

Synthesis, Characterization and Catalytic Activity of MCM-41 Materials Prepared by Various Synthesis and Impregnation Methods

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Introduction

MCM-41 materials belong to the group of mesoporous silicas characterised by a hexagonal arrangement of uniform pores and large surface areas. Since their discovery in 1992 they attracted much attention and were investigated in order to apply as adsorbents, supports and catalysts [1]. The important feature of these sorbents is the possibility of creating the pore dimensions in a wide range from 2 to even 10 nm. It allows application of the MCM materials for some special purposes when wider pores can improve transport into the inner space of their structure, for instance, in selective adsorption or catalytic reactions with large molecules. The engineering of porous structure of ordered silicas may be realised by changing the synthesis conditions, composition of reacting mixture and type of organic template. By incorporation of metal ions into the framework of these sorbents it is possible to improve the catalytic activity of original materials or achieve quite new properties. The catalytically active sites like metal ions can be introduced by applying various methods: direct hydrothermal synthesis, template ion-exchange, impregnation or grafting [1-5]. Regarding large surface areas of MCM-41 materials they may be very catalytically active systems.

Manganese containing porous materials were successfully used in several oxidation processes, e.g. the oxidation of styrene, propene, alkanes, cyclohexane [6-8]. A high catalytic activity of such materials was confirmed in epoxidation of olefins; this process is very important in the syntheses of organic fine chemicals [9,10]. The environment protection is another important field where the catalysts may be effectively used to reduce the emission of toxic substances. Mn-containing systems can be applied for oxidation of such compounds as carbon monoxide, which is emitted in many technological or natural processes. MCM type materials characterised by a developed pore structure may be used as supports for creating modern manganese containing catalysts. Several methods of preparation of metal ion-planted MCM-41 sorbents were investigated with regard to produce the most active catalysts. The possibility of engineering materials with various loadings of manganese ion and the effect of synthesis procedure on the changes of regular hexagonal structure were studied.

In the paper, the investigations of manganese containing mesoporous silicas of MCM-41 type of different pore sizes are presented. Direct hydrothermal synthesis, template ion-exchange method and impregnation were used to introduce Mn atoms on the surface and into the structure of silica skeleton. The obtained materials were characterised by using different physicochemical methods in order to compare their surface and structure properties. It was found that the introduction of manganese to silica structure increases the catalytic activity in the reaction of carbon monoxide oxidation. It is possible to improve the catalytic properties of synthesised MCM-41 materials by introducing other metal ions.

Experimental

Catalyst preparation. The original MCM-41 materials were synthesised using cetyl pyridinium chloride (MCM-41(16)) and octadecyltrimethylammonium bromide (MCM-41(18)) as surfactant templates and TEOS as silica source. In order to wider the pore diameters of MCM-41(18) sorbents 1,3,5-trimethylbenzene TMB was added to a reacting mixture. The preparation procedure followed the method described in the literature [11]. The synthesised material was washed with bi-distilled water, dried and calcined by heating to 550°C at a rate 1°C/min and then kept at this temperature for 6 h.

The manganese ions were introduced into the silica framework by applying the direct hydrothermal synthesis (DHT) (Mn(HT)-MCM(16) and Mn(HT)-MCM(18)) and template ion-exchange (TIE) technique (Mn(TIE)-MCM(16) and Mn(TIE)-MCM(18)) [2,3]. In the DHT method an aqueous solution of manganese (II) nitrate as the metal ion precursor was added directly to the synthesis mixture before the hydrothermal process. Finally the product was filtered, washed, dried at 80°C for 24 h, and calcined at the same conditions as pure MCM-41 materials. In the TIE technique the template cations from the channels of the as-synthesised MCM-41 were exchanged with the metal ions in a solution. In the procedure the weighed sample of the as-synthesised MCM-41 sorbent was added to an aqueous solution of manganese (II) nitrate. The mixture was stirred vigorously at ambient temperature for 1 h, and then kept at 80°C for 20 h. Finally the product was treated as in the case of further materials. The additional sample was obtained by impregnating the original MCM-41(18) material in a solution of manganese salt (Mn(Imp)-MCM(18)). A weighed sample of pure MCM-41(18) support was suspended in an aqueous solution of manganese (II) nitrate, stirred at ambient temperature, dried, and calcined at 550°C for 6 h.

Catalyst characterisation. Various experimental techniques were used to characterise the properties of synthesised materials. The amounts of manganese in the catalysts were determined by applying the X-ray fluorescence (ED-XRF Canberra 1510, USA).

To confirm the regularity of sorbent structure XRD patterns were recorded by the modified diffractometer DRON 3 (Russia) using $\text{CuK}\alpha$ radiation.

The primary mesopore diameter (w_d) was calculated from the XRD (100) interplanar spacing d using the following equation [12]:

$$w_d = cd \left(\frac{\rho V_p}{1 + \rho V_p} \right)$$

where c is a constant equal to 1.213 for cylindrical pores [12], ρ is the pore wall density assumed to be equal to that of amorphous silica – 2.2 g/cm³.

To characterise the surface properties the temperature-programmed reduction (TPR apparatus AMI-1, Zeton Altamira) were used. Before the experiment the samples were heated in the mixture of 5% O₂/He at 500°C for 0.5 h. After cooling the reduction process was conducted in the mixture 6% H₂/Ar. The rate of temperature ramping was 10°C/min.

The catalytic activity was investigated for the oxidation of carbon monoxide by the method of temperature-programmed surface reaction (TPSR). The measurements were conducted in the same TPR apparatus coupled with the mass spectrometer HAL201RC (HIDEN Analytical) using the mixtures of 1% CO/He (20 cm³/min) and 5% O₂/He (20 cm³/min). Before the experiment the samples were heated in the mixture of 5% O₂/He at 500°C for 0.5 h and cooled down. During the oxidation process the catalysts were heated to up to 800°C with 10°C/min. temperature rate increase and then cooled down.

In order to estimate the values of parameters characterising the mesoporous structure of synthesised materials the nitrogen adsorption/desorption at 77 K were determined volumetrically using ASAP 2405N analyser (Micromeritics Corp., USA). Before the experiment the adsorbents were outgassed ($\sim 10^{-2}$ Pa) at 493 K.

The adsorption data were used to evaluate the BET specific surface area, S_{BET} (from the linear BET plots) and the total pore volume, V_t (from the adsorption at the relative pressure $p/p_0=0.98$) [13]. The external (macropore) surface area, S_{ext} , and the primary mesopore volume, V_p , were obtained from the α_s plot method [14]. This method is based on the comparison of nitrogen isotherm on a studied porous solid with the standard isotherm on a reference nonporous adsorbent. This standard reduced isotherm α_s is defined as the ratio of adsorption value corresponding to a given relative pressure p/p_0 and the adsorption value at the point $p/p_0=0.4$ (p is the gas pressure, p_0 is the saturation pressure, $p/p_0=0.4$ is a starting point of isotherm hysteresis loop for nitrogen adsorption). As a reference adsorbent the macroporous silica gel LiChrospher Si-1000 was used [14]. The mesopore structure was characterized by the distribution function of mesopore volume calculated by applying the Barret-Joyner-Halenda (BJH) method [13].

Results and discussion

In Fig. 1 the adsorption/desorption isotherms of nitrogen on all synthesised MCM-41 samples are compared. They show a typical shape for such materials, with a sharp step over a narrow range of relative pressures. In the case of silica with narrower pores prepared by using a template with shorter alkyl chain (MCM-41(16)), the isotherm displays plateau at $p/p_0 < 0.4$. For the MCM-41(18) samples the adsorption step corresponding to nitrogen condensation in primary mesopores is shifted toward higher relative pressures indicating the occurrence of larger pores in this material in comparison to MCM-41(16). The isotherm shapes are different for the samples synthesised in HT and TIE methods. It means that the method of introducing the metal ions to support structure or in its surface influences the structure characteristics of MCM-41 materials significantly. In the case of impregnated sample the nitrogen isotherm gives lower adsorption values over the whole relative pressure range, what is connected with a partial blockage of pores by impregnating medium.

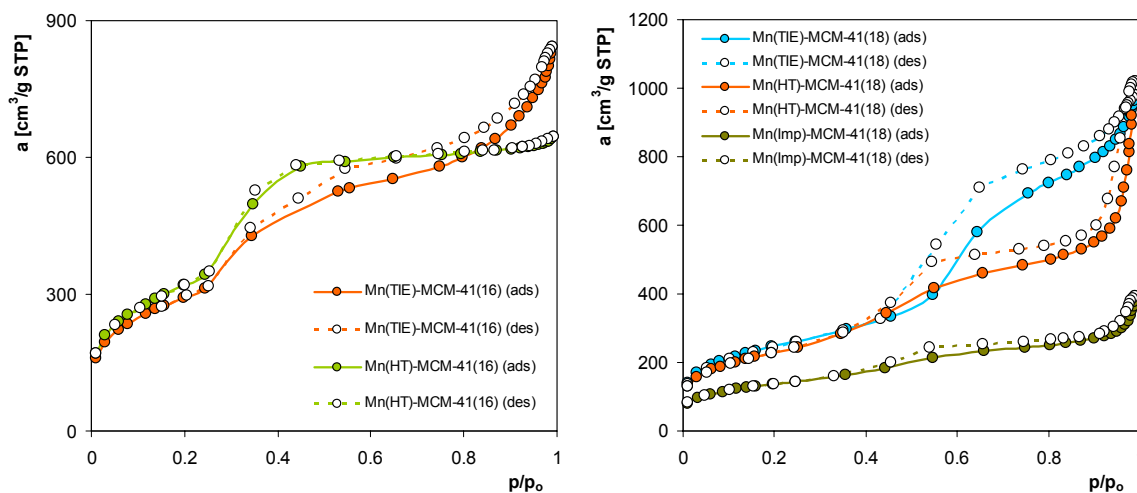


Fig. 1. The nitrogen adsorption/desorption isotherms for synthesised MCM-41 materials.

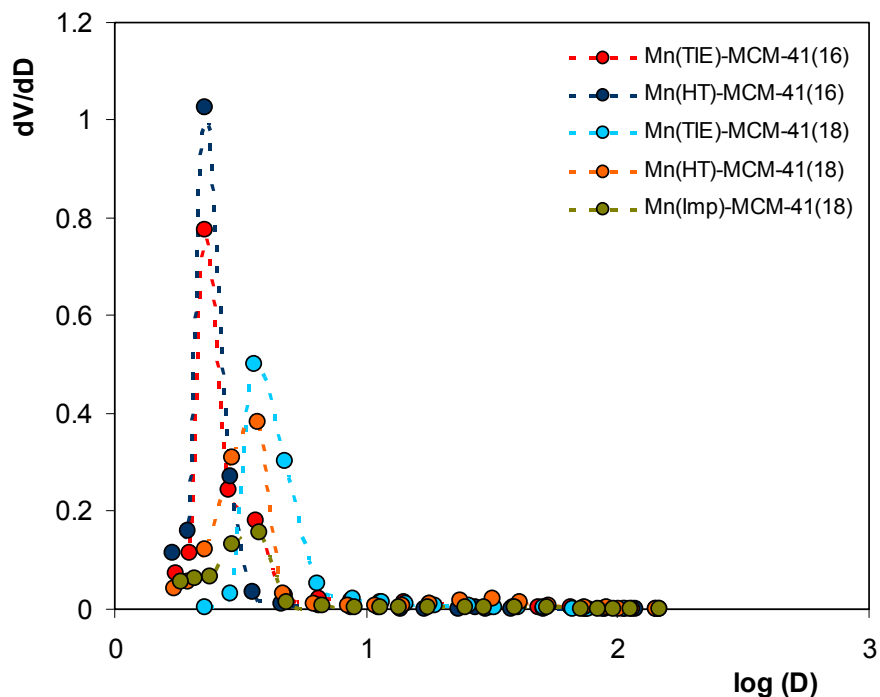


Fig. 2. The pore size distributions for synthesised MCM-41 materials.

The pore size distributions (PSD) calculated by BJH method for MCM-41(16) and MCM-41(18) samples are presented in Fig. 2. Narrow mesopore distributions evidence the uniformity of pore systems of all synthesised materials. The pore distributions for MCM-41(16) samples are shifted toward lower pore diameters. The PSD for MCM-41(18) materials are wider in comparison to MCM-41(16) as a result of using TMB in catalyst synthesis.

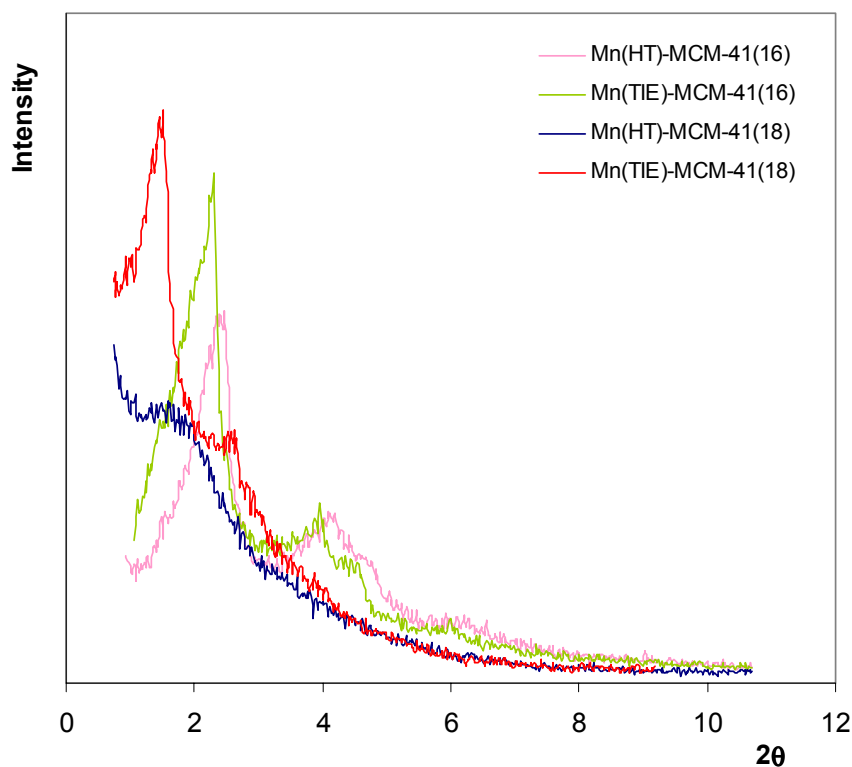


Fig. 3. The XRD patterns for synthesised MCM-41 materials.

In Fig. 3 the XRD spectra are presented for all synthesised sorbents. They feature one prominent peak and two other reflections, which may be attributed to (100), (110) and (200) indices of hexagonal arrangement of pores. The XRD patterns evidence that in spite of the amorphous character of their pore walls the MCM-41 materials show highly ordered arrangement of pores. The (100) peaks are shifted toward lower angles for MCM-41(18) indicating larger unit-cell size for these samples in comparison to MCM-41(16).

The parameters describing the structure of investigated MCM-41 samples calculated from nitrogen isotherm and XRD patterns are presented in Table I. All materials synthesised by HT and TIE methods are characterised by very high values of the specific surface area (S_{BET}) and pore volume (V_t). The volumes of primary mesopores and specific areas are the highest in the case of MCM-41 (16) samples. The mesopore diameters increase successively with template size from MCM-41(16) to MCM-41(18).

Table 1. Parameters characterising structure properties of synthesised MCM materials

Sorbent	%Mn	S_{BET} [m ² /g]	S_{ext} [m ² /g]	V_t [cm ³ /g]	V_p [cm ³ /g]	d_{100} [nm]	w_d [nm]
Mn(TIE)-MCM-41(16)	2.2	1050	208	1.24	0.89	4.23	3.40
Mn(HT)-MCM-41(16)	2.2	1150	48	0.98	0.90	3.86	3.11
Mn(TIE)-MCM-41(18)	2.4	880	300	1.45	0.94	6.22	3.51
Mn(HT)-MCM-41(18)	1.9	815	380	1.3	0.71	4.75	5.08
Mn(Imp)-MCM-41(18)	18.3	487	149	0.54	0.25	-	-

The temperature programmed reduction was applied to investigate the oxidised forms of manganese introduced to silica material by hydrothermal synthesis, template ion-exchange, and impregnation method. In Fig. 4 the TPR curves are compared for all synthesised MCM-41(16) and MCM-41(18) catalysts. The TPR studies reveal the coexistence of various oxide forms in the obtained materials. For the impregnated sample containing larger amount of Mn two-step reduction process is visible, and can be ascribed to the reactions: (I) MnO_2 to Mn_3O_4 , and (II) Mn_3O_4 to MnO . Comparing the sorbents synthesised by HT and TIE methods worse reducibility of samples obtained in HT method was found. Two maxima observed on TPR curves are shifted for Mn(HT)-MCM-41(16) and Mn(HT)-MCM-41(18) samples by about 150°C. Lower reducibility of the oxides can be connected with incorporation of Mn into the silica matrix or with formation of strongly dispersed surface phases. The Mn(TIE)-MCM-41 sorbents can be easier reduced in comparison to the materials synthesised by hydrothermal technique. One may observe two partly superimposed maxima on the TPR curves. Higher reducibility of catalysts synthesised by TIE method may be related to the formation of larger oxide clusters, with weaker interactions the silica support. It was supposed that in the (HT)-MCM materials the oxide phases correspond to oxides with the intermediate composition between Mn_3O_4 and Mn_2O_3 , whereas for TIE sorbents – to oxides between Mn_2O_3 and MnO_2 .

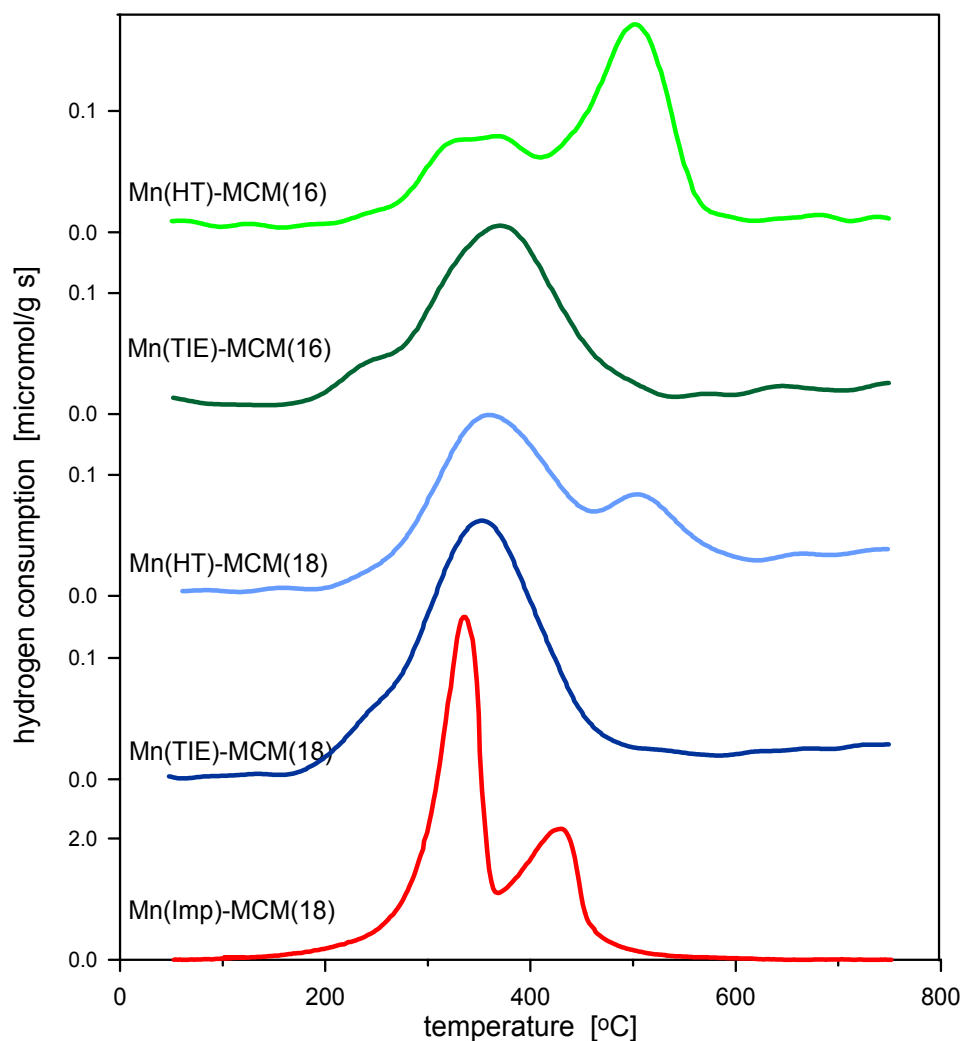


Fig. 4. The TPR curves of the Mn-MCM-41 materials.

In order to estimate the effect of synthesis method on the catalytic activity of synthesised materials the oxidation of carbon monoxide was investigated. In Fig. 5 the oxidation curves are compared for all studied materials. Oxidation of CO in the presence of the materials prepared by HT and TIE methods started at relatively high temperatures, above 200°C. The degree of CO conversion increased with an increase of temperature. In the range of temperatures 400-600°C this growth was hindered. The observed phenomena might be a result of the changes of oxidation number of manganese at different temperatures. The decrease of reaction activity was probably connected with decomposition of some active MnO_x centres and stabilisation of the reduced forms of MnO_x by the silica structure. It was stated, that these processes were reversible. The MCM(16) materials showed higher activity than similar MCM(18). Simultaneously the catalyst obtained by impregnation method showed the greatest oxidation effectiveness and was deactivated at higher temperatures only to an insignificant extent. This indicates on the complexity of factors influencing catalytic performance of the Mn-MCM materials.

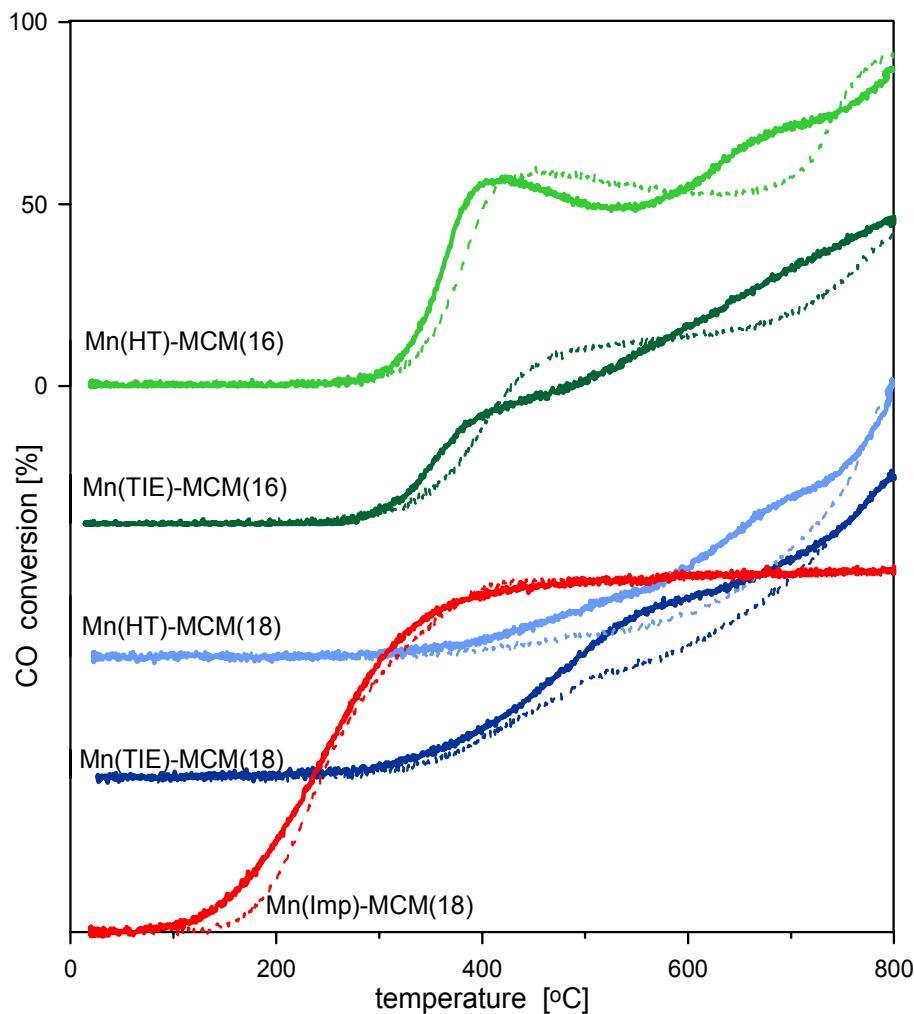


Fig. 5. The temperature programmed oxidation of CO (solid lines - temperature increase, dashed lines - temperature decrease).

Conclusions

- The synthesised manganese containing silicas show the typical features of MCM-41 materials; they are characterised by high values of the specific surface areas and pore volumes, and narrow mesopore distributions; XRD patterns evidence the ordered arrangement of pores.
- The TPR measurements reveal that the oxide phases formed in the hydrothermal synthesis method are strongly bounded to the silica support as compared to that ones in the impregnation or template ion-exchange method. The HT method allows obtaining materials with more stable forms of manganese species located inside the structure or strongly dispersed on the silica surface.
- The catalytic performance of studied materials is connected with the synthesis technique, manganese content, and oxidation reaction conditions. The catalysts with larger amounts of Mn, obtained by impregnation method show the highest activity and high-temperature stability. The decrease of activity at higher temperatures of the materials synthesised by HT and TIE methods may be a result of decomposition and stabilization of MnO_x forms by the silica.

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