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Selective Oxidation of Cyclohexane in Air over Mesoporous Molecular Sieves Ru-doped MCM-48

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Abstract: A series of Ru-doped mesoporous molecular sieves have been synthesized and characterized by XRD, N₂ adsorption/desorption, ICP, FT-IR, FE-SEM, and HRTEM. The characterization results reveal the structure of catalyst and the nature of Ru species. The catalytic performance of the synthesized catalysts has been evaluated for the oxidation of cyclohexane under a mild condition using air as oxidant without any solvent. Catalytic result shows that these catalysts are efficient, and that the behavior of Ru species is different.

Key word: Mesoporous molecular sieves; MCM-48; Characterization; Oxidation of cyclohexane

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The selective oxidation of alkanes under mild condition is still a challenge for chemists, and the activation of C-H bond is the key process. The partial oxidation of cyclohexane is one of the most important reactions because its oxidation products (cyclohexanone, cyclohexanol, so-called K-A oil) are the initial materials to synthesize adipic acid and caprolactam, that are intermediates in the manufacture of nylon-6 and nylon-66 polymers. Previously, the process of cyclohexane oxidation was complex and un-green, and had shortcomings such as serious pollution, low conversion and expensive production cost. At present, an industrial method for the cyclohexane oxidation is carried out with homogeneous catalyst or without catalyst at around 150 °C and under a 1 ~ 2 MPa pressure, which affords a ~ 4% cyclohexane conversion and a 70% ~ 80% selectivity to cyclohexanone and cyclohexanol. Obviously, this process has the drawback of the difficulty of separating the catalyst from the homogeneous reaction system. For the laboratory-scale reaction, benign oxidation of cyclohexane, including heterogeneous catalyst,

solvent-free reaction and clear oxidant such as molecular oxygen, hydrogen peroxide and air, has been reported extensively^[1-11].

As a member of M41s mesoporous molecular sieves family, which was discovered in 1992 by the Mobil group^[12-13], MCM-48 has attracted considerable attention owing to its high surface area, ordered pore channels, and narrow pore size distribution. Although MCM-48 with 3D pore system has some advantages over MCM-41 with 2D hexagonal channel in terms of catalytic and adsorption reactions, more studies have focused on MCM-41 as compared to MCM-48, because the formation of MCM-48 is sensitive to pH value, reaction temperature, reaction time and reagent amount. Even so, a few studies about easy synthesis of MCM-48 have been reported. For example, Schumacher et al.^[14] reported a novel and fast method, which is a modified Stöber synthesis, to synthesize metal-incorporating MCM-48 spheres. Boote et al.^[15] prepared cubic MCM-48 by a rapid and facile way without employing hydrothermal process in 30 min at room temperature.

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Moreover, more efforts have been attempted to enhance the hydrothermal stability and catalytic activity of MCM-48 by doping various elements, including Ti^[16-17], V, Cr^[17], Cu^[18], Al^[19], Boron^[20], Nb^[21] and La^[22], etc.

In an early study^[23], a series of Ru-MCM-48 mesoporous molecular sieves have been synthesized by a facile and rapid way, and their catalytic activity in oxidation of cyclohexane under O₂ was also discussed. With further research, a high conversion of cyclohexane and low selectivity to K-A oil was observed when these samples were used as the catalysts for oxidation of cyclohexane under 1 MPa oxygen at 150 °C. A broad range of complicated oxygenates, including hexanal, butyrolactone, 2-cyclohexene-1-one, cyclohexyl ester, adipic acid, etc, were detected as the main products under the above conditions. In this work, cyclohexane oxidation catalyzed by Ru-doped MCM-48 was carried out in air, instead of pure oxygen, under a mild condition to avoid the deep oxidation. Moreover, the structure of Ru-doped MCM-48 and the nature of Ru species in the catalysts were further characterized by various methods.

1 Experimental

1.1 Catalyst preparation

All reagents used in this work were of AR grade. Details of the synthesis procedure based on the work of Schumacher^[17] and Boote^[18], were as follows: appropriate amount of cetyltrimethylammonium bromide and ruthenium trichloride was dissolved in a mixture of deionized water and ethanol, followed by the addition of aqueous ammonia. After being stirred vigorously at 30 ~ 35 °C for a period of time, TEOS was slowly added to the above mixture under mild stirring. The molar composition of the gel was 0.41 CTAB/ 52 EtOH/ 12 aq. NH₃/ 1.0 TEOS/ 343 H₂O/ 0.003-0.02 RuCl₃. The resultant products were filtered, washed with distilled water, dried at 85 °C overnight and calcined in air at 550 °C for 6 h. According to the different ratios of Si/Ru in the gel, the catalysts were labeled as A (Si/Ru = 300), B (Si/Ru = 200), C (Si/Ru = 100), and D (Si/Ru = 50), respectively. Pure siliceous

MCM-48 was synthesized with the same procedure except that no ruthenium trichloride was added.

1.2 Catalyst characterization

The properties of the Ru-doped MCM-48 and MCM-48 samples were characterized by XRD (Shimadzu XD-3A), N₂ adsorption/desorption (ASAP 2010), ICP (IRIS Advantage ER/S), FT-IR (Bruker, IFS120HRFTIR), FE-SEM (JEOL, JSM-6701F) and HRTEM (JEOL, JEM-2010).

1.3 Catalytic oxidation of cyclohexane

The liquid-phase oxidation of cyclohexane was carried out under vigorous stirring in a 35 mL stainless steel reactor which was heated with an oil bath. In a typical reaction procedure, catalyst (20 mg) was added into the mixture of cyclohexane (2 mL) and *tert*-butyl hydroperoxide (TBHP, 0.1 mL, as the initiator) in the stainless steel reactor, and the mixture was heated to 403 K under stirring in a 1 MPa air atmosphere. After reaction, the steel reactor was cooled in water and the products were directly analyzed by gas chromatography (Techcomp 7890 II using a FID) and GC-MS (Agilent 6890N/5973).

2 Result and discussion

2.1 Characterization of catalysts

In order to obtain information about the principal components of the catalysts, the XRD was used to identify their crystallite phase composition. Obviously, the peaks of ruthenium oxide (Ref. Code 00-040-1) can be found in the XRD patterns of all the catalysts as shown in Figure 1, and the intensities of these peaks increase with increasing Ru content. Combined with the evidence of low-angle XRD and UV-vis in previous report^[23], which proves the incorporation of ruthenium atoms in the framework of MCM-48, this observation confirms that ruthenium species simultaneously present in the framework and on the surface of MCM-48.

Figure 2 shows the N₂ adsorption/desorption results obtained for Ru-doped MCM-48 and MCM-48. For all the samples studied, the isotherms display a typical type IV isotherm of mesoporous materials with steep rises in the relative pressure range of 0.2 ~ 0.3

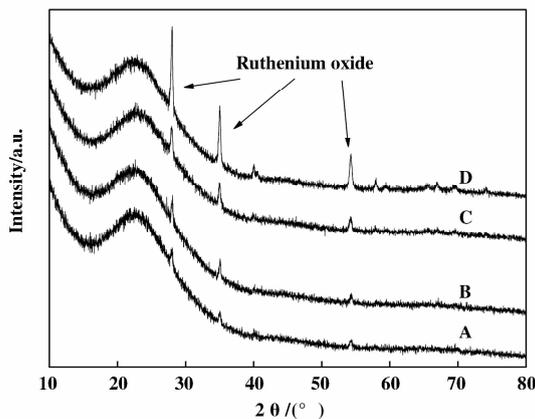


Fig. 1 XRD patterns of Ru-MCM-48 catalysts

due to capillary condensation of nitrogen in the pores^[24]. This suggests that all the samples possess well mesoporous ordering with narrow pore size distribution. BET surface area, pore volume and average pore diameter for all the samples are given in Table 1,

which also includes the Ru content in the samples determined by ICP. The results show the characteristics of mesoporous material, such as high surface area ($> 1\,300\text{ m}^2/\text{g}$) and uniform pore size ($\approx 2.7\text{ nm}$) for both Ru-doped MCM-48 and MCM-48.

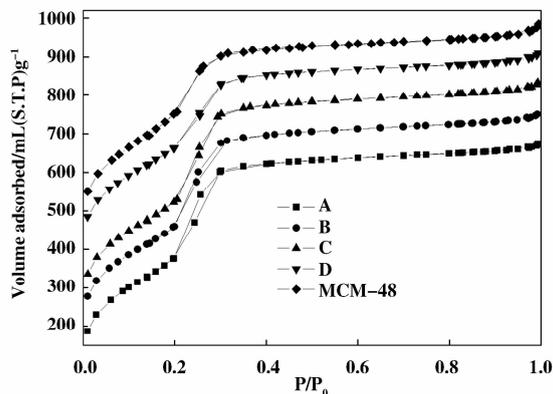
Fig. 2 N_2 adsorption/desorption isotherms of MCM-48 and Ru-MCM-48 catalysts

Table 1 Textual properties of MCM-48 and Ru-MCM-48 catalyst

Catalyst	Ru /%	Si/Ru (in product)	Si/Ru (in gel)	d_{211}^a /nm	a_0^b /nm	S_{BET}^c /($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Average pore diameter/nm
A	0.49	341.32	300	3.32	8.13	1 400	1.17	2.93
B	0.71	234.87	200	3.29	8.06	1 334	1.14	2.97
C	1.38	119.76	100	3.34	8.18	1 385	1.19	2.99
D	2.33	70.03	50	3.37	8.25	1 320	1.08	2.74
MCM-48	-	-	-	3.22	7.89	1 481	1.15	2.53

^a,^[23], d value of peaks (211) in low-angle XRD patterns.

^b, the cell parameter a_0 is calculated from the formula $a_0 = d_{211}6^{0.5}$.

^c, BET surface area.

The FT-IR spectra of all samples are shown in Figure 3. The band at $400 \sim 1\,300\text{ cm}^{-1}$ is attributed to framework stretching vibration area of mesoporous molecular sieves. Generally, the band at 960 cm^{-1} is assigned to Si-OH stretching vibrations in calcined mesoporous molecular sieves. However, it can also be assigned to Si-O-Metal group when metal atoms are doped. Obviously, the intensity of the band at 960 cm^{-1} for Ru-doped MCM-48 catalysts, which increases with the increment of Ru content, is higher than that for MCM-48. In addition, a red shift of this absorption

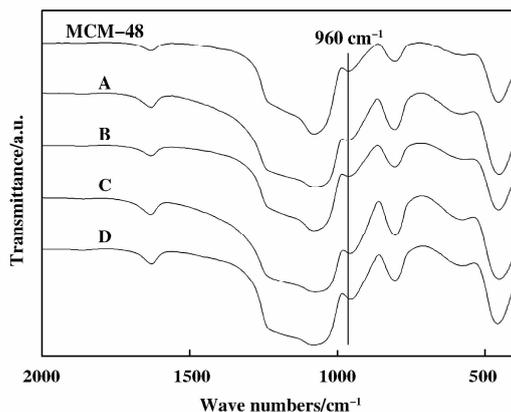


Fig. 3 FT-IR spectra of MCM-48 and Ru-MCM-48 catalyst

band with increasing Ru content was also observed. These suggest the incorporation of Ru atom into the framework of MCM-48 material, consistent with XRD and UV-vis results^[23].

HRTEM and FE-SEM images of pure siliceous MCM-48 and catalyst B are shown in Figure 4. It can be observed clearly from the FE-SEM images that the MCM-48 and catalyst B are composed of nearly-spheri-

cal particles with size ranging from 100 to 700 nm. The similarity in morphology between the two samples suggests the little influence of the doped Ru on the crystallization process. HRTEM photos, which provide the direct observation of morphology, show the highly ordered arrangement of the channels in both MCM-48 and catalyst B. These results are consistent with the observation of low-angle XRD^[23] and N₂ sorption.

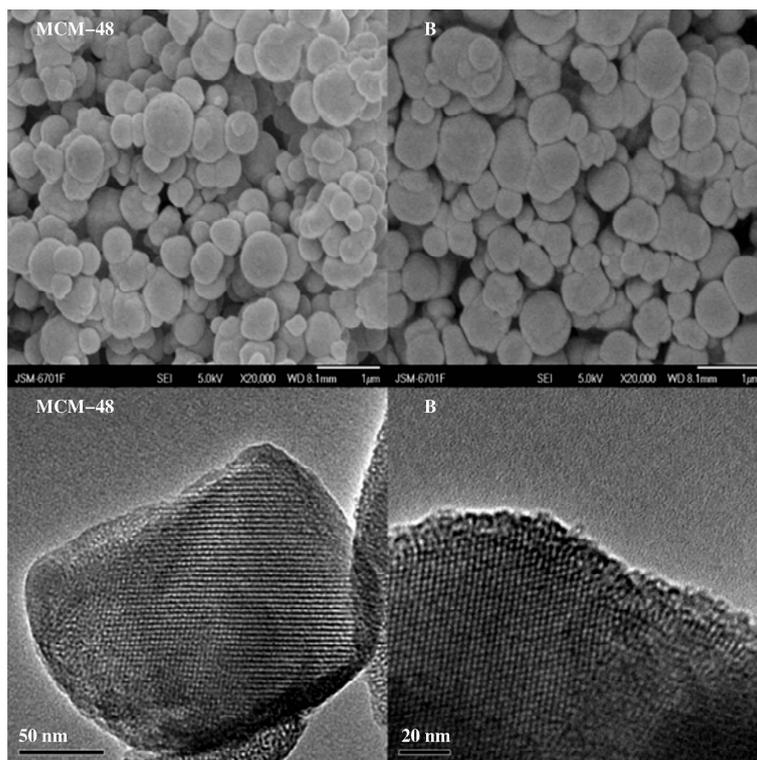


Fig. 4 SEM and HRTEM images of MCM-48 and catalyst B

2.2 Catalytic Results

Figure 5 summarizes the catalytic activities of Ru-doped MCM-48 catalysts in the oxidation of cyclohexane using air as the oxidant and TBHP as initiator without any solvent. For comparison, the data for oxidation of cyclohexane using O₂ as oxidant on catalyst C is also listed in Figure 5. GC-MS indicates that the main products are cyclohexanol and cyclohexanone, and the by-products include adipic acid and some esters. It is found that all the catalysts show a considerable catalytic performance for cyclohexane oxidation by air, and the catalytic activity of the catalysts increase with increasing Ru content. However, the catalysts with high Ru content give a higher ratio of cyclohexanone/cyclohexanol and a higher selectivity to by-pro-

ducts than the catalysts with low Ru content. This could be ascribed to the high content of RuO₂ on the MCM-48 surface which enhances the deep oxidation of the product. It is also found that catalyst C using air shows almost the same catalytic activity as that using O₂ as oxidant, indicating that Ru-doped MCM-48 is an efficient catalyst for cyclohexane oxidation under a mild condition. Moreover, pure siliceous MCM-48 shows no activity for this reaction, indicating that Ru is the active species for cyclohexane oxidation using air as oxidant. For comparison, RuO₂/SiO₂ and RuO₂/MCM-48 prepared by precipitation method with the equal Ru content of catalyst B were also tested for catalytic oxidation of cyclohexane and the results are also listed in Figure 5. Compared with catalyst B, both precipitation

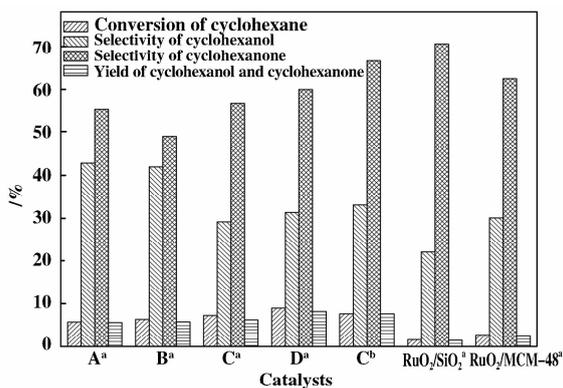


Fig. 5 Catalytic oxidation of cyclohexane over various catalysts by air

^a, reaction conditions: 2 mL cyclohexane, 1MPa air, 0.1 mL TBHP, 20 mg catalyst, 130 °C, 24 h.

^b, [23], reaction condition: 2 mL cyclohexane, 1 MPa O₂, 10 mg catalyst, 150 °C, 4 h

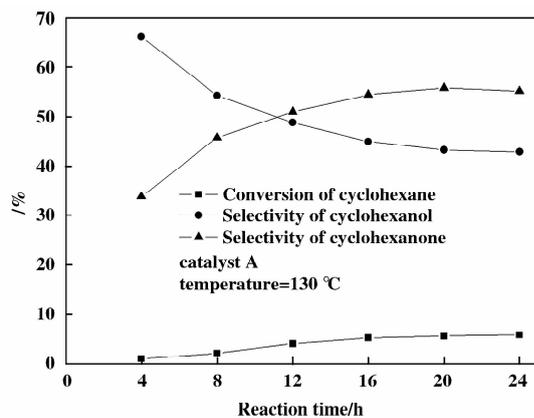
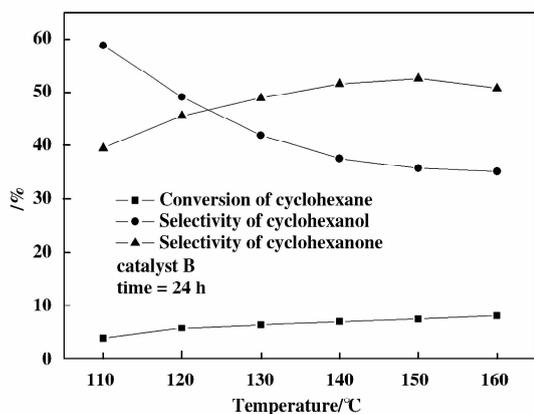


Fig. 6 Effect of reaction time and temperature on the conversion and selectivity

decrease when the reaction was carried out for much longer time or at higher temperature.

In order to evaluate the recyclable potentials of Ru-doped MCM-48 catalysts, catalyst D was separated from the reaction mixture and reused for the cyclohexane oxidation in air. The results for recycling tests are shown in Figure 7. It can be seen that both cyclohexane conversion and total selectivity to cyclohexanol and cyclohexanone decrease slightly with increasing reaction cycles. This could be attributed to the leaching of active Ru species and the shrinkage of the framework during the reaction. The recycling tests revealed that Ru-doped MCM-48 catalysts are very stable and behave truly as heterogeneous catalysts.

samples give a low conversion of cyclohexane and a high selectivity to cyclohexanone. The poor performance of both catalysts can be attributed to RuO₂ that enhanced the deep oxidation of cyclohexanol. In contrast, the Ru-doped MCM-48 show good performance in oxidation of cyclohexane because of the presence of the highly dispersed Ru species in the framework.

Figure 6 illustrates the effect of reaction time and temperature under the conditions described in the chart. With the increase of reaction time and temperature, obviously, the conversion of cyclohexane and the selectivity to cyclohexanone increase, while the selectivity to cyclohexanol decrease. It should be noted that, with the conversion of cyclohexane increasing, the total selectivities to cyclohexanol and cyclohexanone

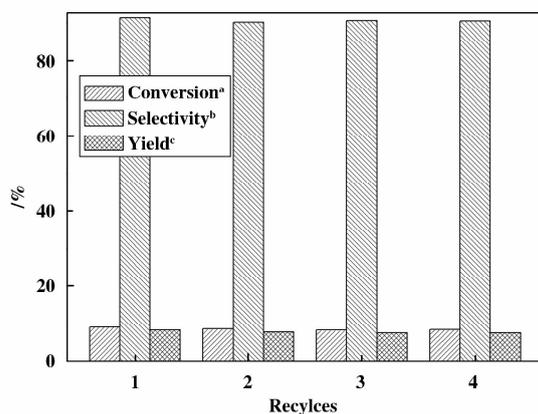


Fig. 7 Leaching and recycling tests over the Ru-MCM-48 catalysts

a: cyclohexane conversion. b: the selectivity of cyclohexanol and cyclohexanone. c: the yield of cyclohexanol and cyclohexanone.

3 Conclusions

In summary, the characterization results prove that the Ru-doped MCM-48 mesoporous molecular sieves synthesized by a rapid and facile way without employing hydrothermal synthesis have good crystallinity, well-ordered mesoporous structure and high surface area. In addition, the ruthenium species simultaneously present in the framework and on the surface of MCM-48. These synthesized mesoporous materials are efficient catalysts for oxidation of cyclohexane using air as the oxidant in a solvent-free system, indicating that Ru-doped MCM-48 is an environment-friendly heterogeneous catalyst. Furthermore, catalytic oxidation results reveal that the highly disperse Ru species in the framework of MCM-48 is more active than the RuO₂ species on the MCM-48 surface and that RuO₂ can lead to the deep oxidation of cyclohexane to produce other oxygenates.

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钌掺杂 MCM-48 介孔分子筛的表征及催化氧化环己烷性能的研究

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摘要: 以在室温条件下快速制备的一系列 Ru 掺杂的 MCM-48 介孔分子筛为催化剂, 进行了无溶剂条件下空气催化氧化环己烷制环己醇和环己酮的反应研究, 并通过 XRD、N₂ 吸附脱附、FT-IR 等多种表征手段对该催化剂进行系统研究. 表征结果表明该催化剂具有典型的 MCM-48 介孔材料结构, 合成过程中加入的 Ru 以不同形态同时存在于催化剂中. 催化反应的结果显示该催化剂在较温和反应条件下具有良好催化活性, 并且不同的 Ru 物种在反应中呈现不同的活性.

关键词: 介孔分子筛; MCM-48; 表征; 环己烷氧化