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ABSTRACT

Since the discovery of the MCM-41 and FSM-16 in the early 1990's of the last century, great and fascinating progress has been made in the design, preparation, characterisation and application of mesoporous silica materials. The mesoporous silica MCM-41 was successfully synthesized and used as the support to immobilize transition metals, such as nickel and ruthenium. High-surface-area supports like mesoporous silica afford highly dispersed metal oxide species which are the key parameter in the rather difficult liquid-phase oxidation of unsaturated alcohols. The synthesized material has high specific surface area, narrow pore size distribution, and large pore with high wall thickness which is very suitable for using as support material. The transitional metals were effectively dispersed on MCM-41 by the direct synthesis method and kept the original 2D hexagonal mesostructure. The obtained nanostructured heterogeneous catalysts were characterized by N₂ adsorption, ultraviolet-visible, XPS and X-ray absorption spectroscopy. X-ray absorption spectroscopy showed the presence of Ru-O bonds, suggesting a higher number of oxidic species. The adopted procedure was simple, green and efficient for unsaturated alcohols oxidation, such as 1-buten-3-ol. The use of a clean oxidant such as H₂O₂ was an important feature of a green chemical reaction since it resulted only water as by-product. The nanostructured heterogeneous catalysts enabled a better accessibility of active sites to bulky substrate molecules, reflected in the high conversions and better selectivity.

INTRODUCTION

MCM-41 (Mobil Composition of Matter No. 41) is a mesoporous material with a hierarchical structure from a family of silicate and aluminosilicate solids that were first developed by researchers at Mobil Oil Corporation and that can be used as catalysts or catalyst supports.

EXPERIMENTAL

Direct synthesis of mono- and bi-metal hybrid materials: Hexadecyltrimethylammonium bromide was dispersed in H₂O and the mixture was stirred for 2 hours at ambient temperature. Sodium silicate solution was added dropwise with stirring and the mixture was stirred for 1 hour. After this time, the metal salt is added and the mixture is stirred for another 2-3 hours mixing continuously, followed by addition of tetramethylammonium hydroxide stirring the mixture for additional 30 minutes. Adjust the pH with concentrated sulphuric acid to 10.5. After 10-15 minutes the pH is checked again and then allowed to stir overnight. Then, the mixture is introduced in the autoclave at 100°C for 5 days. The mixture was then filtered, washed with water, dried and the samples finally were calcinated. The materials obtained are Ru-Cr-MCM-41 and Ru-Ni-MCM-41.

The obtained materials were characterized by SEM, UV-VIS, FT-IR, XPS, EXAFS and N₂ adsorption-desorption and tested in in oxidation of organic compounds in liquid phase (cyclohexene, 1-buthanol, benzyl alcohol), with hydrogen peroxide, and gas phase (CH₄) with air.

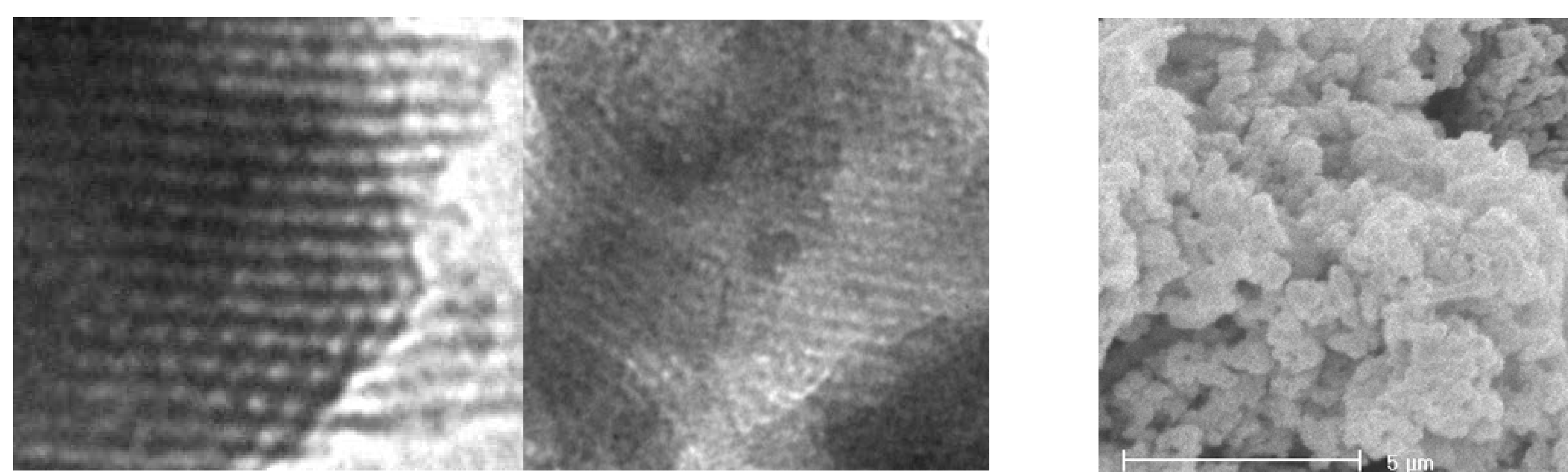
OBJECTIVE

Incorporation of metals into MCM-41 ordered mesoporous network to obtain bimetallic catalysts for oxidation of organic compounds.

RESULTS AND DISCUSSION

The specific surface was calculated using the multilayer adsorption method developed by Brunauer-Emmett-Teller (BET), for relative pressure P/P₀=0,05-0,3. BET surfaces for Ru-Cr-MCM-41 and Ru-Ni-MCM-41 are 768 m²/g and 634 m²/g. These results are in accordance with the pores distribution analysis for the support and the hybrid material, which confirms that these materials are mesoporous materials.

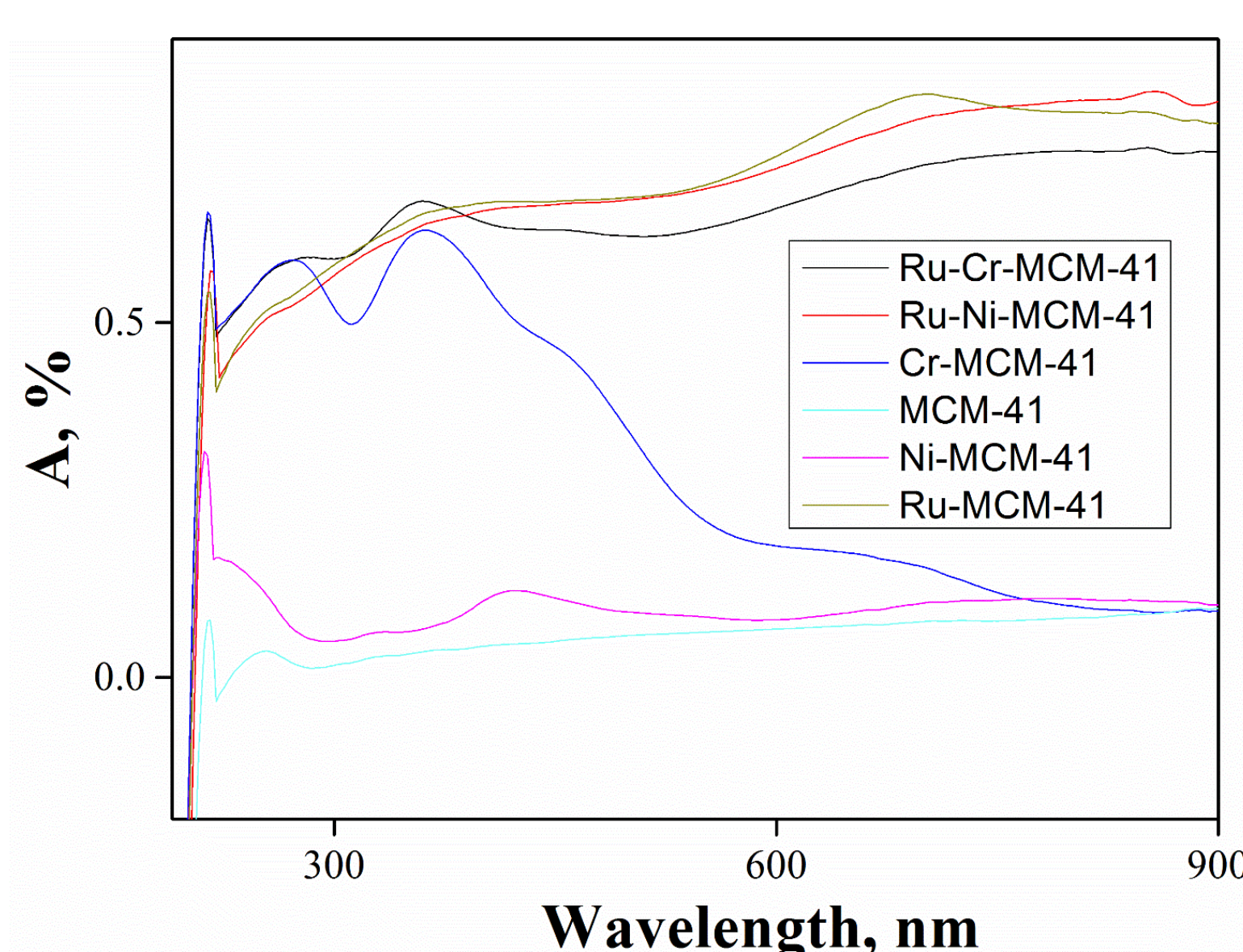
Pores dimensions distribution of supports and catalysts



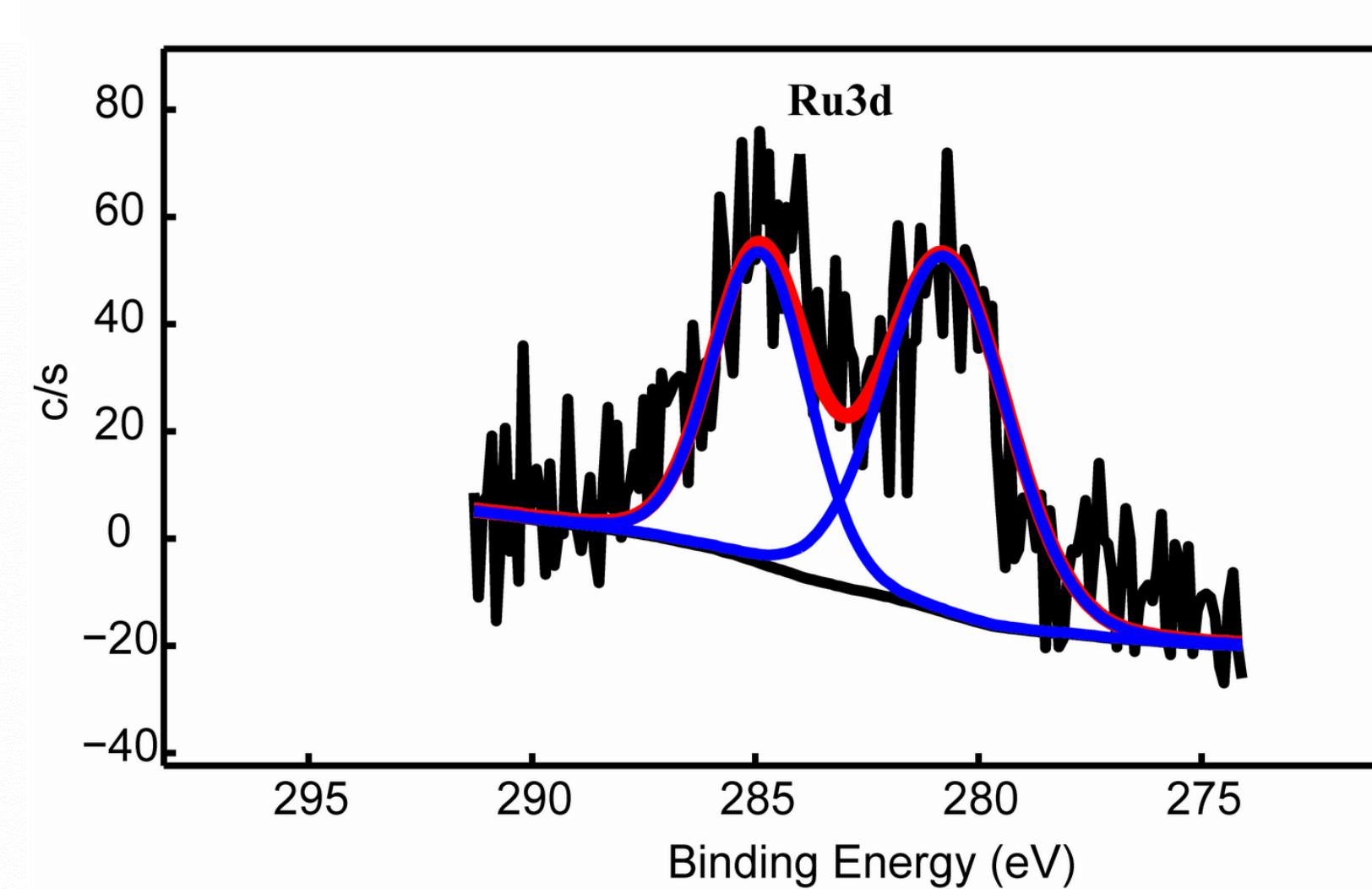
TEM images for Ru-MCM-41 (a) and Ru-Cr-MCM-41 (b)

SEM image for Ru-Cr-MCM-41

The structure of orderly hexagonal MCM-41 mesoporous silica pores is not significantly influenced by ruthenium cations or bimetallic species incorporating. Characterisations of the structure and morphology for the molecular sieve type materials before and after functionalization, revealed the typical ordered mesoporous MCM-41 supports.



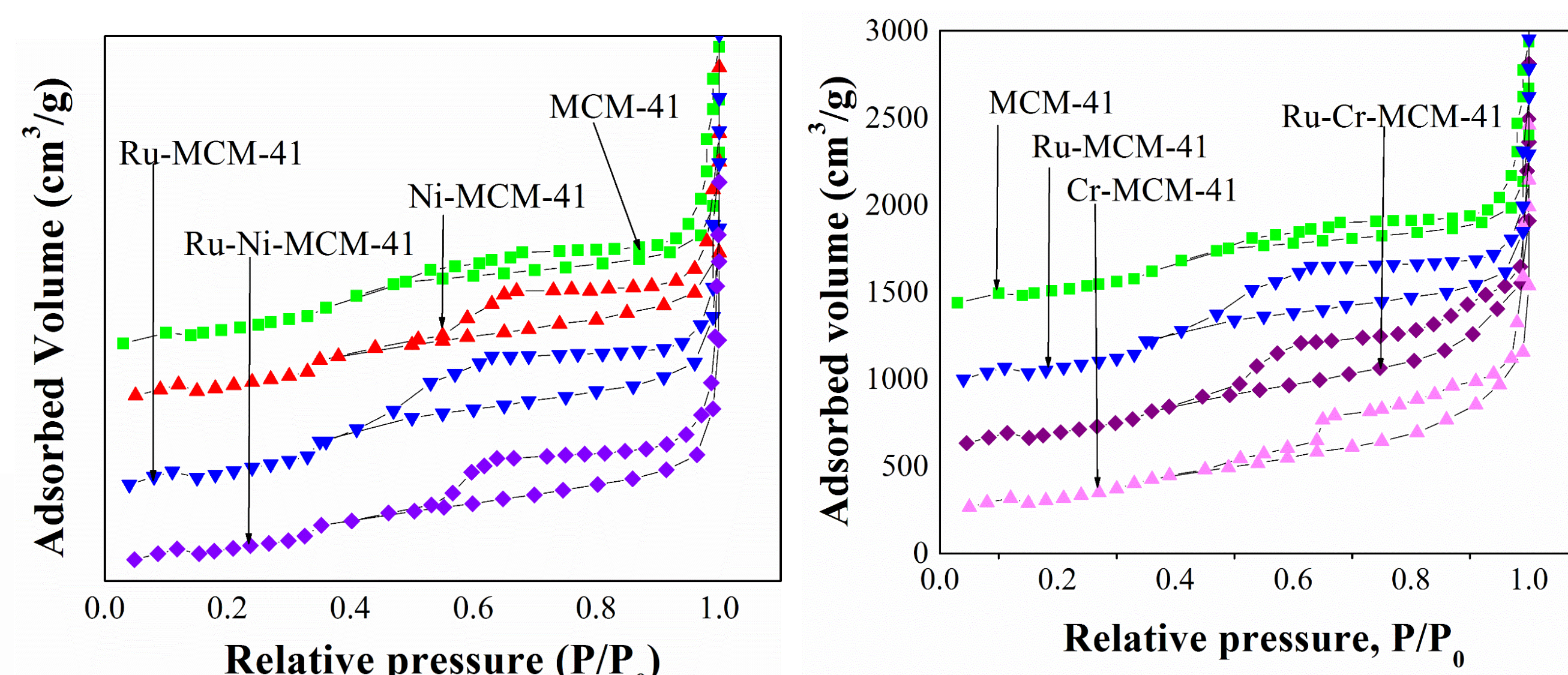
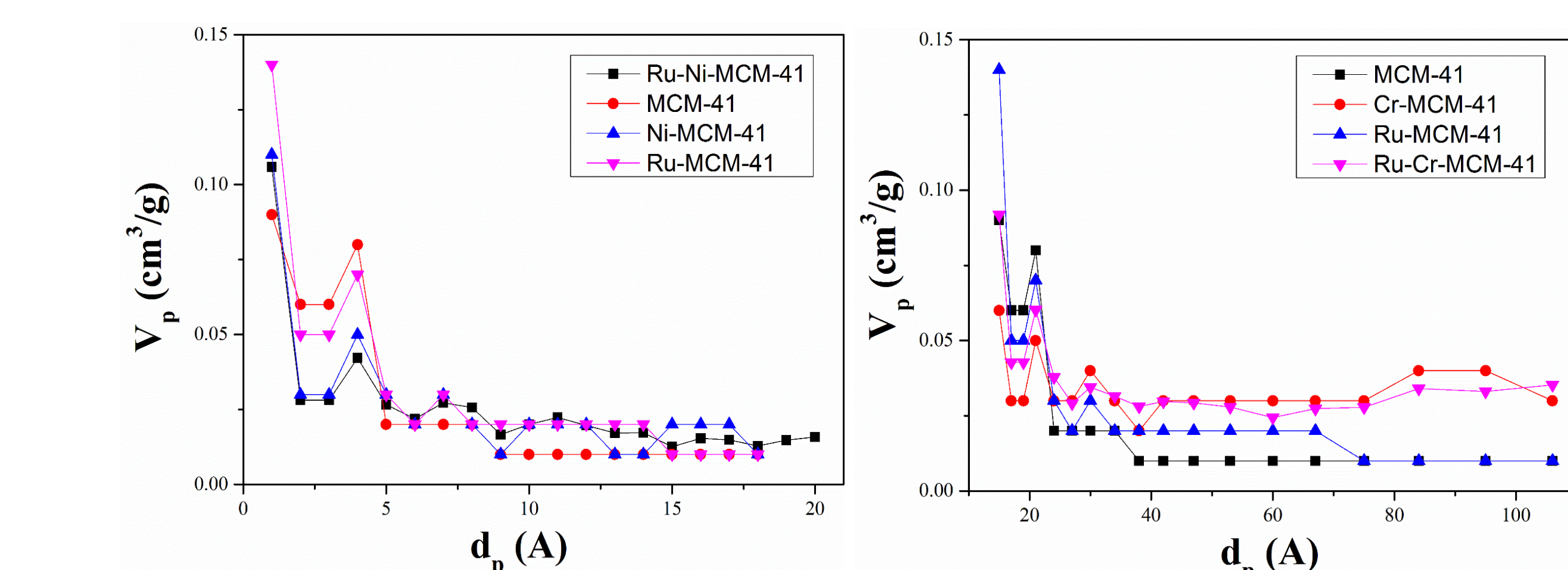
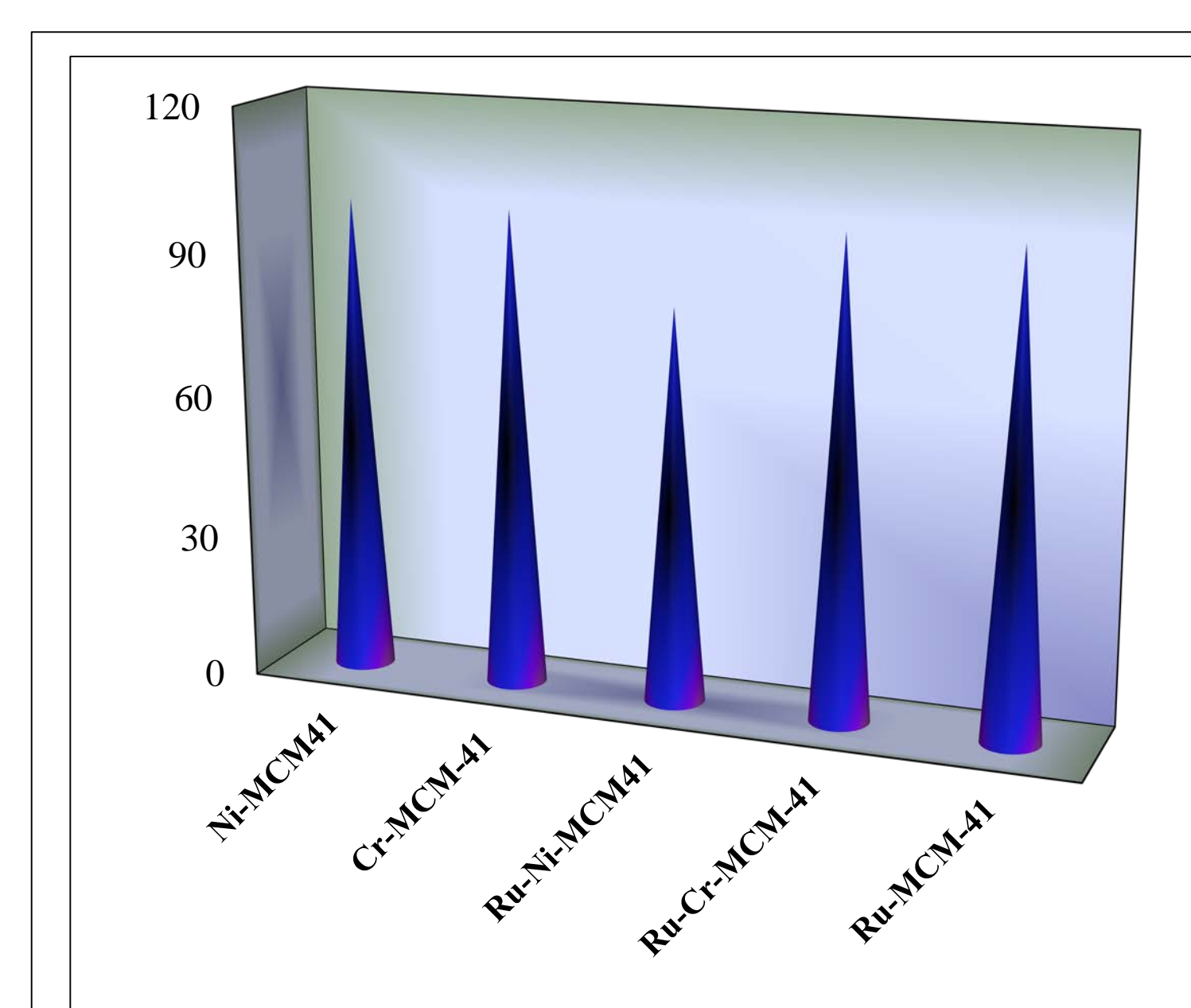
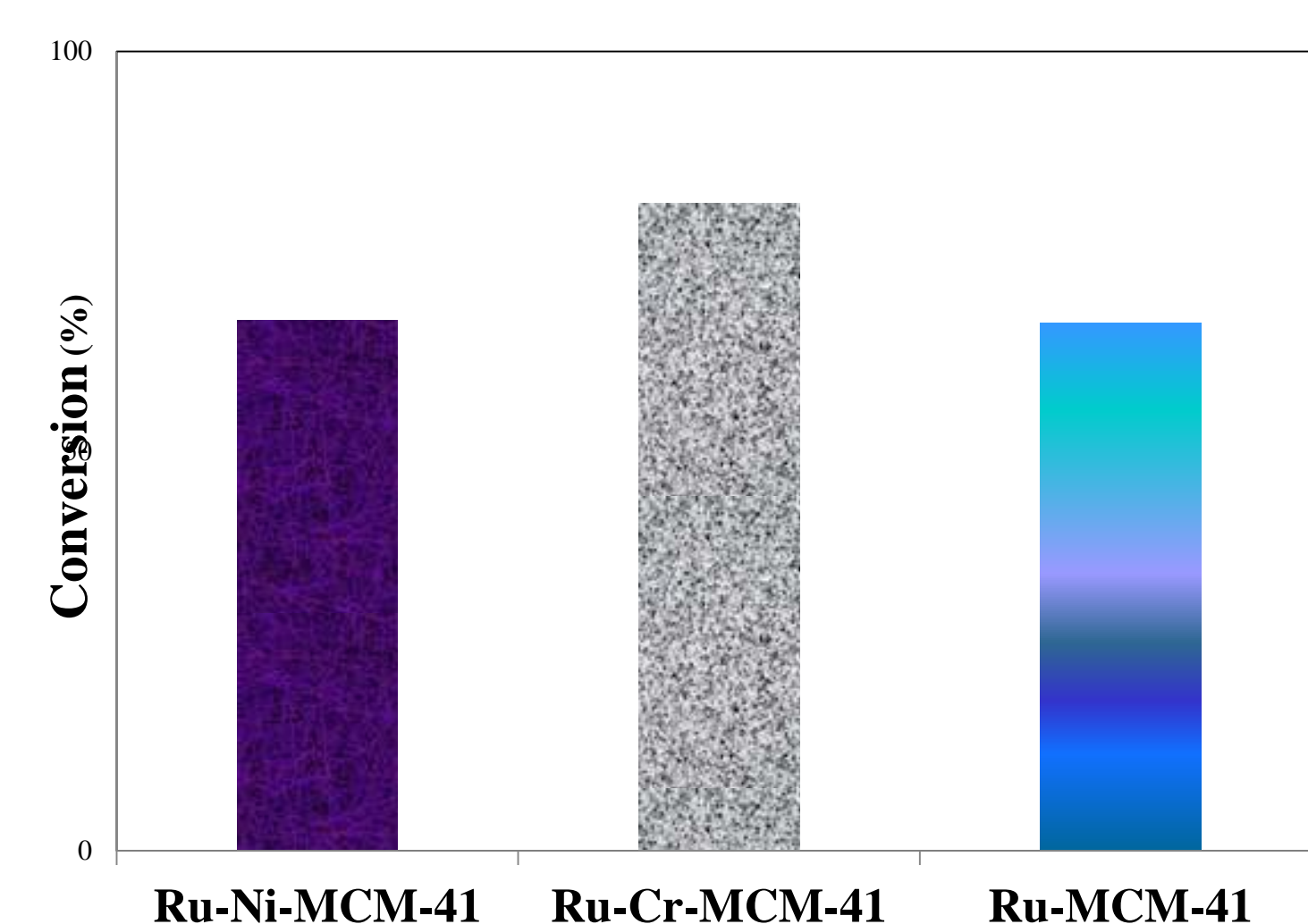
UV-VIS Spectra for catalysts supported on MCM-41



Deconvoluted spectrum of Ru in Ru-Ni-MCM-41

Benzyl alcohol oxidation

N-Buthanol oxidation



Adsorption-desorption isotherms for supports and catalysts

CONCLUSIONS

Mesoporous silica was successfully prepared by hydrothermal synthesis using CTABr as template and Na₂SiO₃ as silica source. The synthesized material had high specific surface area, narrow pore size distribution, and large pore with high wall thickness which is very suitable for using as support material. Transitional metals can be dispersed effectively on MCM-41 by post-synthesis method and still keep the original 2D hexagonal mesostructure. The results of the catalytic tests have shown that they are active and selective catalysts in oxidation reactions of organic compounds. On the other hand, the catalytic activity can be improved with the introduction of the second metal in the system. In the benzyl alcohol oxidation, the highest catalytic activity had the monometallic Ni and Cr systems immobilized on MCM-41 by direct synthesis, the degree of conversion of cyclohexene being around 99 %.

Acknowledgements

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