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Oxidative dehydrogenation of isobutane over Co-MCM-41 catalysts

V. Cortés Corberán [a,*], M.J. Jia [a], J. El-Haskouri [b], R.X. Valenzuela [a],
D. Beltrán-Porter [b], P. Amorós [b]

[a] *Institute of Catalysis and Petroleumchemistry, CSIC, Cantoblanco, 28049 Madrid, Spain*
[b] *Institut de Ciencia dels Materials, Universitat de València (ICMUV), P.O. Box 22085, 46071 Valencia, Spain*

Abstract

Cobalt-containing mesoporous silicates with MCM-41-like structure, with $\mathrm{Si/Co} \geq 49$, are active and selective catalysts for the oxidative dehydrogenation (ODH) of isobutane. The formation of dehydrogenation products is analysed in terms of the nature of the cobalt species, tetrahedral Co(II), and heterogeneously initiated gas-phase reactions inside the mesopores.

Keywords: Oxidative dehydrogenation; Isobutane; Co-MCM-41 catalysts

1. Introduction

Reducible transition metal oxides constitute most of the heterogeneous catalysts for oxidation of hydrocarbons. Their catalytic behaviour depends on the nature of the metal, but it is also extremely dependent on the nature of active oxidic species (oxidation state, coordination sphere, dispersion, and stability), in such a way that supported oxides show a behaviour that may be completely different of that of the bulk oxide. Thus, bulk cobalt oxide and the cobalt-containing perovskite mixed oxides are known to be highly efficient catalysts for total combustion of hydrocarbons. However, cobalt is also an efficient component in molybdate-based catalysts for selective oxidation of olefins and for the oxidative dehydrogenation of propane and isobutane [1,2]. Recently, cobalt oxide supported on titania has been found to be active in the ODH of ethane [3,4].

The introduction of transition metals in the framework of mesoporous MCM-type materials opens new ways to disperse and stabilise active oxidic species, as recently reported on metal-doped mesoporous silicates with MCM-41-type structure. Many cations have been tried to be incorporated into the MCM-41 framework [5]. However, in all cases the total amount of the guest cation that can be introduced by direct (hydrothermal) synthesis is quite limited, leading to the segregation of the excess as a separate oxide phase [5–8]. On the other hand, it is noteworthy that to date catalytic research in the field of alkane oxidative activation on these materials has been almost exclusively devoted to V-containing catalysts [6–9]. Some of us reported for the first time the synthesis of cobalt-containing MCM-41-like mesoporous silicas, by synthesis via the so-called atrane route [2].

We report here for the first time that the incorporation of cobalt into the framework of MCM-41-like silicas produces catalysts that are active and selective for the oxidative dehydrogenation (ODH) of isobutane to isobutene.

2. Experimental

2.1. Catalysts preparation

Cobalt rich mesoporous MCM-41 catalysts were prepared by the atrane route [5] by using of Si and Co atrane complexes (complexes with tri-ethanol amine, TEAH3) as molecular precursors, and CTABr as “supramolecular template”. In a typical synthesis to obtain $\mathrm{Si/Co} = 23$, a mixture of 10.5 ml TEOS and 0.33 g $CoCl_2$ was added to a solution (pre-heated at 180 °C during 5 min) of 22.93 ml TEAH3, and 0.49 g NaOH in 2 ml H_2O, and heated at 150 °C for 10 min. The resulting solution was cooled to

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[*] Corresponding author. Fax: +34-915854760.
E-mail address: vcortes@icp.csic.es (V. Cortés Corberán).

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Table 1
Selected synthetic and physical data for Co-MCM-41 mesoporous catalysts

Si/Co ratio		a[a] (Å)	S_{BET} ($m^2 g^{-1}$)	Pore size[b] (Å)	Pore structure[c]
Starting[d]	Final[e]				
50	155	38.03	909	25.0	Ho
40	98	38.01	662	24.8	Ho
30	49	40.96	526	24.7	Hd
20	23	41.37	479	25.0	W

[a] Cell parameter assuming an MCM-41-like hexagonal cell.
[b] BJH pore sizes estimated from the isotherm's adsorption branch.
[c] According to XRD and TEM: Ho, hexagonal ordered; Hd, hexagonal disordered; W: worm-like.
[d] Molar ratio in the starting mother solution.
[e] Values averaged from EPMA of ca. 50 particles.

60 °C, and then 4.23 g CTABr in 80 ml of water were added while stirring. The mixture is aged at room temperature for 24 h, and then the precipitate filtered and dried in air. To obtain the final catalysts, the obtained mesostructured material is calcined at 550 °C for 7 h in static air. Catalysts samples are denoted as Co-MCM-41(x), where x is the final Si/Co atomic ratio. A pure silica Si-MCM-41 sample was prepared in a similar way for comparative purposes.

2.2. Catalyst characterisation

Elemental composition was determined by EPMA in an electronic microscope Philips SEM-515. Reported Si/Co ratios are calculated averaging the data from some 50 different particles (spot area ca. 1 μm). XRD patterns were registered in 0.02° steps (measuring time 25 s per step) in the angular range 2θ=1–10°, with a Seifert 3000TT diffractometer, using Cu Kα radiation. TEM micrographs were obtained with an electronic microscope Philips CM-10, operated at 120 kV. UV-Vis diffuse reflectance spectra were registered with a Shimadzu UV-250 1 PC instrument. Adsorption–desorption isotherms of nitrogen were carried out in a Micromeritics ASAP 2010 instrument. Table 1 summarises the main synthesis variables and physical data of some selected samples of the prepared Co-MCM-41 catalysts.

2.3. Catalytic tests

Catalyst samples (0.2 g) were tested for the ODH de isobutane in a tubular, fixed-bed continuous reactor at 425–550 °C using an iC_4H_{10}–O_2–He feed (molar ratio 27:13.5:59.5), with on line GC analysis of reactants and products. Void volume of the reactor was filled with SiC bits. To check the contribution of homogeneous reactions in the gas phase in the absence of catalysts, similar tests were conducted by substituting SiC bits for the catalyst. Conversion, selectivity and yields were calculated on a C-atom basis, and expressed as mol%. In all tests, mass and carbon balances were within 100 ± 5%.

3. Results and conclusions

EPMA analysis (Table 1) showed that all the samples are chemically homogeneous (spot area ca. 1 mm) with a regular distribution of Si and Co atoms throughout the inorganic walls. All the solids prepared, i.e., mesostructured (prior to calcination) and mesoporous (after calcination), display XRD patterns with at least one strong reflection at low 2θ angle values (reflection (1 0 0) of the MCM-41 hexagonal cell) and at least other three features of lower intensity (reflections (1 1 0), (2 0 0) and (2 1 0), characteristic of mesoporous silicas, with the only exception of the material with the maximum cobalt content (Si/Co = 23) for which the peaks are broadened. The general features of the XRD patterns are kept after surfactant evolution during calcination, but a significant loss of order is observed for the mesoporous solids when comparing their patterns with those of the respective mesostructured solids. The relative intensity and resolution of the reflections decrease after template removal. In the case of the mesoporous catalysts, an hexagonal ordered (Ho) array is achieved up to cobalt contents defined by the ratio Si/Co = 98. Further increase of the cobalt content increases progressively the disorder of the hexagonal array (Hd) leading to a highly disordered wormhole-like (W) pore system for the ratio Si/Co = 23: Ho ($\infty \geq$ Si/Co $\geq$ 98) → Hd (Si/Co = 49) → W (Si/Co = 23). TEM images (not shown for lack of room) fully correlate with XRD observations.

All catalyst samples show typical Type IV N_2-isotherms with one well defined step at intermediate partial pressures ($0.3 < P/P_0 < 0.45$), related to the capillary condensation of N_2 inside the mesopores. Only sample Co-MCM-41(49) isotherm showed a small hysteresis loop at $P/P_0 = 0.4$–0.6, which indicates a partial narrowing or blocking of the pores. On the other hand, while incorporation of Co atoms practically do not affect the pore size, BET area and pore volume decrease gradually as the Co content increases. This evolution indicates a relative loss of order and regularity in the pore system according to XRD and TEM data.

Samples with Si/Co ratios ≥49, having the typical low-angle XRD pattern characteristic of hexagonal MCM-41 solids, were tested as catalysts for the oxidation of isobutane. The absence of reflections at $2\theta > 10°$ and the chemical homogeneity of every sample (from EPMA) indicate that no segregation of cobalt oxide crystallites occurs in these catalysts.

In the reaction conditions used, both Co-MCM-41 samples (Si/Co = 49 and 98) were active for the target reaction already at 400 °C, its activity increasing with reaction temperature (Table 2). Start-up activity initially decreased, but reached a steady-state value after 1 h on stream at 525 °C. No change of BET surface area was observed after the catalytic tests. A higher Co content (Si/Co = 49) gave an activity around 20% higher at the lower temperatures (Table 2), although the BET area was lower (Table 1).

Table 2
Catalytic behaviour for the selective oxidation of isobutane over Co-MCM-41 catalysts[a]

Si/Co ratio	Reaction temperature (°C)	Conversion (%)		Selectivity (%)								Yield (%)	
		iC_4H_{10}	O_2	$iC_4H_8^=$	MAL[b]	ACT[c]	C_3H_6	HCHO	CO	CO_2	Others[d]	$iC_4H_8^=$	MAL
98	425	3.2	13.6	25.1	22.8	8.1	2.1	11.3	10.4	16.2	4.0	0.8	0.7
	450	4.6	21.2	25.4	23.2	6.4	3.3	9.9	11.2	17.2	3.4	1.2	1.1
	475	6.2	30.2	26.1	21.7	4.8	4.5	8.8	12.4	17.8	3.9	1.6	1.3
	500	8.7	41.4	26.6	20.5	3.7	6.9	7.3	12.8	17.6	4.6	2.3	1.8
	525	12.3	54.5	27.2	19.0	3.1	10.3	5.6	13.8	16.2	4.8	3.3	2.3
49	425	4.0	18.0	25.9	17.6	6.6	2.4	6.0	12.1	25.5	3.8	1.0	0.7
	450	5.7	29.4	25.9	16.0	4.9	3.5	5.0	13.1	27.9	3.7	1.5	0.9
	475	7.8	40.6	25.8	15.4	3.3	4.6	4.7	14.2	28.3	3.8	2.0	1.2
	500	10.0	52.2	26.1	14.1	2.7	6.7	4.1	14.7	27.6	3.9	2.6	1.4
	525	12.4	66.9	26.7	13.2	2.1	9.5	3.7	15.3	25.2	4.2	3.3	1.6

[a] Reaction conditions: iC_4:O_2:He $= 27.0:13.5:59.5$ (mol%), $W/F = 12\ g_{cat}\ h/(mol_{C4})$.
[b] MAL: methacrolein.
[c] ACT: acetone.
[d] Acrolein, acetaldehyde, ethylene, etc.

Unexpectedly, not only carbon oxides but also isobutene, methacrolein (MAL) and other oxygenates were formed (Table 2). The combined selectivity to dehydrogenated products (as MAL should be a product of isobutene selective oxidation) approaches 50%. At similar conversion levels, the higher Co content did not modify the olefin selectivity but decreased the selectivity to methacrolein. These dehydrogenated products may not be explained as due to the non-catalysed gas-phase homogeneous reaction, because, in the absence of catalyst, the conversion was roughly one order of magnitude lower, even at 525 °C (Fig. 1). The low selectivity to carbon oxides must be due to the nature of the cobalt centres. The main feature of the UV-Vis diffuse reflectance spectra of the catalysts (not shown) is the a broad band with three maxima at 545, 600 and 640 nm, assigned to the transition $^4A_2 \rightarrow {}^4T_1(P)$ in Co(II) systems with tetrahedral environments. This means that catalysts Co-MCM-41 with $Si/Co \geq 23$ present a unique tetrahedral coordination of the Co(II) centres. This type of Co^{2+} species has been found to be active and selective for the ammoxidation of ethane on Co-containing zeolites with MFI and BEA structures [10]. While CoAPO-5 shows poor activity and low olefin selectivity in the ODH of propane [11], CoH-containing zeolites BEA, MFI, MOR and FER have been found active for the ODH of ethane and propane [12], but no product of the selective oxidation of the olefin was detected. The activity of these Co-containing zeolites having similar Co/Al ratios is influenced by their topology in the order: BEA > MFI ⋙ MOR > FER. These results point to an additional factor, besides the nature of the cobalt centre, to be influencing the catalytic behaviour.

On the other hand, interestingly, the pure MCM-41 silica sample showed some activity itself, producing also dehydrogenation products; its selectivity varies with isobutene conversion degree following a trend similar to that found for Co-MCM-41 with $Si/Co = 98$ (Fig. 1), although operating at much higher temperatures. This result seems to reveal an influence of the reactivity inside the confined space of the mesopores, that could be analysed in terms of heterogeneously initiated, radical gas-phase homogenous reactions, as previously observed for the partial oxidation of propane to acrolein [13]. In this way, activation of the

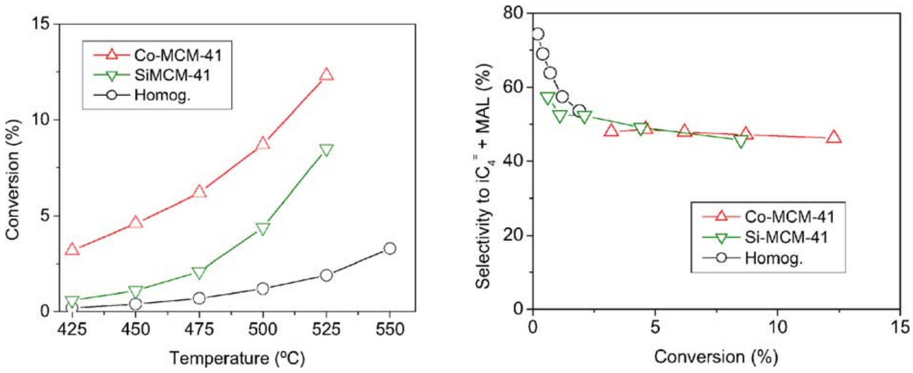

Fig. 1. Conversion (left) and selectivity to dehydrogenated products (right) in the ODH of isobutane over Co-MCM-41 ($Si/Co = 98$) and its Si-MCM-41 homologue. Reaction conditions: iC_4:O_2:He $= 27.0:13.5:59.5$; $W/F = 12\ g_{cat}\ h/(mol_{C4})$.

alkane molecule would take place on centres located on the inner pore wall, generating radical species that would either react inside the void volume of the mesopores (acting as “nano-reactors”) or interact with another centre of the pore wall. The observed variation of the selectivity to methacrolein with the Co content could be explained in this way: a higher number of active centres will increase the probability of further oxidation of the formed methacrolein. Further studies are in progress to clarify the mechanism.

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