

Catalytic activity of Co/MCM-41 and Co/SBA-15 materials in toluene oxidation

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Abstract Cobalt-containing MCM-41 and SBA-15 mesoporous materials were prepared by the pH-adjusting of the impregnation solution. The modified materials were investigated by X-ray diffraction, N₂ physisorption, temperature-programmed reduction, DR UV–Vis diffuse reflectance, and FT-IR spectroscopy of adsorbed pyridine. The pH of the impregnation solution influences the surface charge of the mesoporous support and therefore determines the strength of interaction between the cobalt precursor and the mesoporous support. The formation of different cobalt oxide species in different ratios, depending on the pH of the impregnation solution, was established for both materials. The modified Co/MCM-41 and Co/SBA-15 materials were active in toluene oxidation. Their catalytic activity is predetermined by the nature, the reducibility, and the dispersion of the obtained cobalt oxide species.

Introduction

Mesoporous silica materials with regular pore structure, such as MCM-41 and SBA-15, have recently attracted attention because of their applicability as model mesoporous materials in catalysis [1–4]. The removal of volatile organic compounds (VOCs) from emissions is of

considerable interest due to the harmful effects of these pollutants. Recently, strict regulations on the environmental standards in several countries have initiated concerns on the pollutants control requiring a 40% reduction in VOC emissions by 2010. Among the VOCs, toluene is one of the targeted components, which is produced from the petrochemical industry, pressing, and printing. The catalytic oxidation is an alternative to the incineration process for the destruction of VOCs. The activity of the catalysis is an important factor determining the effectiveness of this technique. The transition metal-modified (Co, Ni, Mo, V, etc.) mesoporous silicas are appropriate catalysts for VOC oxidation [2, 5–7]. Among them, cobalt-containing catalysts show the best catalytic activity and selectivity. It is well known that the nature and dispersion of the cobalt oxide species are the key factors determining the activity and selectivity of the supported catalysts [8, 9]. The nature of the precursor [10–12], the preparation method [10, 12, 13], the support [10, 14–23], the metal loading [12, 17, 19, 20], and the preliminary treatments [14, 19, 24–28] have influence on the state of the cobalt oxide species. The high surface area of the mesoporous MCM-41 and SBA-15 materials ensure higher cobalt oxide dispersion compared to conventional SiO₂ [16, 29, 30]. For the preparation of highly active catalysts in toluene oxidation, it is important to obtain easily reducible and finely dispersed Co₃O₄ particles [2]. In the case of Co/SiO₂, the nature of the formed cobalt species was found to depend on the amount of silanol groups, the polarity of the solvent, and the pH of the impregnation solution [13]. In our previous article [28] it was also found that the amount of surface silanol groups in the mesoporous MCM-41 and SBA-15 materials modified their catalytic properties in hydrogenation reaction through its effect on cobalt particle dispersion and reducibility. The presence of silanol groups increases the metal support

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interactions and leads to lower reducibility of the formed cobalt oxide species [13, 28]. The preliminary silylation of SBA-15 support is a way of reducing the cobalt oxide–support interaction enhancing the reducibility of the cobalt oxide species [29]. Ming and Baker [31] reported the influence of pH of the impregnation solution on the formation of the hardly reducible cobalt silicate. At $\text{pH} \geq 5$ they observed the reaction of cobalt ions with the surface of silica gel forming various cobalt silicates.

The aim of this article is to study the effect of pH of the impregnation solution on the formation of cobalt oxide species with different nature, reducibility, and dispersion on MCM-41 and SBA-15 silica materials. The catalytic performance of the modified samples was studied in total oxidation of toluene.

Experimental

Sample preparation

The parent silica MCM-41 and SBA-15 materials were synthesized by hydrothermal procedure according to [32, 33], respectively. *N*-hexadecyltrimethylammonium bromide ($\text{C}_{16}\text{TMABr}$), Pluronic P123 [triblock copolymer ($\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$)], tetramethylammonium hydroxide (TMAOH), and fumed silica or tetraethylorthosilicate (TEOS) were used as templates and silica sources, respectively. Synthesis mixtures with the following relative molar compositions were prepared:

MCM-41: 1.0 SiO_2 : 0.25 $\text{C}_{16}\text{TMABr}$: 0.2 TMAOH: 35 H_2O .

SBA-15: 4 g $\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$: 0.24 HCl: 0.04 TEOS: 6.67 H_2O .

After drying, the as-synthesized samples were calcined in air for template removal at 773 or 723 K for MCM-41 and SBA-15, respectively.

Wet impregnation with 0.028 M Co-nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck) was applied for loading 5.5 wt% Co at various pH values (1.5–5). The pH of the impregnation solution was adjusted by adding drops of nitric acid. The modifications are designated as Co/MCM-41(*X*) and Co/SBA-15(*X*) where *X* = 1.5; 3 or 5 is the pH value of the impregnation solution.

The cobalt salt decomposition was carried out in situ in air at 673 K for 2 h with a heating rate of 10 K/min.

Characterization

X-ray diffractograms were recorded by Philips PW 1810/1870 diffractometer applying monochromatized CuK_α radiation (40 kV, 35 mA). In situ X-ray diffraction (XRD)

measurements were carried out in an HT1200 Anton Paar chamber pretreating the samples at 673 K in air.

Nitrogen physisorption measurements were carried out at 77 K using Quantachrome NOVA Automated Gas Sorption Instrument. The pore-size distributions were calculated from the desorption isotherms with the non-local density functional theory (NLDFT) method [34].

Diffuse reflectance spectra of the samples in the UV–Vis region were registered using a Beckman 5720 UV–Vis spectrophotometer equipped with an integrating sphere. A BaSO_4 disk was used as reference. All spectra were recorded under ambient conditions.

FT-IR experiments were performed with Nicolet Compact 400 spectrometer by the self-supported wafer technique with pyridine (Py) (0.07 kPa) as probe molecule. The spectra were normalized to 5 mg/cm^2 weight of the wafers for comparison.

The reducibility of Co-modified samples was investigated by temperature-programmed reduction (TPR) technique in H_2/Ar flow (10:90, 20 mL/min) using a conventional TPR apparatus equipped with a heat conductivity cell and a trap for removal of released water. The reduction of the cobalt oxide species was estimated by measuring the hydrogen uptake of the samples.

Catalytic activity measurements

Prior to the catalytic experiment the samples were pretreated for 1 h in air, at 673 or 573 K in order to decompose the salt precursor. The reaction of toluene oxidation was studied at atmospheric pressure using a fixed-bed flow reactor and air as carrier gas. The air stream passed through a saturator filled with toluene and equilibrated at 273 K ($p_{\text{toluene}} = 0.9$ kPa). The activity was determined in the temperature interval of 473 to 620 K at WHSV of 1.2 h^{-1} . Online analysis of the reaction products was performed using gas chromatograph HP 58 90 series II equipped with a 25-m PLOT Q capillary column.

Results and discussion

Physico-chemical properties of the Co-modified MCM-41 and SBA-15 samples

XRD data of the impregnated Co/MCM-41 and Co/SBA-15 samples (data not shown) with the intense (100) and higher Miller indices reflections in the low 2θ region confirm the preservation of the hexagonal structure after the modification. Diffraction peaks of Co_3O_4 at higher diffraction angles cannot be detected by in situ XRD of the Co/MCM-41 samples after the salt decomposition (data not shown). Very broad reflections with low intensity, typical

of Co_3O_4 , are evident only for Co/SBA-15(3) and Co/SBA-15(5) samples. Thus, the determination of the Co_3O_4 particle size by XRD method applying the Debye–Scherer equation was not possible.

The nitrogen adsorption and desorption isotherms of all modified samples are presented in Fig. 1. The isotherms of the modified Co/MCM-41 samples exhibit a sharp increase at a relative pressure of $p/p_0 = 0.2$ – 0.4 , which is associated with capillary condensation of N_2 in the channels with narrow pore size distribution (Fig. 1). The position of this step is shifted to higher relative pressure for the Co/SBA-15 samples (Fig. 1), indicating the presence of larger pores (Table 1). The isotherms of parent and modified MCM-41 are reversible and do not show any hysteresis loop, whereas the isotherms of the parent and modified SBA-15 exhibit a H2-type hysteresis loop, which is a typical feature of this type of mesoporous material. The calculations by NLDFT method show that Co/MCM-41 and Co/SBA-15 samples have narrow pore size distribution with a maximum at about 4 and 7 nm, respectively (Table 1). The specific surface area of the modified Co/MCM-41 and Co/SBA-15 mesoporous materials (S_{BET}) is slightly lower than that of

the parent ones. The pore diameter of MCM-41 and SBA-15 samples has not changed after the impregnation procedure.

The FT-IR spectra of the modified materials in the region of 2000 to 400 cm^{-1} are used for the characterization of Co-modified molecular sieves (data not shown). The asymmetric stretching vibrations (Si–O–Si) appear at about 1090 cm^{-1} for MCM-41 and at 1075 cm^{-1} for SBA-15. The slight shift of this band, observed for the cobalt-modified MCM-41 and SBA-15 samples, is an indication that a part of the cobalt is incorporated into the mesoporous framework and Co–O–Si bonds are formed. According to the literature [35] in the case of transition metal-modified mesostructured silicates the appearance of the band at 968 cm^{-1} can be associated with the formation of a M–O–Si bond and the presence of silanol groups as well.

DR UV–Vis spectra (Fig. 2) recorded at room temperature are used for the characterization of the nature and the coordination of cobalt oxide species in the Co-containing MCM-41 and SBA-15 samples. The presence of a triplet at 540, 585, and 630 nm can be assigned to the electronic ligand-field ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition for tetrahedrally

Fig. 1 N_2 adsorption isotherms of the calcined parent and cobalt-modified mesoporous silica materials

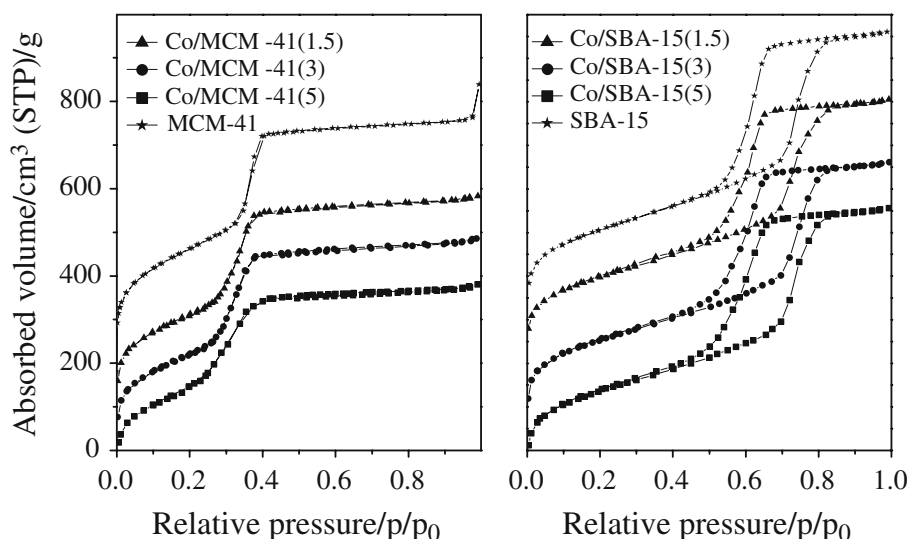


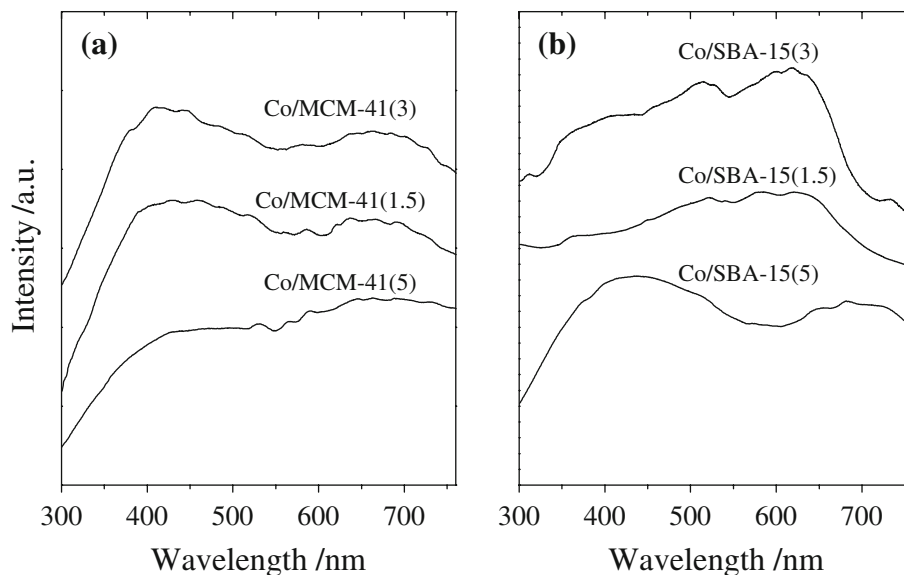
Table 1 Physico-chemical characteristics of the parent and the cobalt-modified samples

Sample	pH	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	H_2 uptake ^a (mmol/g)	Extent of reduction ^b (%)
MCM-41	–	1023	0.90	4.2	–	–
Co/MCM-41(5)	5.0	861	0.70	4.2	0.06	5.2
Co/MCM-41(3)	3.0	892	0.80	4.1	0.18	14.7
Co/MCM-41(1.5)	1.5	902	0.81	4.1	0.15	12.3
SBA-15	–	856	1.1	7.0	–	–
Co/SBA-15(5)	5.0	794	1.0	7.0	0.19	15.4
Co/SBA-15(3)	3.0	787	1.0	7.0	0.13	10.5
Co/SBA-15(1.5)	1.5	763	0.93	7.0	0.12	9.7

^a Calculated from the area of the TPR curve in the range of 373 to 923 K, related to sample weight calcined at 1273 K

^b Calculated from the H_2 uptake related to the total amount of cobalt (0.93 mmol/g), assuming that 4 mmol H_2 is needed for the reduction of 1 mmol Co_3O_4 to Co^0

Fig. 2 DR UV–Vis spectra of cobalt-modified MCM-41 (a) and SBA-15 materials (b)

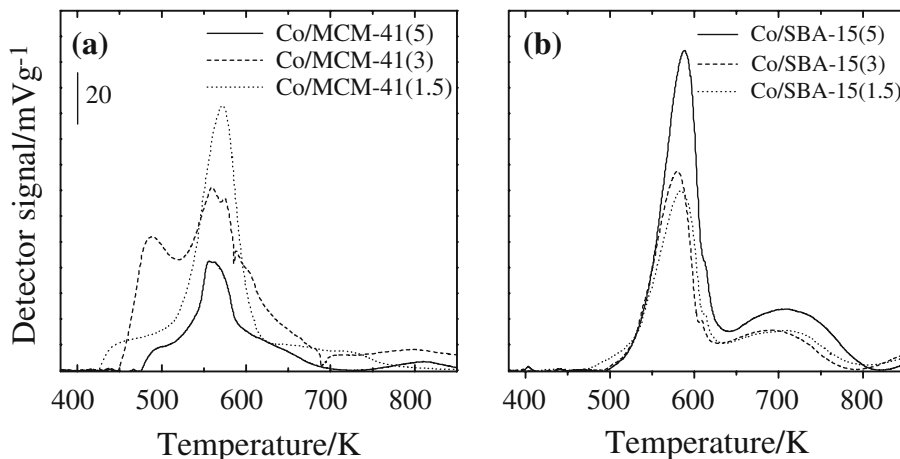


coordinated Co^{2+} , whereas the absorption band around 420 nm can be attributed to octahedrally coordinated Co^{3+} in the mixed spinel oxide Co_3O_4 [30]. The DR UV–Vis spectrum of Co/MCM-41(3) displays a more intensive absorption band at 420 nm typical of the octahedrally coordinated Co^{3+} in Co_3O_4 in comparison to that of the Co/MCM-41(5) (Fig. 2). In the case of cobalt-containing SBA-15 samples this band is the most intensive for the Co/SBA-15(5) sample. The differences in the nature of the cobalt oxide species, registered by DR UV–Vis spectroscopy, can be correlated well with the color of the samples, for example Co/MCM-41(3) is black (octahedrally coordinated Co^{3+} in Co_3O_4), whereas the Co/MCM-41(5) sample is blue (tetrahedrally coordinated Co^{2+}).

The TPR data of the modified samples show the presence of cobalt oxide species reducible at different temperature intervals (Fig. 3) and different extents, up to 923 K (Table 1). The TPR curve of Co/MCM-41(3) exhibits four peaks: the first peak is centered at 470 K and

three overlapping peaks in the range of 520 to 650 K (Fig. 3a). These reduction peaks can be ascribed to the reduction of Co_3O_4 particles in a two-step process [36–38]. Obviously, these reduction features indicate that during the calcination easily reducible Co_3O_4 particles have been obtained. They are most probably formed as a result of weak interaction between the cobalt aqueous complexes and the support at pH = 3 and as a consequence the major part of them is reducible at low temperature. The TPR curves of Co/MCM-41(5) and Co/MCM-41(1.5) samples show one reduction peak at about 550 K (Fig. 3a). Considering the amount of consumed H_2 (Table 1) higher extent of reduction was achieved for Co/MCM-41 sample prepared at pH = 3 in comparison with other Co/MCM-41 samples. The TPR curves of the Co/SBA-15 samples show one highly intensive peak at 580 K and one small peak at about 700 K (Fig. 3b). In this case pH = 5 of the impregnation solution is proved to be the most appropriate value for the formation of higher amount of easily

Fig. 3 TPR profiles of the Co-containing samples after oxidative pretreatment at 673 K



reducible cobalt oxide species. According to the literature [36, 37], the remaining cobalt oxide species should exist as Co-silicate like species reducible above 873 K. The metal ion deposition during the impregnation process of the silica support with an ionic solution [31] is strongly affected by the pH value of the impregnation solution. Strong cobalt–support interaction could occur at pH = 5 when MCM-41 is used as a support, which is probably a reason for the lower reducibility of Co/MCM-41(5). However, in the case of Co/SBA-15, the impregnation at pH = 5 leads to weaker cobalt–support interaction.

To explain the differences in the cobalt precursor–support interactions, the surface active centers were investigated by means of FT-IR spectroscopy. The spectra of the parent materials possess a highly intensive band at 3740 cm^{-1} and a broad band in the $3690\text{--}3450\text{ cm}^{-1}$ region (data not shown) which is typical for the isolated silanol groups and the silanol groups involved in hydrogen bonding in mesoporous silicas, respectively [37]. The comparison of the spectra for the parent MCM-41 and SBA-15 materials shows significantly higher amount of SiOH groups on SBA-15. The intensity of SiOH bands is decreased in a different extent after the modification with cobalt. These differences could be due to the different participation of the surface silanol groups in the impregnation process, in dependence on the pH value of the impregnation solution. The FT-IR spectra of the adsorbed pyridine on the modified samples can be used for more detailed characterization of the cobalt oxide species interacting with the silica supports (Fig. 4). The bands at $1450/1610\text{ cm}^{-1}$ can be attributed to pyridine, coordinatively bound to Lewis acid sites, for example, coordinatively unsaturated cobalt oxide species connected to the silica support. The intensity of these bands is higher in the case of Co/MCM-41(5) than that of Co/MCM-41(3). This effect can be due probably to the more intensive cobalt–support interactions during impregnation at pH = 5 in contrast to the impregnation at pH = 3. Co/MCM-41(3) sample shows the highest extent of reduction as a result of the less intensive cobalt–support interactions. The spectrum of Co/SBA-15(5) also shows higher intensity of the bands at $1450/1610\text{ cm}^{-1}$ in comparison to the spectrum of Co/SBA-15(3). The higher amount of SiOH groups in SBA-15 (Fig. 4) probably favors the formation of higher amount of tetrahedrally coordinated Co^{2+} ions, interacting with the silica support. When the silica support is impregnated by an ionic solution, the adsorption of ions is strongly affected by the surface charge of the support [31]. Silanol groups possess amphoteric character and can exist in the form of SiOH , SiO^- , or SiOH_2^+ species, depending on the pH of the impregnation solution. Therefore the mechanism of the deposition of cobalt ions depends strongly on the pH of the impregnation solution. If the pH of the

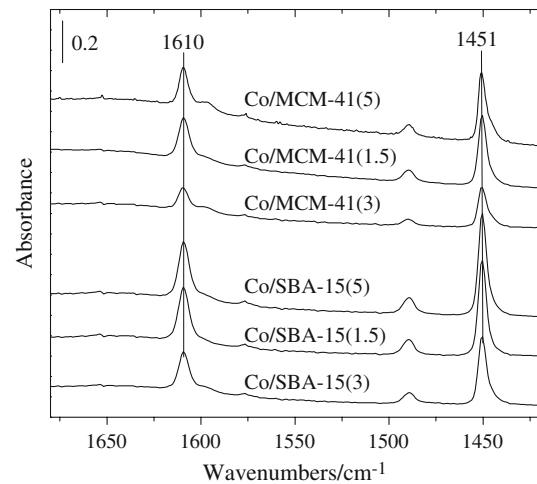


Fig. 4 FT-IR spectra of adsorbed pyridine on cobalt modified MCM-41 and SBA-15 samples. Samples were pretreated in vacuum at 673 K, Py was adsorbed at 473 K and desorbed in HV at 373 K

impregnation solution is ≥ 5 , cationic exchange between the negatively charged silica and the positively charged cobalt ions is the predominating process, resulting in the formation of cobalt silicates and hydrosilicates. Below the isoelectric point of silica (pH < 2) there is no surface reaction between the positively charged silica and the cobalt ions, even adsorption is suppressed, deposition of poorly dispersed cobalt oxide phase can be expected. At pH = 2–5, when the silica surface is slightly negatively charged, adsorption is favored and the dispersion of cobalt oxide can be enhanced. According to Li et al. [36], the interaction of the cobalt precursor with the support can lead to the simultaneous formation of surface bound Co^{2+} ions and cobalt silicates, the latter being not or very hardly reducible. A part of the formed cobalt silicate can be embedded in the silica walls and therefore it cannot be detected by FT-IR method using adsorbed pyridine as a probe molecule. The Co^{2+} species are reducible at lower temperature in comparison to cobalt silicate.

Summarizing the results of physico-chemical characterizations, the different interactions of the cobalt oxide species with the silanol groups of the support depending on the pH value of the impregnation solution resulted in different reducibility of the samples. The formed cobalt oxide species (Co_3O_4 , Co^{2+} , and Co-silicate like species) possess diverse reducibility and dispersion as the TPR data show. The highest amount of Co_3O_4 particles are obtained in the case of Co/MCM-41(3) prepared at pH = 3, whereas the highest amount of cobalt silicate could be formed in the Co/MCM-41(5) sample, impregnated at pH = 5. The presence of larger quantity of silanols in SBA-15 leads to the formation of higher amount of surface bound Co^{2+} ions, resulting in an intensive Lewis acidic band (coordinatively unsaturated cobalt oxide species) in the FT-IR

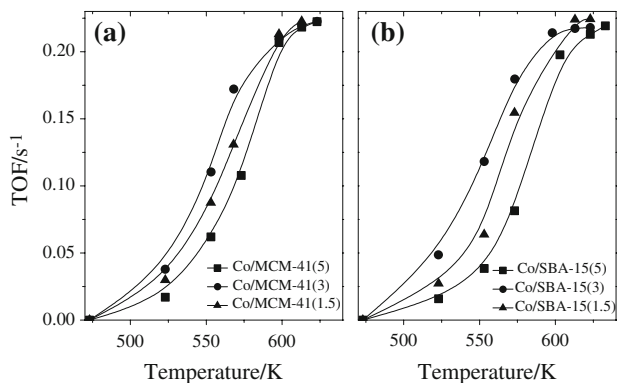


Fig. 5 Toluene conversion versus reaction temperature over the Co/MCM-41 and Co/SBA-15 catalysts, oxidized at 673 K

spectra of Co/SBA-15(5). Lou et al. [39] found that the largest amount of cobalt species incorporated into the siliceous framework of Co-SBA-15 are obtained at pH = 6.5 by direct synthesis procedure.

Catalytic study

In Fig. 5 the results of the catalytic oxidation of toluene as a function of reaction temperature (450–620 K) on all samples pretreated at 673 K in air are shown. It has to be noted that CO₂ and water were the only products formed in the investigated range of temperature. The samples, prepared at pH = 3 of the impregnation solution, show the highest catalytic activity in toluene oxidation for both supports. The shift of the conversion curve for the Co/MCM-41 and Co/SBA-15 samples, prepared at pH = 5 and pH = 1.5 to the higher temperature, is an evidence for their lower catalytic activity in comparison to their analogs, prepared at pH = 3.

The temperature of the oxidative pretreatment has a notable influence on the nature and dispersion of the cobalt oxide species formed upon the precursor decomposition [13]. The catalytic activity of the selected samples oxidized at 673 and 573 K is compared in Fig. 6. Mild oxidative pretreatment at 573 K has a favorable effect on the formation of catalytically active cobalt oxide species for both types of mesoporous supports. Besides, this influence is stronger when SBA-15 is used as a support. According to Van Steen et al. [13], the higher temperature for oxidation pretreatment leads to stronger metal–support interaction and to the formation of hardly reducible cobalt oxide particles.

Summarizing the catalytic performance and the physico-chemical characterization of the modified materials, we could conclude that the samples containing higher amount of easily reducible Co₃O₄ particles show higher catalytic activity. According to the Mars-van Krevelen mechanism,

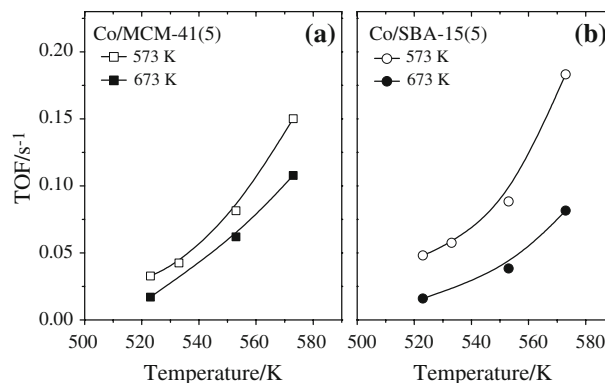


Fig. 6 Effect of the pretreatment temperature on the catalytic activity

which is usually realized during the toluene oxidation [2, 40–43], participation of oxygen from the solid catalyst is of key importance. The higher catalytic activity of Co/MCM-41(3) and Co/SBA-15(3) could be assigned to the easier release of oxygen from the Co-oxide species. However, in the case of Co/SBA-15(5) the higher extent of reduction does not lead to higher catalytic activity, more probably due to the simultaneous presence of Co₃O₄ and Co²⁺, latter being less active in toluene oxidation. In Fig. 7, the results of the catalytic oxidation of toluene as a function of temperature on both supports prepared at pH = 3 and pH = 5 and oxidized at 573 K are presented. In this case the mild oxidative treatment resulted in higher catalytic activity for Co/SBA-15(5). The higher oxidation temperature probably leads to further transformation of finely dispersed Co₃O₄ particles to cobalt silicate. Such transformation, depending on the calcination temperature, has been reported also by Van Steen [13].

Conclusions

The effect of the post-synthesis modification with cobalt via wet impregnation of mesoporous MCM-41 and SBA-15

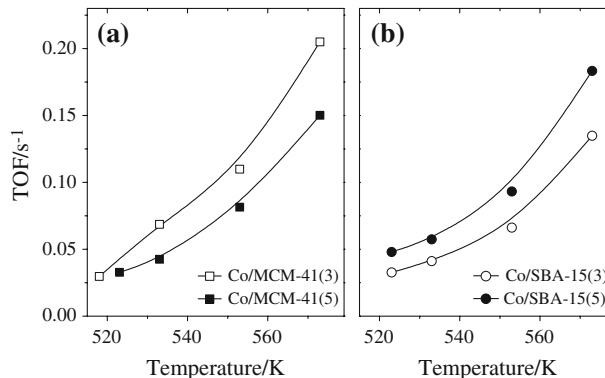


Fig. 7 Catalytic activity of the cobalt modified samples prepared at different pH values and oxidized at 573 K

materials at different pH values of the impregnation solution was studied. The mechanism of cobalt deposition depends on the pH of the impregnation solution. Cobalt oxide species with different nature (Co_3O_4 , Co^{2+} , and Co-silicate like species) are formed as a result of different interactions with the support. These species possess diverse reducibility and dispersion. The highest catalytic activity is observed for both type of samples prepared at $\text{pH} = 3$ due to the presence of easily reducible and finely dispersed Co_3O_4 particles. Mild oxidative pretreatment has a favorable effect on the formation of easily reducible and finely dispersed cobalt oxide species active in total toluene oxidation for both supports.

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