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Metal states in cobalt- and cobalt–vanadium-modified MCM-41 mesoporous silica catalysts and their activity in selective hydrocarbons oxidation

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Abstract

MCM-41 mesoporous molecular sieves with various V and Co loading were obtained by hydrothermal synthesis. The structural regularity and morphology of the resultant materials were characterized by XRD, TEM, SEM and N_2 adsorption. The information about the nature, co-ordination and location of the metal species were obtained by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRS). These methods indicated different localization of the cations in extra-framework positions or in the skeleton of the molecular sieves. In the low loaded cobalt catalysts, Co^{2+} in tetrahedral position was observed. The increase in metal content led to the appearance of Co^{3+} in Oh symmetry. In both cases, the cobalt ions were placed outside of the silica framework. Vanadium in the bimetallic samples was incorporated inside the framework of the molecular sieves and on the channel walls. V^{5+} was in tetrahedral symmetry. Cobalt in the bimetallic samples was presented as Co^{2+} in Td symmetry. When Co and V were introduced together in the starting gel, a lower quantity of vanadium was incorporated into the mesoporous sieve. The modified MCM-41 molecular sieves obtained by hydrothermal synthesis were active in selective oxidation of styrene to benzaldehyde and of benzene to phenol.

Keywords: Vanadium; Cobalt; VCo-MCM-41 catalysts; Metal state; Hydrocarbon oxidation

1. Introduction

Transition metals substitution for silicon in molecular sieves such as hexagonally ordered MCM-41 represents an interesting direction for development of novel catalysts that show remarkable activity and selectivity in oxidation of organic compounds [1–4]. The catalytic properties are mainly attributed to the position and coordination of the transition metal ions into the molecular sieve framework. Therefore, the characterization of transition metal states is very important issue of their study.

It is well known that the formation of various surface phases during preparation of vanadium and cobalt catalysts depends strongly on the support, metal loading, method of preparation, and pre-treatment [5–7]. The high surface area of MCM-41 mesoporous sieves and the presence of uniform hexagonal arrays of mesopores provide new opportunities for transition metal incorporation. It is possible to obtain metal heteroatoms as framework tetrahedral T atoms, bound in defect sites of the framework, anchored to the surface, extra framework counter ions or extra framework oxides. The metal ions incorporated in the framework of mesoporous MCM-41 molecular sieves provoke equally Lewis acidity and oxidizing properties. Incorporation of a second metal might therefore create

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catalysts with new redox and acid properties [8–10]. Vanadium-containing MCM-41 has received particular attention since many oxidation catalysts contain V as active component [11]. In the V-MCM-41 catalysts prepared by hydrothermal synthesis [12–14], vanadium occurs mainly as isolated tetrahedrally coordinated V^{5+} species incorporated in the pore wall or anchored to the pore wall.

The aim of the present investigation is to shed some light on the state of cobalt and vanadium in monometallic (Co-, V-MCM-41) and bimetallic (VCo-MCM-41) catalysts with different metal loading prepared by direct hydrothermal method and their behavior in hydrocarbons oxidation by H_2O_2.

2. Experimental

2.1. Synthesis

Co-, V-MCM-41 and VCo-MCM-41 molecular sieves were synthesized by hydrothermal treatment [15,16] on the basis of molar gel composition of 1.0 SiO_2:x M:0.48 CTMAB:0.28 Na_2O:3.7 TMAOH:222.0 H_2O, where $x = 0.02$–1.0 for Co-MCM-41 (samples assigned from Co1 to Co5 in Table 1) and 0.4 for VCo-MCM-41 (samples assigned from VCo1 to VCo3). Co/V molar ratio was varied between 0.3 and 3 in the synthesis gel (0.3 for VCo1, 1 for VCo2, and 3 for VCo3). The obtained gels were sealed into Teflon-lined steel autoclaves and heated 5 days at 373 K. The solid products were recovered by filtration, washed and dried at air. The as-synthesized samples were heated in flow of N_2 and then calcined in air at 823 K. The description of the samples is given in Table 1. The reagents used for catalysis preparation were sodium silicate (25.5–28.5 silica), cethyltrimethylammonium bromide (CTMAB, Aldrich), tetramethylammonium hydroxide (TMAOH solution 25% in water, Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (Merck), $VO(SO_4)_2 \cdot 5H_2O$ (Merck).

2.2. Characterization

The obtained materials were characterized by X-ray diffraction (XRD) (Philips PW 170 diffractometer), N_2 adsorption–desorption (Micromeritics-Tristar 3000), scanning electron microscopy (SEM) (Philips XL-20 microscope), transmission electron microscopy (TEM) (Tecnai Philips microscope) with accelerating voltage of 100 kV, temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and Diffuse reflection spectroscopy (DRS). TPR was carried out in equipment described elsewhere [17] using a flow mixture 10% H_2 in Ar at 10 ml/min, temperature ramp of 10 K/min to 973 K. Prior to the TPR experiment the samples were treated in Ar for 1 h at 423. The amount of Co and V in the catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (ARL 3410). XPS spectra were recorded on ESCALAB-MkII (VG Scientific) electron spectrometer with base pressure 1×10^{-8} Pa, following the technique given in [18]. The energy positions of photoelectron line were determined with respect to the reference C 1s line (BE 285 eV). Diffuse reflectance spectra of the samples were recorded at room temperature on a Beckman 5270 spectrophotometer. $BaSO_4$ was used for a reference.

2.3. Catalytic test

Mono- and bimetallic catalysts were tested in oxidation of aromatic hydrocarbons (benzene and styrene) with hydrogen peroxide. Reactions were performed in a round bottom flask using 30 wt.% aqueous H_2O_2 as oxidant. The reactant mixture of substrate, oxidant and solvent were added to 70 mg catalyst and heated, during 24 h, at constant temperature of 343 K and under magnetic stirring. The molar ratio substrate/acetonitrile/H_2O_2 was 1/1.8/3 for styrene oxidation and 1/–/3, for benzene oxidation. After reaction, the mixture was cooled down to room

Table 1
Characteristics of the Co-, V- and VCo-MCM-41 catalysts

Sample	Designed metal content in the samples[a] (wt.%)		Metal content in the calcined samples[b] (wt.%)		Percentage of the immobilized metal (b/a) (%)		a_0 (nm)	S_{BET}, (m^2/g)	$\varnothing_{BJH}$ (nm)
	Co	V	Co	V	Co	V			
MCM-41	–	–	–	–	–	–	4.6	1050	2.7
Co1	1.8	–	1.34	–	74	–	4.6	990	2.8
Co2	3.6	–	3.23	–	90	–	4.7	900	2.8
Co3	5.5	–	4.59	–	83	–	4.7	640	2.7
Co4	7.4	–	6.28	–	85	–	4.8	570	3.0
V	–	1.6	–	1.13	–	71	4.5	1050	2.7
VCo1	2.7	0.78	2.23	0.23	83	29	4.7	950	2.8
VCo2	1.8	1.6	1.15	0.61	64	38	4.6	1010	2.8
VCo3	0.9	2.5	0.76	0.78	84	31	4.7	970	2.7

a_0 – cell parameter (calculated from $a_0 = 2d_{100}(3)^{-1/2}$) (nm).
S_{BET} – BET surface area (m^2/g).
$\varnothing_{BJH}$ – pore diameter (nm).
[a] Calculated from SiO_2/M^{n+} molar ratio in the mother liquor.
[b] Obtained by chemical analyses.