Catalytic behaviour of chromium supported mesoporous MCM-41 silica in the oxidative dehydrogenation of propane

J. Santamaría-González, J. Mérida-Robles, M. Alcántara-Rodríguez, P. Maireles-Torres,
E. Rodríguez-Castellón and A. Jiménez-López *

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

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A series of chromium supported mesoporous MCM-41 silica catalysts (0.5–6 wt% Cr) were prepared and tested in the oxidative dehydrogenation of propane between 350 and 550 °C. The catalytic activity, observed at temperatures as low as 350 °C, can be well explained on the basis of the existence of highly dispersed and reducible chromium species.

Keywords: chromium supported catalysts, MCM-41, oxidative dehydrogenation of propane, mesoporous solids

1. Introduction

Upgrading of light alkanes is one of the main challenges of the refining and petrochemistry industries because it supposes adding value to cheap feedstocks. In this line transformation of such compounds in olefins or by partial oxidation in aldehydes or acids represents two processes very studied [1]. Dehydrogenation of alkanes in inert atmosphere is an industrial reaction to obtain alkenes for polymerization and other organic syntheses [2]. Although this reaction is very selective to olefins, it suffers from high deactivation by coking and from the high endothermicity of the reaction, making necessary the use of catalysts and supports with high thermal stability.

Dehydrogenation of alkanes can be also accomplished under oxidative conditions, an exothermal reaction which takes place at much lower temperatures than that of pure dehydrogenation. However, the main limitation of this process is the parallel total oxidation reaction leading to CO_x formation. Vanadium and molybdenum oxides are the most commonly used active phases supported on a varied set of materials [3–6].

It has been extensively proved that the effectiveness of this type of catalysts depends upon the dispersion degree of the active phase. Recently we have found that nanoparticles of chromia [7] or mixed gallium oxide/chromia [8] intercalated between the layers of α-zirconium phosphate, which originate porous materials with large specific surface areas, are quite active in the oxidative dehydrogenation of propane at temperatures as low as 400 °C.

On the other hand, Mobil scientists have reported, at the beginning of 90s, the synthesis of a new family of mesoporous solids denominated as MCM-41 [9]. They exhibit a hexagonal arrangement of cylindrical channels of which the diameters can be tuned between 16 and more than 100 Å. However, in spite of their very high specific surface area they exhibit a low acidity when they are based on a silica matrix. Therefore, many efforts have been devoted to the introduction in both the silicate framework or on the internal silicate surface of different metal atoms such as Al, Ti, V, Zr and Cr in order to impart acid and/or redox properties to the resulting mesoporous structures [10].

We have previously reported that structurally chromium-doped mesoporous MCM-41 silicas are catalytically active in the dehydrogenation of propane, in oxidative and non-oxidative conditions [11]. In the present work we describe the results of the study of the catalytic behavior in the oxidative dehydrogenation of propane of catalysts based on chromia supported mesoporous silica, in which the chromium content ranged between 0.5 and 6 wt%. The chemical and structural characterization of these catalysts has been previously reported [12] and these results will be used in order to establish a correlation of their catalytic activities with properties such as the degree of chromia dispersion, reducibility of chromium species or acidity of catalysts.

2. Experimental

Mesoporous silica, Si-MCM-41, has been prepared by adding an aqueous solution of cetyltrimethylammonium chloride (Aldrich, 25 wt%) to an ethanolic solution of tetraethoxysilane (Aldrich, 98%, 20.4 ml TEOS in 33 ml ethanol). The surfactant : Si molar ratio was 2. The pH was adjusted to 11 by addition of an aqueous solution of tetramethylammonium hydroxide (Aldrich 25 wt%, 5 ml). After stirring the resulting gel at room temperature for three days, a solid was recovered by centrifugation, washed with ethanol and water, air-dried and finally calcined in air at 550 °C.

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* To whom correspondence should be addressed.

Chromium-impregnated samples were prepared by using the incipient wetness method. Thus, 1 g of calcined mesoporous silica was treated with 1.8 ml of chromium nitrate aqueous solution containing the desired amount of chromium. Water was then evaporated in an oven at 60 °C and the dry material was then heated at 550 °C for 5 h in air. The samples are designated hereinafter as xCr-MCM were x means the total weight percentage of chromium.

All catalysts were characterized by X-ray diffraction using a Siemens D501 diffractometer (Cu K_α source) provided with a graphite monochromator. Textural parameters have been obtained from N_2 adsorption–desorption isotherms determined using a glass conventional volumetric apparatus at 77 K, after outgassing the catalysts at 200 °C and 10^{-2} Pa overnight. Pore size distributions were calculated with the Cranston and Inkley method for cylindrical pores [13]. UV-vis spectroscopy studies were carried out in diffuse reflectance mode with a Shimadzu MPC 3100 spectrophotometer and taking $BaSO_4$ as reference. The X-ray photoelectron spectra (XPS) were recorded with a Physical Electronics 5700 instrument provided with a multichannel hemispherical electron analyzer, the band-pass energy being 29.35 eV. The Mg Kα X-ray excitation source ($h\nu = 1253.6$ eV) was at a power of 300 W. The pressure in the analysis chamber was maintained below 1.3×10^{-7} Pa during data acquisition. The binding energies (BE) were obtained with ±0.2 eV accuracy and charge compensation was done with the adventitious C 1s peak at 248.8 eV. Thermal-programmed desorption of ammonia (NH_3-TPD) was used to determine the total acidity of the catalysts. Before the adsorption of ammonia at 100 °C the samples were heated at 500 °C in a He flow (35 ml min^{-1}) for 1 h. The NH_3-TPD was performed between 100 and 500 °C, with a heating rate of 10 °C min^{-1}. The evolved ammonia was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) provided with a thermal conductivity detector.

Temperature-programmed reduction (TPR) of thermally treated impregnated samples was performed between 100 and 700 °C, using a flow of Ar/H_2 (40 cm^3 min^{-1}, 10% of H_2) and a heating rate of 10 °C min^{-1}. Water produced in the reduction reaction was eliminated by passing the gas flow through a cold finger (−80 °C). The consumption of hydrogen was controlled by an on-line gas chromatograph provided with a TCD.

Catalytic activity in the dehydrogenation of propane under oxidative conditions was measured in a fixed-bed quartz U-tube microcatalytic flow reactor working at atmospheric pressure. Samples were previously treated at 400 °C under a He flow (30 ml min^{-1}) for 1 h. The gas reaction mixture was constituted of 7.06 mol% propane in O_2/N_2 (19.5/73.4 mol%) and a total flow rate equal to 28.32 ml min^{-1}. The F/W values ranged between 4.27 and 21.86 mol-C_3 h^{-1} g^{-1}. In these conditions, both external and internal diffusional limitations were absent. Analysis of the products was performed using an on-line gas chromatograph (Shimadzu GC-14B) provided with a column (7 m in length and 5 mm internal diameter) filled with sebaconitrile and a flame ionization detector. The analysis of CO_2 was carried out on-line with a packed column Poropack A (2.5 m in length, $1/8''$ OD) and using a TCD.

3. Results and discussion

In a previous communication, the structural characterization of different chromium supported catalysts has been extensively reported [12]. Thus, powder X-ray diffraction and N_2 adsorption–desorption at 77 K results have shown the structural stability of the MCM-41 silica support after the impregnation process. Regarding the BET surface areas and pore volume of the catalysts, they are slightly modified after impregnation with respect to those of the pristine mesoporous silica, the values ranging between 833 and 895 m^2 g^{-1} and between 0.570 and 0.646 cm^3 g^{-1}, respectively. Moreover, XRD data and infrared spectroscopy have only proved the existence of chromium oxide crystallites for catalysts with Cr content higher than 1.5 wt%.

XPS analysis has been employed to obtain information of superficial composition of catalysts and, therefore, of chromium dispersion. The absorption curves in the region of Cr $2p_{3/2}$ showed an asymmetric peak centered at 576.5 eV assigned to Cr(III), which can be deconvoluted in two components, one main at low energy (576.7 eV) due to Cr(III) and another small at high binding energy (578.9 eV) assigned to Cr(VI). The percentage of contribution of Cr(VI) to the total area changes with the chromium loading, being higher at low loading of chromium, as observed in other catalytic systems [14].

The presence of Cr(VI) species has been corroborated by UV-vis spectroscopy (figure 1). As it is known, Cr(VI) in tetrahedral coordination, as in CrO_4^{2-} ions, exhibits two intense charge transfer bands close to 280 and 370 nm, whereas octahedral Cr(III) shows three bands due to $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions which appear near to 350, 400–500 and 600–700 nm, respectively. The UV-vis spectra of catalysts reflect the coexistence of both Cr(VI) and Cr(III) species because a band at 269 nm (Cr(VI)) appears, which decreases in intensity as the chromium loading increases. The group of three bands at 354–360, 400 and 600 nm is typical of octahedral Cr(III); these bands became more intense with the chromium content.

Figure 2 shows the H_2-TPR curves of the chromium supported silica MCM catalysts. In all cases, the reduction of chromium species is accomplished in two distinctive steps. A first consumption of hydrogen can be observed which takes place at low temperature (310–350 °C) and could be attributed to the reduction of chromium species in high oxidation states to Cr(III). The second band at higher temperature (400–450 °C) is assigned to the reduction of Cr(III) to Cr(II). The H_2-TPR curve of the 1.5Cr-MCM catalyst shows the highest area of the band corresponding to the more reducible Cr species. In effect, this catalyst has the highest percentage of chromium dispersed but without presence of chromia crystallites.

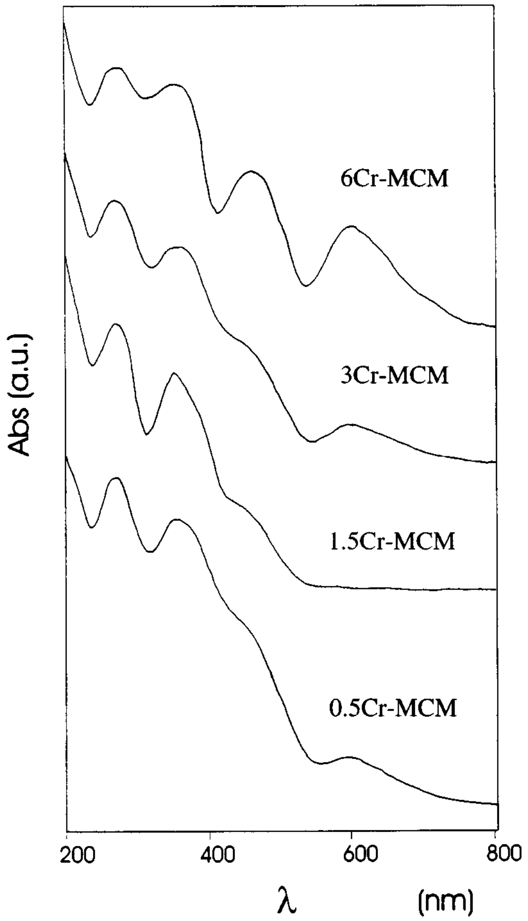

Figure 1. UV-vis diffuse reflectance spectra of chromium supported silica MCM catalysts with different wt% Cr.

In contrast to the pristine silica MCM-41, chromia supported silica catalysts are solid acids, as deduced from NH_3-TPD. Thus, total amounts of desorbed ammonia, between 100 and 500 °C, ranged between 177 and 640 μmol g^{-1}, decreasing with the chromium loading. This evolution has been justified as a result of the dispersion degree of the active phase, the lowest acidity being found for the sample with 6 wt% Cr which, at the same time, revealed in its XRD pattern the formation of microcrystallites of chromia on the support surface.

Catalytic data

This new group of catalysts based on chromia supported on silica MCM materials with chromium loading of 0.5, 1.5, 3 and 6 wt% has been tested in the oxidative dehydrogenation of propane at different temperatures. The silica MCM support was inactive; therefore, the observed catalytic activity of chromia-containing solids must be associated to the presence of chromium species. Propene and CO_x were the main products formed during the oxidation of propane on these catalysts, whereas O-containing organic compounds were not detected. Furthermore, under the described experimental conditions a small deactivation occurred depending on the catalyst; in consequence all the experimental data have been taken after 120 min of time on stream.

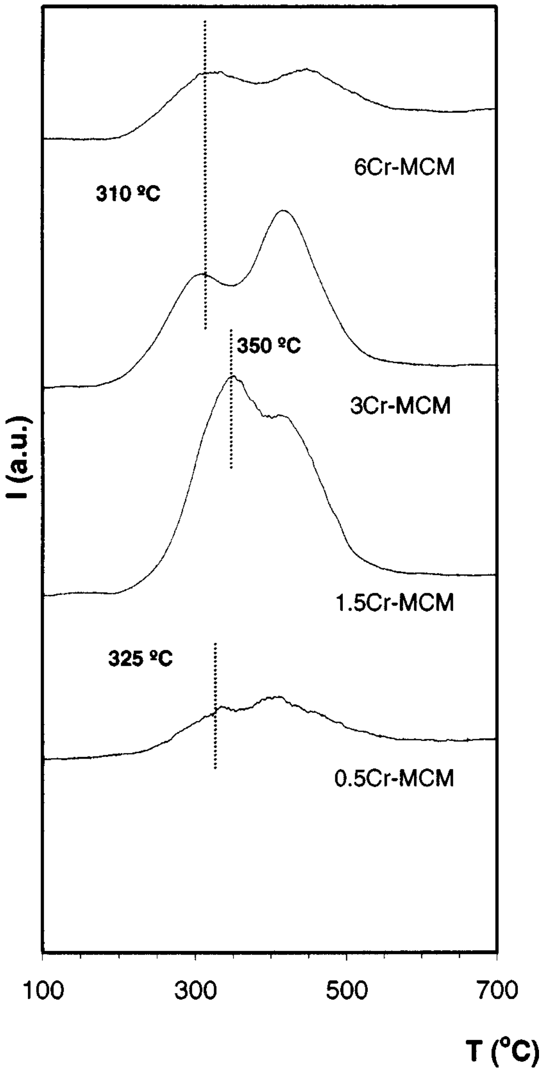

Figure 2. H_2-TPR profiles of the hydrogen consumption of the chromium supported silica MCM catalysts.

The variation of the propane conversion as a function of the reaction temperature of chromia supported silica MCM-41 catalysts (figure 3) reveals that the propane conversion depends upon the chromium content and for each catalyst increases with temperature. On the other hand, the 1.5Cr-MCM catalyst exhibits the maxima values of conversion in the whole range of temperatures studied. Table 1 compiles the catalytic data for the propane oxidation at 500 °C and the selectivities to the main reaction products along the group of catalysts. The rate of propene formation increases with the chromium loading up to the 1.5Cr-MCM sample, and then it is maintained in a lower value, close to 2.2 μmol g^{-1} s^{-1}, for higher chromium contents. These results are expected since Cr(III) species are the active centers in this reaction and the dispersion degree of chromium rapidly decreases for loadings higher than 1.5 wt%. The appearance of microcrystallites of Cr_2O_3 in the XRD patterns of these latter catalysts has confirmed this assumption. This

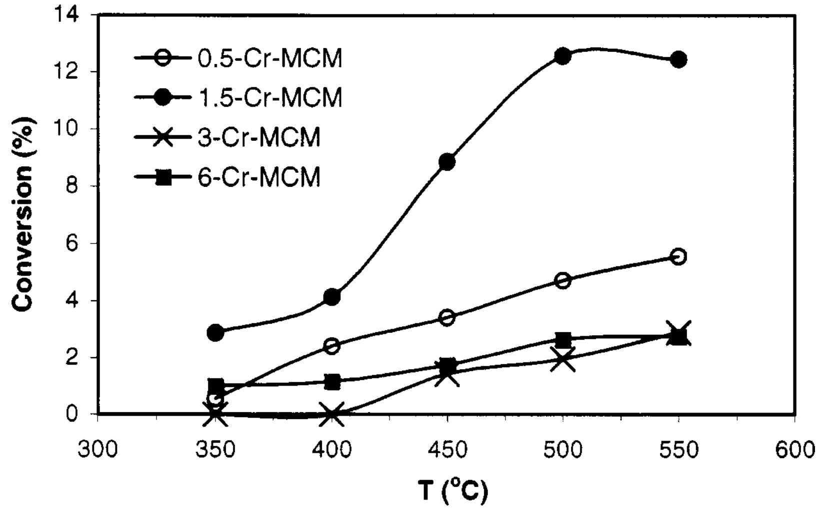

Figure 3. Conversion of propane as a function of the reaction temperature during the oxidative dehydrogenation of propane on chromium supported silica MCM catalysts. ($F/W = 13.73$ mol-C_3 h^{-1} g^{-1}.)

Table 1
Catalytic behavior of chromium supported silica MCM catalysts in the oxidative dehydrogenation of propane at 500 °C, after 120 min on-stream ($F/W = 13.73$ mol-C_3 h^{-1} g^{-1}).

Catalyst	Conversion (%)	Selectivity (%) Propene	CO	CO_2	Rate (μmol-C_3H_6 g_{cat}^{-1} s^{-1})	TOF $\times 10^{20}$ (μmol-C_3H_6 at-Cr^{-1} s^{-1})	Yield (%)
0.5Cr-MCM	4.7	19.4	49.4	31.0	1.8	3.11	0.9
1.5Cr-MCM	12.4	18.4	49.9	31.4	4.6	2.65	2.3
3Cr-MCM	1.9	56.8	14.1	28.4	2.2	0.63	1.1
6Cr-MCM	2.6	38.6	42.0	19.0	2.1	0.30	1.0

fact has already been described by other authors, who found that the presence of chromia crystallites had a negative influence on the formation rate of olefins [15]. On the other hand, the existence of an intense peak at low temperature (ca. 350 °C) in the TPR curves of the 1.5Cr-MCM sample indicates that its reducibility is very high. Therefore, the redox properties of these catalysts, which are correlated with the dispersion degree of the active phase, can well account for their catalytic activity in the oxidative dehydrogenation of propane.

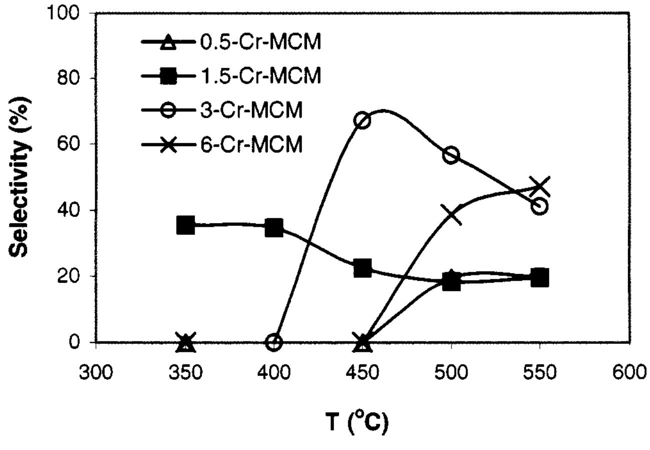

Figure 4. Dependence of selectivity to propene on the reaction temperature in the ODH of propane. ($F/W = 13.73$ mol-C_3 h^{-1} g^{-1}.)

Turnover frequencies (TOF), considering only the activity of Cr species, decrease with the chromium content due to its lower dispersion degree. Thus, the samples with 3 and 6 wt% of Cr content which have low dispersion exhibit the lowest turnover frequency values. The variation of the selectivity to propene with the reaction temperature can be observed in figure 4. It is noticeable that only the 1.5Cr-MCM catalyst produces propene in the whole range of temperatures studied. The other catalysts only generate CO at temperatures lower than 450 °C. On the other hand, the selectivity to propene decreases with the reaction temperature, clearly indicating that the higher the temperature the higher the rates of secondary reactions, in which the formation of CO_x products takes place. The evolution of the selectivity with the conversion has been studied in detail on 1.5Cr-MCM (figure 5). All the curves obtained at different temperatures show a rapid decay with conversion, indicating that the formation of CO_x products takes place. Thus, only for conversion percentages lower than 5% the selectivity values are important.

On the other hand, the values of the propene yields in the oxidative dehydrogenation reaction are lower than those found on chromia and mixed chromia/gallia pillared α-zirconium phosphate where a high dispersion of chromium was attained, and the formation of chromia crystallites was never found [7,8]. Moreover, the experimental yield values observed in our chromia supported silica MCM catalysts

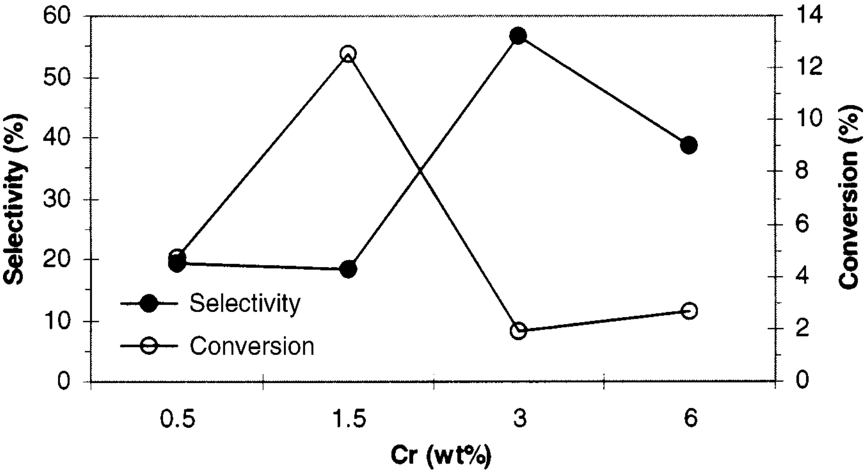

Figure 5. Variation of the conversion of propane and the selectivity to propene versus the chromium loading. ($F/W = 13.73$ mol-C_3 h^{-1} g^{-1}) at 500 °C.

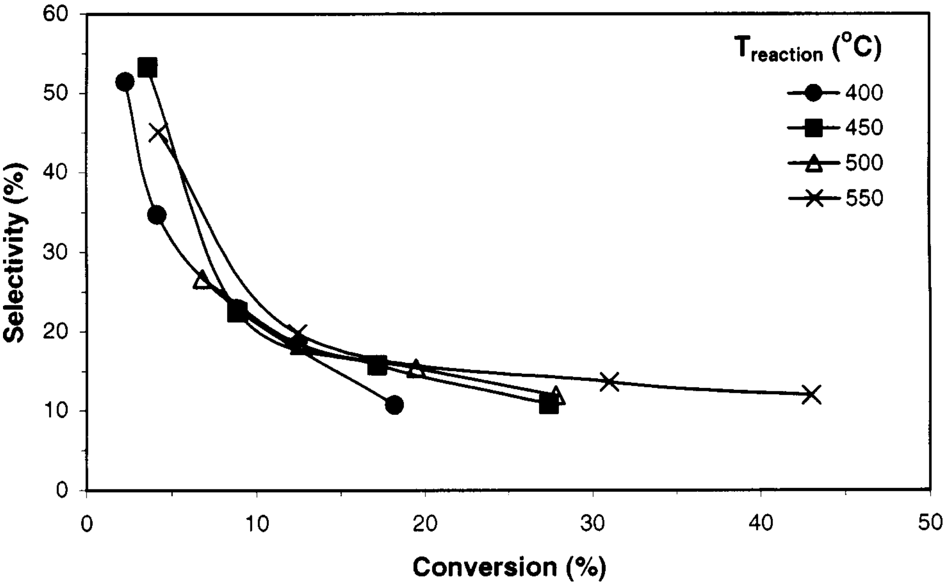

Figure 6. Selectivity to propene as a function of the propane conversion on 1.5Cr-MCM catalyst at different temperatures. ($F/W = 13.73$ mol-C_3 h^{-1} g^{-1}.)

are also lower than those of chromia supported on titania and zinc oxides [16]. The low interaction between chromia and the silica MCM support could account for these moderate yields. It seems to be largely accepted that the interaction between the active phase and the support depends on the different acid–base character. Thus, the interaction is stronger as the difference in acid–base nature is more important [17].

The yields of propene are maximum at 500 °C, therefore, we have chosen this temperature to compare all the catalysts. Figure 6 shows the evolution of the selectivity and the conversion versus the chromium content at this temperature. It can be observed that the most selective samples are those catalysts with 3 and 6 wt% Cr which at the same time are the less active. This behavior could be related to the dispersion of the active phase and their acidic properties. Indeed, the samples with higher chromium content show the lower acidity values, the formed olefin is thus rapidly desorbed increasing the selectivity. This correlation between acidity and selectivity has been previously found in the same catalytic reaction on chromia/gallia pillared materials [8].

Finally, we have studied the influence of the contact time (F/W values) on the activity of the 1.5Cr-MCM catalyst. It can be observed in figure 7 that spatial velocities higher than 13.73 mol-C_3 h^{-1} g^{-1} do not increase the rate of propane formation.

In conclusion, catalysts based on chromia supported on a mesoporous silica MCM-41 support behave as moderately active in the oxidative dehydrogenation of propane. This behavior is a consequence of the low dispersion degree attained on this siliceous support. Only the catalyst having a chromium loading of 1.5 wt% shows good activity, with a yield to propene of 2.5%. Moreover, this catalyst exhibits

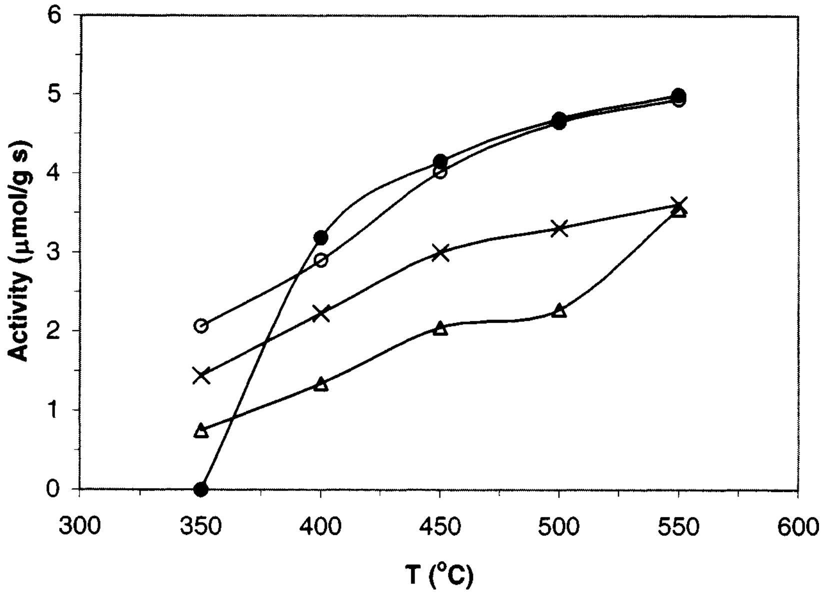

Figure 7. Influence of the contact time (F/W) on the dehydrogenation rate at different temperatures during the ODH of propane on the 1.5Cr-MCM catalyst: 21.86 (●), 13.73 (○), 7.53 (×) and 4.27 (△). (F/W in mol-C_3 h^{-1} g^{-1}.)

better performance than a structurally Cr-doped MCM-41 silica with similar chromium content [11]. In order to improve the catalytic activity of this family of materials new experiments are being carried out to modify the affinity of the support for the chromium species and the acidity of the active phase.

Acknowledgement

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