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Influence of MCM-41 Silanol Number on Vanadia Deposition by Molecular Designed Dispersion Method

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The dispersion and the loading of metals on support materials have great importance in the design of catalysts. Two MCM-41 supports having similar morphology, porosity characteristics and different OH/nm^2 values were synthesized, in order to study the influence of silanol number on vanadia deposition. VO_x supported MCM-41 catalysts were prepared through the molecular designed dispersion method (MDD) in liquid phase using vanadyl acetylacetonate. Different techniques such as X-ray diffraction, N_2 adsorption/desorption, UV - VIS and TGA were used for characterization of support materials and VO_x/MCM-41 catalysts. All results indicate that the MCM-41 silanol number strongly influence the loading of vanadia.

Keywords: silanol number, dispersion method (MDD), MCM-41 catalysts

The most striking fact about the MCM-41 material is that, although composed of amorphous silica, it displays an ordered structure with uniform mesopores arranged into a hexagonal, honeycomb-like lattice. MCM-41 is a proper porous matrix for the design of catalysts by introducing or grafting metal ions, metal oxides, metal or organometallic complexes or other type of active species. There have been essentially three approaches to the insertion of metal oxides: impregnation, melting oxide inclusion, and solid-state reaction (Zhao et al 1996). Until now, only a few published papers have documented the correlation between the MCM-41 silanol number and vanadia loading by MDD method (Zhao et al 1997).

In this paper we discuss the influence of hydroxyl number of the support on vanadia loading by the molecular designed dispersion method. Two MCM-41 supports, possessing different OH numbers, were synthesized at room temperature. The vanadyl acetylacetonate was deposited in two ways: at room temperature and with a decreasing temperature gradient (from 318K).

Experimental part

Two MCM-41 supports (S1 and S2) with similar morphology, porous features and different OH number, were synthesized. The former support (S1) was prepared according to the recipe of Liu et al (2003). For former support (designated S2) the molar composition: SiO_2:0.12CTAB:0.25Na_2O:136H_2O was realized using cetyltrimethylammonium bromide (CTAB), tetraethyl-orthosilicate (TEOS) from Acros Organics. The mixture was further stirred for 1h followed by aging at room temperature for 72h. The final product was filtrated, washed, dried at room temperature and calcined at 550°C. Vanadia was deposited on the mesoporous supports by the MDD method using vanadyl acetylacetonate (Van Der Voort et al 1997). The obtained VO_x samples were noted S1V and S2V, respectively.

The vanadia loaded on the final catalysts was determined colorimetrically at 450 nm, on a NICOLET EVOLUTION 500 UV-VIS device. The X-ray diffractions were recorded on a Philips PW 1830 powder diffractometer (45 KV, 25 mA), using Ni filtered Cu_a (0.154 nm) radiation. N_2 adsorption/desorption measurements were performed on a QUANTACHROME Autosorb 1. The SEM images were obtained using a JSEM 5510 microscope, operating at an accelerating voltage of 15kV. The number of silanols per unit surface area on the pore surface was determined (Blitz et al 1998) and correlated with the weight losses in TGA measurements of the modified supports. TGA measurements were performed on a Mettler TG50 thermobalance, equipped with a M3 microbalance and connected to a TC10A processor.

Results and Discussions

XRD patterns of the supports are typical for hexagonally ordered mesoporous materials (fig. 1). A strong (100) reflection at 2θ = 2.46 and 2.58 have been observed for each support. Two other peaks at 2θ between 4 and 6, attributed to the (110) and (200) reflections are also present. SEM images prove that the S1 and S2 samples have the same morphology (fig. 2.).

The N_2 adsorption/desorption isotherms of S1and S2-supports, S1V and S2V-systems, of type IV in IUPAC classification show a capillary condensation at a relative pressure (P/Po) between 0.2 and 0.3 (not shown).

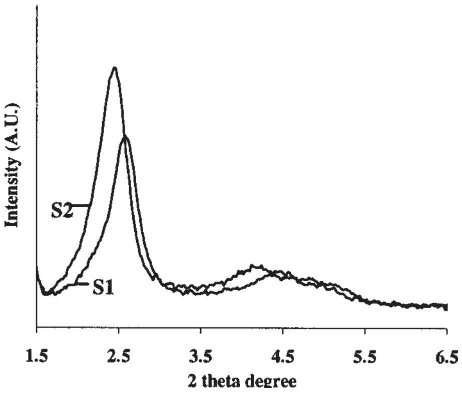

Fig. 1. XDR patterns of the supports

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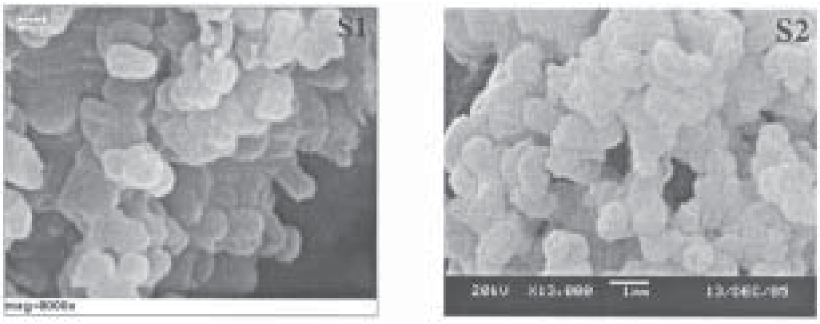

Fig. 2. SEM images of the support

Table 1
CHARACTERISTICS OF THE SUPPORT MATERIALS, S1V AND S2V

Samples	mmol V/g support	S_{BET} (m^2/g)	Total pore Volume (cc/g)	Pore diameter (Å)	Particles size (μm)	OH/nm^2
S1	0	1250	0.885	23.6	1-2	2.81
$S1V_{0.66}$	0.079	1220	0.862	22.6	-	-
$S1V_{14.66}$	0.424	1190	0.855	22.5	-	-
S2	0	1100	0.786	23.6	1-2	2.23
$S2V_{0.66}$	0.058	1030	0.753	22.1	-	-
$S2V_{14.66}$	0.246	960	0.707	20.3	-	-

Table 2
VANADIUM CONTENT, ATOMS/nm^2 SUPPORT

Initial V concentration (mmol/l)	α S1	α S2
0.66 RT	0.038	0.031
6.00 RT	0.145	0.116
10.0 RT	0.193	0.132
14.66 RT	0.204	0.134
0.66 G	0.046	0.046
6.00 G	0.173	0.159
10.00 G	0.222	0.203
14.66 G	0.238	0.217

RT - room temperature; G - Gradient

Increasing metal loading, a gradual decrease in surface area and pore volume was observed, but the porosity characteristics of the materials after deposition were maintained very high, indicating that no structural degradation took place. The characteristics of the supports before and after deposition of vanadia are presented in table 1.

The α-value, number of V atoms per nm^2, (table I) was calculated by dividing the V loading by the specific surface area of the support before deposition: $V(mol/g) \cdot N_A)/S(nm^2/g)$ (Meynen et al 2005). In this way, vanadium loading on the different supports could be compared, in a straightforward way, even if the studied supports have differences in surface area. As shown in tables I and II vanadia loading on the S1 support is higher than on S2 support, both at room temperature and under temperature gradient conditions, despite similar porous characteristics and morphology. These results suggest that the vanadia loading is strongly influenced by the silanol number of the support.

Conclusions

MDD vanadia loading, on MCM-41 supports with similar morphology, porosity and different silanol number, was compared. Our results showed that with higher OH number of the support, higher is the quantity of vanadium which could be introduced, despite of similar porous characteristics and morphology. These results have been verified both at room temperature and gradient temperature conditions. It was demonstrated that the MCM-41 silanol number strongly influence the MDD loading of vanadia.

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