

O23: Microwave improve fats speed chemistry: a new technique in oxidation of benzylic alcohols on composites materials Cr (ZSM-5/MCM41)

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Abstract:

Direct oxidation of benzylic alcohols to their corresponding ketones on Cr(ZSM-5/MCM41) composite materials catalyst with t-BuOOH as terminal oxidant is carried out under microwave irradiation in high yield and with high stereoselectivity. Then the ketones were obtained under solventless conditions on silica gel media, with 80% yield and reaction time 10 min. The Composite materials Cr-(MCM41/ZSM5) used were exchanged at low content of chromium and containing both micropores and mesopores structures and were very selective and stable for this type of reaction. High conversion rates compared to the others catalysts was obtained.

Keywords: benzylic oxidation, microwaves, composite materials; catalyse, chromium exchange

Introduction:

The objective of using microwave as an energy source for chemical reactions concerning solid catalysts has been checked up intensively in this recent years [1,2]. These studies show that in some cases the reaction rates are improved while in others the product selectivity changes when microwave radiation is used instead of conventional heating. Whether this is due to faster and selective dielectric heating provided by microwave or due to any specific microwave effect (e.g.: specific bond activation), is a subject of discussion [3–7]. A profit of microwave heating compared to other heating methods is that any substance with high dielectric loss factor can combine easily with microwave radiation and gets heated. Microwave heating can be very useful for otherwise relatively slow reactions. Since the first publications on the application of microwave-assisted organic synthesis in the mid-1980s,

[7] this technology has been developing rapidly organic synthesis under solventless conditions. And is encouraged for environmental protection reasons [8]. In the first experiments, Geeye, and Giguere could record dramatic accelerations in some traditional organic reactions [9,10] hence microwave technology can reduce the reaction times and energy consumption and may lead to an increase in yields and selectivity in some cases [11]. Heterogeneous catalysis has also proved to be very effective in enhancing selectivity. Zeolites and mesoporous materials have been successfully employed in the selective oxidation of

aromatics, alcohols and alkenes [12] and for some chemical applications [13]. A great number of examples of reactions were described in the organic synthesis [14]: the reactions of cyclic additions[15], the synthesis of the radio-isotopes[16], the chemistry of the fluorine[17-18], polymers[19], heterocyclic chemistry [20-21]carbohydrates[22], homogeneous and heterogeneous catalyse [23], medical and combinative chemistry [24] and green chemistry [25-26]. However the use of solvents in this type of reactions led to problems of safety, because some explosions were noted [9,10], the later developments showed that reactions free from solvents can solve these problems of safety, facilitate and reduce the number of the preparatory stages of the reactions.

In this work direct oxidation of benzylic alcohols to their corresponding ketones on

Cr (ZSM-5/MCM41) composite materials catalyst with t-BuOOH as terminal oxidant is used as a model reaction to determine the influence of microwave irradiation on catalytic reactions of organic compounds. The choice of this model reaction is not only due to the economic and scientific importance of the reaction but also due to the fact that this reaction has been investigated extensively in the past 20 years [27,28].

The oxidation reaction was carried out free from solvents.

The composite materials used as catalyst were molecular sieves with a bimodal pore size distribution, combining the advantages of both the microporous and the mesoporous materials. This two-fold molecular sieve might have potential applications in adsorption and catalysis [29]. For instance, these materials proved to be also active for solid acid catalysts [30]. From catalytic point of view, the composite materials Cr-(50-MCM41/ ZSM5) prepared by our research was investigated on the oxidation reaction of the benzylic alcohols.

2. EXPERIMENTAL SECTION:

2.1 The chemicals:

The chemicals used for the syntheses were colloidal solution of silica (Ludox HS40 Dupont, 40%SiO₂, 60%H₂O), tetrapropylammonium bromide (TPABr (γ7%, Aldrich) cetyltrimethylammonium bromide (CTAC Br) (98%, Fluka), sodium aluminates NaAl₂O₃ (65% Al₂O₃, 27% Na₂O, Aldrich), sodium hydroxide (98%, Fluka) and deionised water.

The products of exchange were the salts of chromium nitrate (>99 %, Aldrich), the deionised water and the MeNH₂ (40wt % in water, Fluka).

2.2 The catalyst preparation:

A synthesis procedure described earlier [31] was modified for mixtures of the C₆[C₆H₁₃(CH₃)NBr] and C₁₄[C₁₄H₂₉(CH₃)₃NBr] templates/surfactants. The concentrations of ammonium were scaled according to: C₆ (wt) + C₁₄ (wt)= 100%, where C₆ (wt) =50% and C₁₄ (wt) =50%

A synthesis of the composite materials Al MCM41/ ZSM5 were obtained by two step procedure:

Solution A: The mixture of the template agents were dissolved in water under magnetic stirring at room temperature for 15 min.

Solution B: For the preparation of aluminosilicate material: aluminate sodium used as source of Al was added to sodium hydroxide and subsequently dissolved in water at 50°C for 10 min. Then a solution of silica Ludox 40 was added to the previous solution under stirring with magnetic stirrer at room temperature for 15min.

The solution B was poured onto the solution A drop wise under continuous stirring for 24h at room temperature.

The gel of the surfactants/silica mixture obtained has the following composition: 100 SiO₂, 1Al₂O₃, 20 Na₂O, 20 TPA₂O, 20CTA₂O, 7000H₂O.

Finally the gel mixture was transferred into the tubes of glass Pyrex sealed by Teflon ribbon in order to avoid the losses of material during the heating. The tubes were placed vertically into beakers and were introduced into the drying oven. Then the gel was crystallised at the temperature of 130°C under static conditions and atmospheric pressure for 4 days. The resulting solids were recovered by filtration, completely washed with distilled water 3 to 4 times and then dried to 100 °C overnight. The calcination of the as-synthesised materials was carried out at 500 °C with heating rate of 3 °C/min in air for 6 h to remove the template molecules. The obtained solid is denoted 50(MCM41/ZSM5).

The cationic exchange of the 50(MCM41/ZSM5) by chromium ions was obtained by the following procedure: 1gram of the calcined product was ion exchanged in 100 ml of a solution of 0.5 M NaCl for 24 h at ambient temperature and pH = 5 –6, This initial Na⁺ ion-exchange was followed by a second (24h) under gentle agitation in fresh solutions, to obtain Na-50(MCM41/ZSM5).

The Na-50(MCM41/ZSM5) samples were subsequently exchanged with Cr³⁺ ions, again with 1 gram solid in 40 ml solution of 0.1M Cr(NO₃)₂. The chromium ion exchanges were done under stirring at 50°C for 3h. The pH control was employed throughout all ion-exchanges and the pH value was adjusted to the desired range (5-6) by adding MeNH₂ (40wt % in water) before introducing the solid. The final solid was recovered by filtration, washed several times with de-ionised water and dried (150°C, 5 h) before being analysed by various characterisations. The chromium exchanged composite material obtained is denoted Cr-(50-MCM 41/ZSM5).

2.4 catalyst characterisation:

The Cr (50-MCM41/ZSM5) was characterized by powder X-ray diffraction using a Philips PW 1801/29 diffractometer with CuK α radiation. The similarity of the intensity of the main peaks of Cr (50-MCM 41/ZSM5) and (50 MCM 41 /ZSM5) spectra indicated that the alteration of the structure in the course of the ion exchanges is not significant (Figure 1 and 2).

Specific surface area and pore volume measurements were obtained from volumetric nitrogen adsorption using ASAP 2010 instrument. Nitrogen adsorption measurements were

performed at liquid nitrogen temperature. The BET surface area measured was 560m²/g (figure 3).

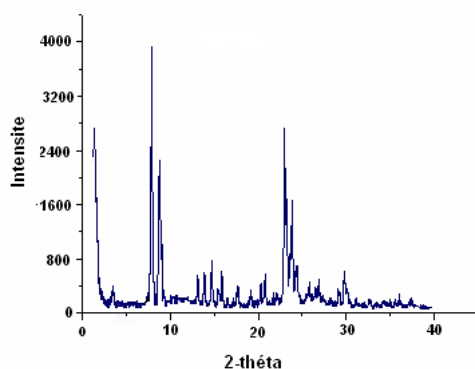


Figure.1: X-rays diffraction patterns
of calcined 50-(MCM 41 /ZSM5)

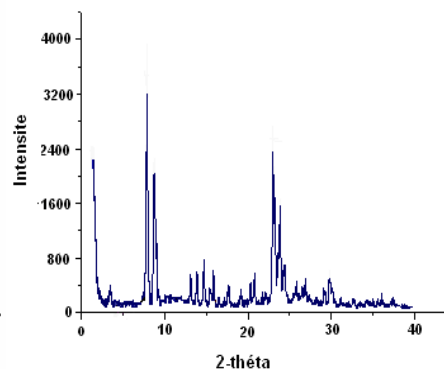


Figure 2: X-rays diffraction patterns
of Cr (50-MCM 41 /ZSM5)

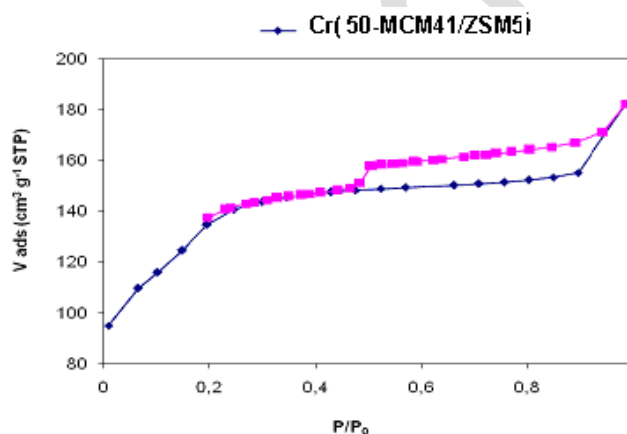


Figure.3: the BET surface area of Cr (50-MCM 41/ZSM5)

2.5. Catalytic testing:

The oxidation procedure:

The oxidation of the secondary benzylic alcohols over the Cr-(50- MCM41/

ZSM5) catalysts was performed by using the following procedure: A mixture of the secondary benzylic alcohol as substrate (1mmol), 70% aqueous t-BuOOH, (4mmol) +Cr-(50- MCM41/ ZSM5) (5mg) was closely mixed with silica gel (5mg) and it is introduced into the vessel of 50 ml in the machine of microwave(Discover, CEM-SP1245 model, USA).

The reaction conditions were recorded on the machine; the temperature of 100°C is selected under an atmospheric pressure. The oxidation was done under backward flow without solvent (dry). The reaction is stopped after 10 min. The reactional mixture obtained is filtered on column Al₂O₃ an aluminium, rinsed with ether diethylic to eliminate the t-BuOOH (which does not have reacted) the characterization of the obtained product is carried out by the chromatography GPC phase and the spectroscopy mass.

3. RESULTS AND DISCUSSION:

Table 1: Oxidation of benzylic alcohols on the microwaves (Discover, CEM-SP1245 model)

Substrate	Product (% conversion)
Benzohydrol	Benzophénone (100)
Trans2 phenyl1 Cyclohexanol	Trans2 phenyl1 Cyclohexanone (56)
Cyclopropyl phenyl carbinol	Cyclopropyl phenyl cétone (95)
Méthyl p tolyl carbinol	Méthyl p tolyl cétone (99)
1phenyl -1propanol	1phenyl -1propanone (95)
1-indanol	1-indanone (99)

Taking into account the results of the analyses by gas chromatography and mass spectrometry, we noted that the composite material Cr (50-MCM41/ZSM5) was very selective catalyst for the oxidation of benzylic alcohols to the corresponding ketones. Total conversions were obtained for drastic timing 10mn only. However for the case of the trans2 phenyl1 Cyclohexanol, the conversion was only 56%.

4. CONCLUSIONS:

The technology of microwaves can reduce the reaction times and the energy consumption and can lead to an increase in the outputs and selectivity of the oxidative reactions

The use of composite materials with feeble chromium content and the realization of these reactions in dry medium, in an environment free from organic solvent are another behaviour and aspect of green chemistry [31, 32]

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