



Preparation, Characterization and Catalytic Performance of Bimetallic Ti-Co-MCM-41 Catalysts

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Ti-Co-MCM-41 molecular sieve catalysts were synthesized using the impregnation method. The catalysts were characterized by X-ray diffraction, UV-visible, Fourier transform infrared spectroscopy and low temperature N₂ adsorption-desorption. Their performance in 4-*tert*-butylbenzaldehyde synthesis was evaluated in mild conditions by oxygen oxidation 4-*tert*-butyltoluene. The results showed that the catalysts had large surface area and pore size and contained titanium and cobalt with four ligands, which formed the catalysts of high catalytic activity. The conversion rate of 4-*tert*-butyl toluene was improved by 38 %, the selectivity of 4-*tert*-butyl benzaldehyde was improved by 85 % and the yield of 4-*tert*-butyl benzaldehyde was up to 35 %.

Keywords: Ti-Co-MCM-41, Molecular sieve, Grafting, Impregnation, Catalytic activity.

INTRODUCTION

4-*tert*-Butyl benzaldehyde is an important intermediate of medicines, dyes, flavors, fragrances and other fine chemical products and its synthesis methods mainly include chemical oxidation, O₂ (air) oxidation, H₂O₂ oxidation, electrochemical oxidation and so on¹⁻⁴. At present, benzyl chloride hydrolysis method is widely used in industrial production. However, this method brings great environmental pollution and new green synthesis techniques need to be developed in order to solve the problem. Since 1992, the United States of America Mobil company has invented M41S series of mesoporous molecular sieves which show attractive prospect for shape selective catalytic oxidation of organic macromolecular material and the synthesis and application of Ti mesoporous molecular sieve have become a hot spot⁵. A variety of mesoporous molecular sieves with Ti appeared in succession, such as Ti-MCM-41^{6,7}, Ti-HMS^{8,9} and Ti-SBA-15¹⁰, which exhibited good catalytic performance in many oxidation reactions. Besides, cobalt-based inorganic or organometallic compounds as catalysts are also widely used in catalytic oxidation reaction^{11,12}.

As a candidate for catalyst carrier, the mesoporous silica MCM-41 contains rich silicon hydroxyl and has larger specific surface area and pore size, which can play a unique role in the catalytic reaction. In this paper, the active atoms of Ti and Co were modified in molecular sieve carrier by virtue of grafting method and impregnation method and the catalyst of Ti-Co-

MCM-41 with double active components was obtained, which was proved to have high activity and selectivity.

EXPERIMENTAL

Preparation of Si-MCM-41: 65 g deionized water and 2 g CTAB were added to the three-necked flask of 500 mL. The mixture was heated to 40 °C and then stirred for 0.5 h. After CTAB was dissolved completely, 20 g aqueous ammonia was added to the mixture under continuous stirring for 0.5 h. Then, 8.5 g TEOS was dropped slowly into the mixture and the mixture was strongly stirred for 2 h. The reaction mixture was aged at ambient temperature for 24 h and then crystallized at 110 °C for 24 h in the reaction kettle. The crystalline product was recovered by filtration, washed with deionized water, air-dried and calcined in air at 300 °C for 2.5 h and 650 °C for 3.5 h successively. Thus, the white powder product named Si-MCM-41 mesoporous silica material was obtained¹³.

Preparation of Ti-MCM-41: Titanocene dichloride was added to chloroform under stirring to realize complete dissolution of titanocene dichloride in the chloroform and the mixture was marked as solution A. The prepared Si-MCM-41 powder was added to chloroform and then triethylamine was slowly dropped into the mixture under continuous stirring. The obtained mixture was marked as solution B. After that, solution A was dropped into solution B and the reaction mixture was strongly stirred for 3 h. Then the mixture was recovered by

filtration, air-dried and calcined in air at 500 °C for 2 h and 650 °C for 3.5 h. Thus, the white powder product named Ti-MCM-41 mesoporous silica material was obtained. Samples with different titanium contents can be obtained by changing quality ratio of the reactants.

Preparation of Ti-Co-MCM-41: The calcined Ti-MCM-41 was stirred in a solution of $\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in 30 mL glycol to steep the Ti-MCM-41 sample fully. The obtained mixture was first vacuum-desiccated at 250 °C for 4 h and then calcined in air at 550 °C for 4 h. Samples with different cobalt contents can be obtained by changing quantity ratio of the reactants.

Characterization of the catalyst: Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-2500 X-ray diffraction equipped with $\text{CuK}\alpha$ radiation and Ni filter. The diffraction data were collected every 0.02° at a scan speed of $1^\circ (2\theta)/\text{min}$ from 1 to 8° and the experimental conditions were as follows: voltage 40 kV, current 100 mA.

N_2 adsorption-desorption isotherms were recorded at 77 K on a Micromeritics ASAP 2020. The samples were dried at 200 °C for 5 h before test. BET surface areas were calculated from the linear part of the BET plot and pore size distributions were calculated using the adsorption branches of the N_2 isotherms and the BJH method. UV-visible diffuse reflectance spectra were obtained on a Lambda 650S spectrometer and the referenced BaSO_4 were used for the measurements. Element content of the products was determined using JSM-6460 scanning electron microscope (SEM) and JSM-6460 energy spectrum analysis (ESA). Fourier-transform infrared spectroscopy (FT-IRS) was recorded by a VERTEX 70 infrared spectrometer with scanning range of $2000\text{--}500\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was recorded by a VG ESCALAB5 multi-function electronic energy spectrometer with $\text{AlK}\alpha$ ray under CAE mode. The spectrometer was operated with a tube voltage of 9 kV, tube current of 18.5 mA and overpass energy of 500 eV. C-1s scan of every level was used as an internal reference to correct the shift in binding energies of the present level caused by charging effect.

Catalytic testing: Catalytic reaction was performed in a three-necked flask equipped with a condenser and thermometer. The catalytic performance of each sample was tested in the liquid phase with vigorous stirring. The oxidation of 4-*tert*-butyl toluene was carried out at 70 °C for 8 h by adding 0.4 mmol TBHP and O_2 to a mixture which contained 6.7 mmol 4-*tert*-butyl toluene, 150 mg of catalyst and 15 mL of acetonitrile. After the reaction, the catalyst was filtered off, washed with methanol and dried at 100 °C in air overnight, while the reaction liquid was qualitatively analyzed with GC-MS and quantitatively analyzed with GC equipped with a HP-5 capillary column and a flame ionization detector (FID), respectively.

RESULTS AND DISCUSSION

Catalyst Structure: Fig. 1 shows XRD patterns of the samples. It can be seen that the samples all have a strong diffraction peak at about 2° and two small peaks between 3° and 5.5° , which is consistent with previous reports. The samples present six mesoporous structures of MCM-41 molecular sieve and have better long-range order and crystallinity. The

absorption peak intensity of the modified sample decreases and the peak position also slightly migrates, which indicates the metallic elements have entered into the framework of zeolite and changed the long-range order of silicon molecular sieve.

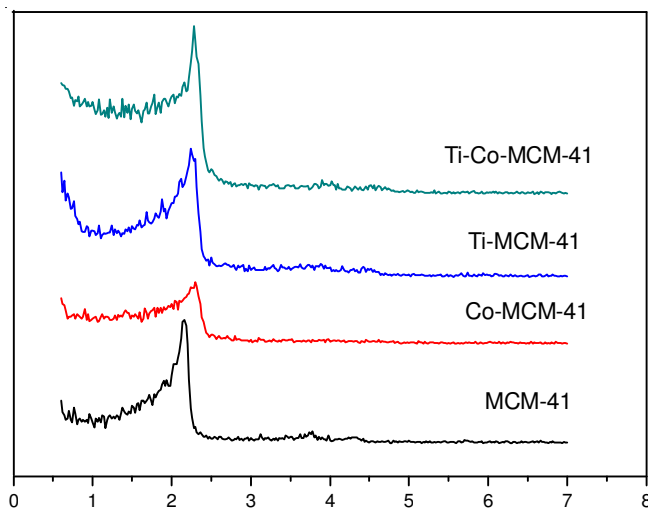


Fig. 1. XRD patterns of the samples

Pore structure and specific surface area: The nitrogen adsorption-desorption isotherms of sample is shown in Fig. 2. The sample exhibits typical IV isotherms as expected for mesostructured materials, which indicates the structure of catalyst remains intact after loading the active components in the carrier.

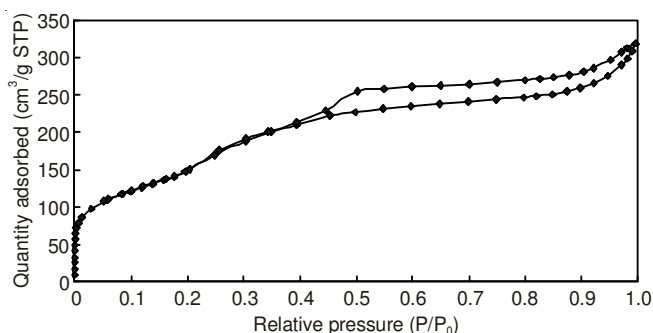


Fig. 2. N_2 adsorption-desorption isotherm of Ti-Co-MCM-41

The textural properties of the catalyst sample are listed in Table-1 and the figures indicate the prepared Ti-Co-MCM-41 catalyst has larger specific surface area, pore volume and pore size, which means the catalyst has good adsorption and catalytic performance.

TABLE-1
PORE STRUCTURE ANALYSIS OF Ti-Co-MCM-41

Sample	SBET (m^2/g)	Pore volume (cm^3/g)	BJH pore size (nm)
Ti-Co-MCM-41	598.0	0.49	3.4

Infrared spectroscopy: Infrared spectroscopy provides structure information of molecular sieves in the $1400\text{--}400\text{ cm}^{-1}$ region. Fig. 3 shows FT-IR spectra of Ti-MCM-41, Ti-Co-MCM-41 and MCM-41 and two bands appear at the same

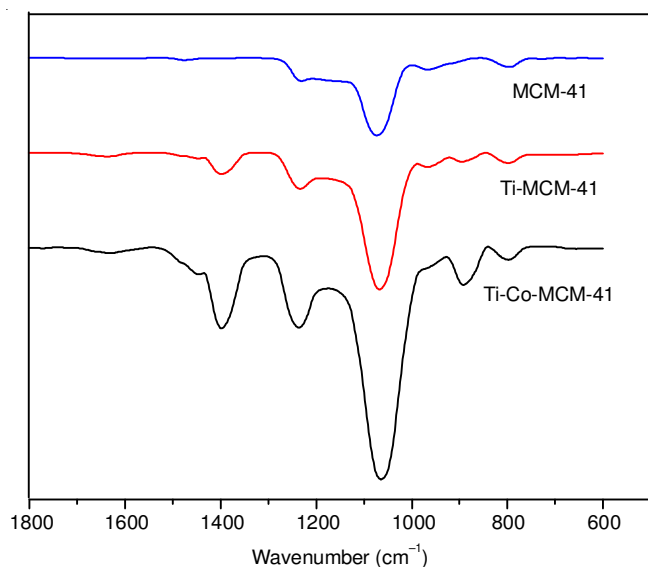


Fig. 3. FT-IR spectra of the samples

position of MCM-41, Ti-MCM-41 and Ti-Co-MCM-41 spectra, of which 1085 cm^{-1} absorption peak is attributed to the asymmetric stretching vibration of Si-O-Si bond and 800 cm^{-1} absorption peak may be caused by the symmetric stretching vibration of Si-O-Si bond.

After introducing titanium into MCM-41, the larger titanium atoms can make the molecular sieve asymmetry structure increase and induce distortion and vibration of the silicon oxygen tetrahedron, which results in the intensity enhancement of Si-O-Si bond at 1085 cm^{-1} . This is an indirect evidence that titanium has entered into the molecular skeleton. In addition, the vibration absorption peak of Ti-O-Ti bond is not found at 652 cm^{-1} , which indicates titanium exists in the skeleton state. After cobalt is introduced into Ti-MCM-41, no new absorption peaks appear in the spectrum of Ti-Co-MCM-41, while the characteristic absorption peak of Ti-Co-MCM-41 is enhanced obviously, which indicates cobalt also exists in the skeleton state.

Scanning electron microscope: The morphology of the catalysts was observed by SEM and the images are shown in Fig. 4. The particle size of the two catalysts both ranges from 0.5 to $1\text{ }\mu\text{m}$ and the pore structure is distinct. Compared with MCM-41, the morphology of Ti-Co-MCM-41 does not change after the active components are loaded.

Diffuse reflectance ultraviolet-visible absorption spectroscopy: Diffuse reflectance UV-visible absorption spectroscopy has been widely used in analyzing silica-based mesoporous molecular sieve which contains heteroatoms. The UV-visible spectra of TiO_2 should have three obvious peaks at 398 , 517 and 638 nm according to the reported literatures. However, as Fig. 5 shows, the three obvious peaks do not appear, which means titanium has not formed TiO_2 . After titanium is introduced into MCM-41, the strongest UV-visible absorption peak of Ti-MCM-41 is at 220 nm and it is the characteristic peak of four coordinated titanium, which indicates titanium atoms have entered into MCM-41 framework of zeolite. After cobalt is introduced into Ti-MCM-41, the main absorption peak of the sample migrates to 222 nm and an acromion appears, which should be the characteristic absorption band of cobalt element.

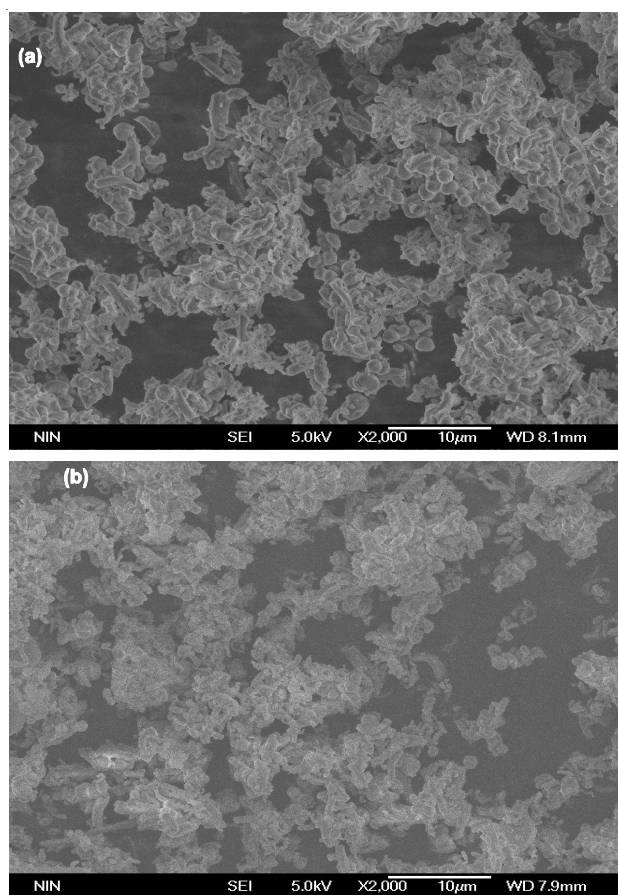


Fig. 4. SEM images of (a) MCM-41 and (b) Ti-Co-MCM-41

That is to say, cobalt atoms have also entered into the framework of molecular sieve.

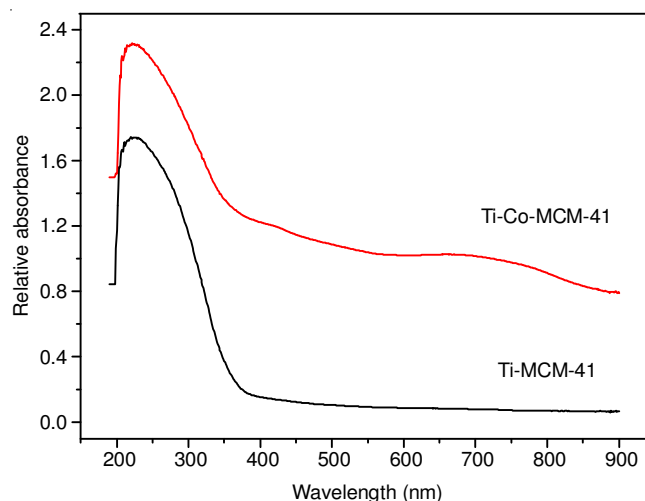


Fig. 5. UV-visible spectra of the samples

X-ray photoelectron spectroscopy analysis: Chemical state information of the active components in the catalysts was analyzed by XPS and Fig. 6 presents the XPS spectra of Ti and Co by scanning the entire spectrum. It can be seen that Ti photoelectron intensity is highest at 458.31 eV and Co photoelectron intensity is highest at 782.61 eV . According to the standard spectra, titanium exists in tetravalent ion state and cobalt remains in trivalent ion state. The results indicate titanium

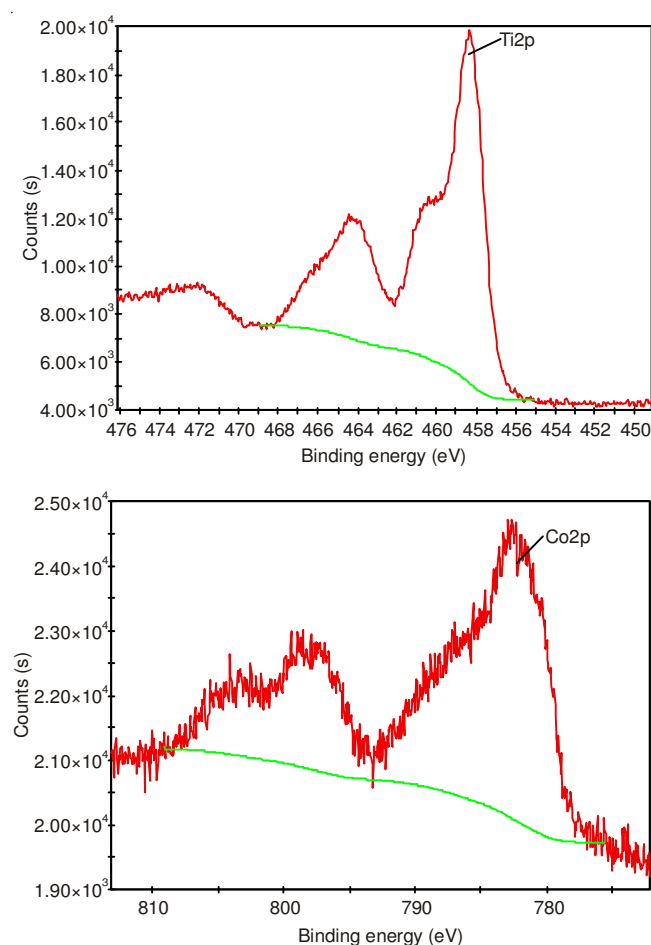


Fig. 6. XPS spectra of (a) Ti and (b) Co for the catalyst

and cobalt have both entered into the molecular sieve framework, which accords with the previous infrared spectrum analysis.

Catalytic performance: The catalyst activity of Ti-Co-MCM-41 with different titanium and cobalt contents is shown in Table-2. The raw material conversion rate is very low in blank experiment, while the conversion and selectivity are improved obviously after adding the samples, which verifies their catalytic role. However, the performance of the catalyst is closely related with the content of titanium and cobalt. Whether the quantity of catalyst is low or too high, the selectivity and conversion rate is low and higher yield can be obtained only when the quantity is appropriate. Combined with the analysis results of catalyst characterization, it can be deduced that part of active components of the high load catalyst do not exist in the skeleton state and that they do not have catalysis for the reaction, which leads to a lower yield.

Conclusion

A series of catalyst samples of Ti-Co-MCM-41 with different titanium and cobalt contents were obtained and most of the titanium and cobalt entered the framework of molecular sieves without damaging the molecular sieve structure severely.

TABLE-2
EFFECTS OF THE CATALYSTS ON THE
OXIDATION OF 4-*tert*-BUTYL TOLUENE

Catalyst	ArCH ₃ conversion (%)	ArCHO selectivity (%)	ArCHO yield (%)
Blank	2.99	36.2	1.08
3Ti-4Co-MCM-41 ^a	31.94	83.5	26.7
4Ti-4Co-MCM-41	38.89	86.2	33.5
5Ti-4Co-MCM-41	32.14	84.1	27.0
4Co-MCM-41	9.19	80.6	7.4
5Ti-MCM-41	19.05	91.8	17.5
3Ti-3Co-MCM-41	28.36	76.5	21.7
3Ti-5Co-MCM-41	29.41	74.5	21.9
4Ti-3Co-MCM-41	38.81	76.3	29.6
4Ti-5Co-MCM-41	32.23	75.2	24.2

^aNote: The 3Ti-4Co-MCM-41 in the table denotes the catalyst has a titanium content of 3 % and cobalt content of 4 %; ^bNote: Reaction conditions were as follows: *p-tert*-butyl toluene 1 g, acetonitrile 15 mL, catalyst 0.15 g, oxygen 2 mL/min, accelerator 0.06 g, reaction temperature 70 °C, reaction time 8 h

The catalyst samples had larger specific surface area and pore size and the content of active components could satisfy with the requirements, which showed good adsorption capability and catalytic activity. Catalytic experiments demonstrated that the prepared catalyst was effective for catalytic oxidation of 4-*tert*-butyl toluene to 4-*tert*-butyl benzaldehyde and 4Ti-4Co-MCM-41 had higher conversion rate and selectivity, with the yield of 4-*tert*-butyl benzaldehyde up to 35 %.

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