. The Ru-MCM-48 was characterized by IR and surface area analysis. Hydrogenation reactions were carried out at room temperature by taking 1 mmol of acetophenone and 0.2g of Ru-MCM-48 in a PARR hydrogenation apparatus for 6 hours. The products formation was monitored with GCMS



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#### INTRODUCTION

In 1932, Mc Bain Coined the term “Molecular Sieve” to define certain Porous solid materials that act as a sieve on a molecular dimension, when he observed that a material called chabazite had a Property of selective absorption of molecules smaller than 0.5 nm in diameter. The Mesoporous material discovered by Mobile Researchers (Kresge et al., 1992; Beck et al., 1992) in 1992 designated as M 41S. Three main subgroups of M 41S are (a) Hexagonal MCM-41 with one-dimensional Pores (b) Cubic MCM – 48 with three dimensional pores and (c) Thermally unstable lamellar MCM – 50. Wide range of Pore sizes (1.5 – 7 nm), high surface area (700 – 1300 m<sup>2</sup>g<sup>-1</sup>) (Gomez et al., 2004; Nath and Ganguli, 2012), possible local structure modification and thermal stability makes these mesoporous material attractive to study adsorption, separation, ion exchange and as host structure (Koyano and Tatsumi, 1996; Gaydhankar et al., 2005; Vidya et al., 2004) for nano materials. MCM-48 belongs to the space group *Ia3d* and the incorporation of Ru nano particles into the structure results in good hydrogenation catalysts (Zhao et al., 1998).

#### Experimental

##### Preparation of Ruthenium nano particle

0.1855 g of Ruthenium Chloride (RuCl<sub>3</sub>) and 0.41625 g of Polyvinylpyrrolidone (PVP) were dissolving in 75 mL of Ethylene glycol under stirring at 473 K for 3 hours. The colour change from dark red to light yellow and then finally to dark brown when colloidal solution of Ru-nano cluster were formed (Yan et al., 2001; Chen et al., 2008).

##### Preparation of Ru-MCM-48

MCM-48 was hydrothermally synthesised as per literature method (Sun and Coppens, 2002). The Ru-MCM-48 was prepared by stirring 1g of calcined MCM-48 (Xu et al., 1998; Yan et al., 2001) with 20 ml 0.05 M colloidal solution of Ru-nano cluster for 4 hours at room temperature. The product was filtered, washed with alcohol and dried.

##### Characterization

##### UV-VIS Spectroscopy

The UV-Vis spectrum (Fig.1) of the nano solution (Chen et al., 2009; Rose and Wilkinson, 1970) before heating shows the

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peak at 350 nm gradually decreases after heating which indicates the formation of Ru colloids. On heating a broad band with a maximum at 392 nm develops, giving the material a deep yellow colour.

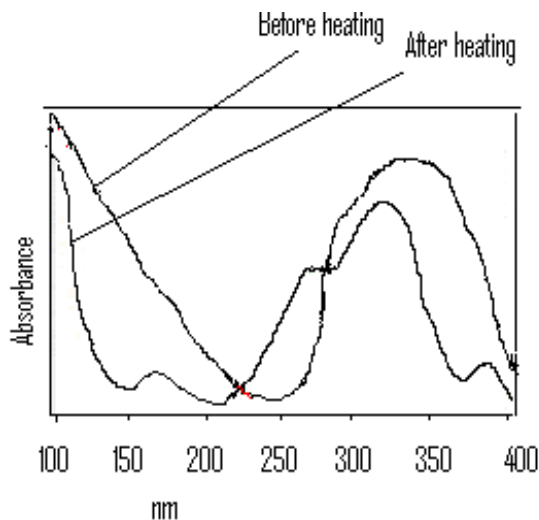


Fig.1. The UV-Vis spectrum of the Ru- nano solution

**IR Study:** The IR band (Fig.2) at  $458\text{ cm}^{-1}$  for the silica structure may overlap with that of the ruthenium complex,  $957\text{ cm}^{-1}$  arises from Si-O stretching in Si-OH groups. The band at  $957\text{ cm}^{-1}$  is likely to be due to a Si-O stretching vibration perturbed by Ru. The important bands at 1248 and  $1075\text{ cm}^{-1}$  can be assigned to the Si-C and Si-O-Si bonds respectively. The band at  $1630\text{ cm}^{-1}$  is due to bending mode of adsorbed water molecules. The bands at 1407, 791 and  $693\text{ cm}^{-1}$  suggest the presence of organic fragments. The sharp decrease in the intensities  $2842$  and  $2971\text{ cm}^{-1}$  indicates the removal of surfactants.

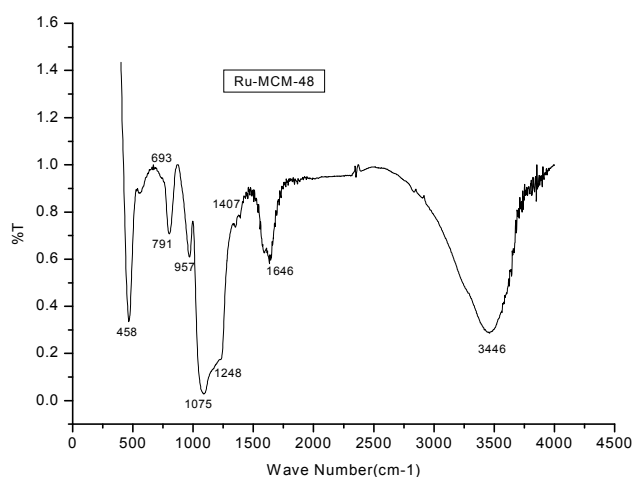


Fig.2. IR Spectra of Ru-MCM-48

**DRS study:** The DR UV-Vis spectra (Fig.3) of Ru-MCM-48 showed a large absorption at about 280 nm, which is due to the electronic transition from  $\text{O}^{2-}$  to  $\text{Ru}^{4+}$  in tetrahedral coordination and the band at 350 nm that contain a series of d-d transition will be attributed to the Ru in the framework. But in case of MCM-48 such characteristic absorbance were not observed. This demonstrates the incorporation of ruthenium into the framework of MCM-48 materials (Luo et al., 2009).

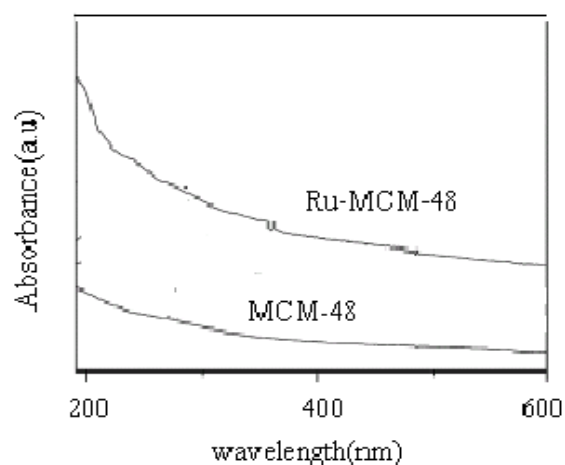


Fig.3. The DR UV-Vis spectra of Ru-MCM-48 and MCM-48

**XRD Study:** The crystallinity of the molecular sieves was characterized by X-ray diffraction (XRD) (Fig.4) studies. As shown in Fig.4 the characteristic peak at 2.6 and peak at 3.1 which are indexed to the (211) and (220) reflections, respectively. Several other peaks are observed in the range of 4-6 which belong to the cubic  $la3d$  symmetry of typical mesoporous molecular sieves.

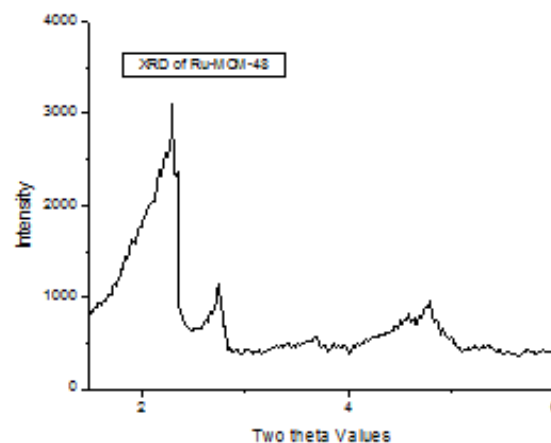


Fig.4. XRD of Ru-MCM-48

**SEM Study:** The spherical morphology of Ru-MCM-48 is clearly visible in the SEM image (Fig.5)

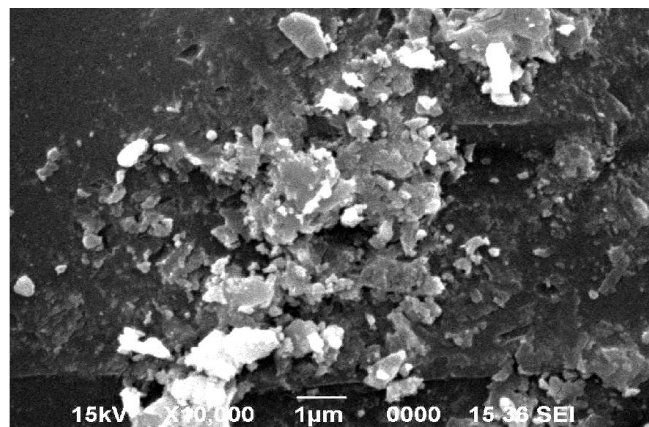


Fig.5. SEM of Ru-MCM-48

**N<sub>2</sub> adsorption/desorption isotherm:** The N<sub>2</sub> adsorption/desorption isotherm for Ru-MCM-48 shows (Fig. 6) a typical type IV isotherm with steep rises due to capillary condensation, which is characteristic of the mesoporous materials. The position of inflection between the relative pressures  $P/P_0 = 0.2-0.4$  region depends on the diameter of mesopores, and its uniform pore size distribution. The hysteresis loop at a relative pressure  $P/P_0=0.5-1.0$  is due to interparticle porosity. The BET surface area was  $422 \text{ m}^2 \text{ g}^{-1}$ . The pore volume and average adsorption pore diameter of Ru-MCM-48 are  $0.305 \text{ cm}^3/\text{g}$  and 2-3 nm respectively.

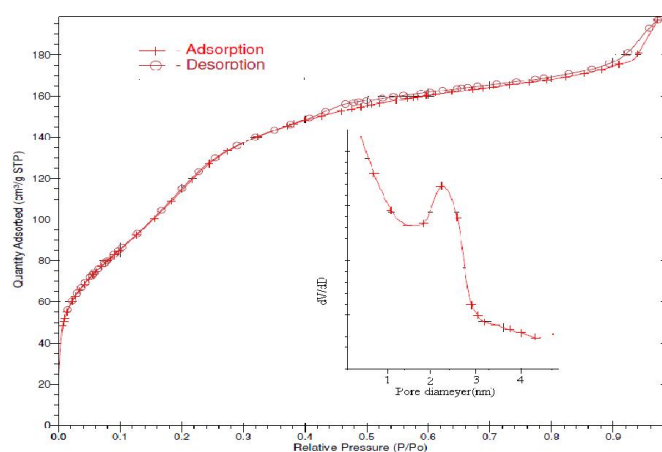


Fig.6. N<sub>2</sub> adsorption/desorption isotherm of Ru-MCM-48

### Catalytic study

**Hydrogenation Reaction:** Hydrogenation reactions were carried out at room temperature by taking 1 mmol of acetophenone in 50 mL of methanol and 0.2 g of Ru-MCM-48 in a PARR hydrogenation apparatus for 10 hours. The products formation (1-hydroxyphenyl ethane) was identified with GCMS and the product percentages are shown in table 1.

Table 1.(Product % yield)

Time (hrs)	1	2	4	6	10
Product (%) yield with Ru-MCM-48	30	40	68	91	91
Product (%) yield with SBA-15 supported norephedrine					85

The reaction was completed in 6 hours and the yield was 91%, but when the same reaction was carried out by SBA-15

supported norephedrine as per literature (Jin et al., 2005) then the yield was 85% in 18 hours. Hence the former was better hydrogenation catalyst than the later.

### Conclusions

Ruthenium nano particles supported on MCM-48 is a good catalyst for hydrogenation reaction.

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