Short communication

Influence of V-sources on the catalytic performance of VMCM-41 in the selective oxidation of methane to formaldehyde

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ABSTRACT

VMCM-41 catalysts from two different tetravalent vanadium sources, hydrothermally synthesized after a mild gelation step at room temperature, were used as catalysts for the selective oxidation of methane to formaldehyde. Vanadyl acetylacetonate as VMCM-41 precursor, facilitates highest VO$_x$ density with predominance of monomeric and a small portion of low-oligomeric VO$_x$ species. It produces CH$_2$O in high yield and the highest space time yield (STY$_{CH2O}$) reaches 5.3 kg$_{CH2O}$·kg$_{cat}^{-1}$·h^{-1} at 600 °C (rate of formation, r$_{CH2O}$ of 363 h^{-1}). VMCM-41 synthesized from vanadyl sulfate hydrate precursor contains a more significant portion of low-oligomeric species. With a lower V loading, these VO$_x$ species are significantly less active resulting in a maximum STY$_{CH2O}$ of 2.7 kg$_{CH2O}$·kg$_{cat}^{-1}$·h^{-1} at 625 °C (r$_{CH2O}$ of 243 h^{-1}).

1. Introduction

Formaldehyde production through oxidation of methanol, which itself is produced from synthesis gas, is characterized by low exergy of about 43.2% [1]. As a consequence, the direct catalytic conversions of methane to methanol or formaldehyde became a challenging aim in C1-chemistry [1–6]. Catalysts with highly dispersed vanadium and molybdenum oxide species are known for their selectivity directing properties in the oxidation of methane to formaldehyde [7–10]. The most efficient vanadium based catalysts contain highly dispersed monomeric isolated and/or low-oligomeric VO$_x$ species on mesoporous silica supports, e.g. SBA-15 or MCM-41 [11–15]. Such VO$_x$ species are crucial to form formaldehyde and minimize consecutive oxidation to carbon oxides. In addition, VO$_x$ species partially carrying acidic V-OH groups were supposed as the active site [8,9,14,16,17].

Synthesis methods of V containing MCM-41 [9,13,14,18] as well as specific synthesis parameters, which could influence the structure and nature of VO$_x$ species, such as ageing temperature and time [19], V content [20–22], Si or V sources [20,23–28] and pH adjustment [20,29] are well reported before.

Gucbilmez et al. found that if ammonium metavanadate, NH$_4$VO$_3$, was used as vanadium source in hydrothermal synthesis of VMCM-41,

the V/Si ratio in the solid structure was about five times lower than the corresponding value obtained with VOSO$_4$ as V precursor [23]. Selvam and Dapurkar reported that the tetravalent vanadium sources, such as VOSO$_4$ and VO(acac)$_2$ provide a maximum of vanadium incorporation in the silicate framework of MCM-41, due to the formation of monomeric VO$_4^{3-}$ ions in the synthesis gel [24]. In case of VMCM-41 prepared by pentavalent vanadium sources like NaVO$_3$ and NH$_4$VO$_3$, both monomeric VO$_4^{3-}$ and binuclear V$_2$O$_7^{4-}$ ions were formed in the synthesis gel. Noteworthy, V$_2$O$_7^{4-}$ species hinder the incorporation of vanadium into the silicate matrix, leading to a lower V content in the solid. These attempts resulted in excellent active catalysts for cyclohexane oxidation in the presence of methyl ethyl ketone as initiator, i.e. conversion of cyclohexane and selectivity of cyclohexanol were over 90% [24]. Wu et al. reported that the in situ formation of vanadium tartrate in the synthesis gel provides the incorporation of a large amount of tetrahedral monomeric as well as small chain, oligomeric V(IV) species in MCM-41 [27]. This generates a good catalytic performance in cyclohexane oxidation without initiator, i.e. 22.6% cyclohexane conversion and 99.5% selectivity for cyclohexanone plus cyclohexanol.

In this study VMCM-41 was synthesized hydrothermally after a mild gelation step at room temperature with two different tetravalent

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vanadium sources, namely $VOSO_4$ and $VO(acac)_2$. The different sources lead to different VO_x species whereas the $VO(acac)_2$ derived VMCM-41 is most suitable for the catalytic selective oxidation of methane to formaldehyde among all one-pot derived analogues.

2. Experimental

2.1. Catalysts preparation

6.6 mmol of N-cetyl trimethyl ammonium bromide (CTAB, ACROS, 99.9%) was dissolved in 110 ml of deionized water under stirring. Subsequently, 4.91 g ammonium hydroxide solution (25% NH_3, Chem Solute) and 43 mmol tetraethyl orthosilicate (TEOS, Fluka, 99%) were added slowly to the CTAB solution. To this mixture 1.8 mmol of vanadium sources, $VOSO_4 \cdot 3H_2O$ (Aldrich, 99%) or $VO(acac)_2$ (Merck Schuchardt, 98%) in 10 ml deionized water were added. The further gelation process was carried out under stirring at room temperature for 18 h. For a sequent hydrothermal ageing step, the gel was filled in a 180 ml Teflon-lined autoclave and treated for 3 h at 80 °C. After gelation and ageing, the resulting mixtures were filtered and the solid samples were washed with deionized water consecutively. The obtained VMCM-41 products were dried at 105 °C for 6 h. The samples were calcined at 575 °C for 10 h in air.

The denotation of the samples bases on the source of vanadium. "V-a" and "V-s" stands for $VO(acac)_2$ and $VOSO_4 \cdot 3H_2O$ used as sources, respectively. Powder X-ray diffraction (XRD), nitrogen adsorption at low temperature and transmission electron microscopy (TEM) were applied to reveal the structural and morphological properties of the samples. The vanadium contents were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) and the Si content was determined by means of Atom Absorption Spectroscopy (AAS). The coordination environment of V species was analyzed by Ultraviolet–visible spectra (UV–vis) and their reduction behavior were investigated by means of temperature programmed reduction in H_2 (H_2-TPR). Details of the characterization of the catalyst can be found in the ESI.

2.2. Catalytic oxidation of methane

Catalytic oxidation of methane was carried out in a horizontal fixed bed plug flow reactor consisting of a quartz tube with an inner diameter of 8 mm. Experiments were performed with 50 mg of the respective unclassified catalyst (particles of about 100 × 300 nm) placed in the center of the quartz tube, fixed by quartz wool. Behind the catalyst bed the inner diameter of the reactor decreases to 4 mm. Oven temperatures were controlled by a thermocouple in the middle of the catalyst bed.

The catalytic performance was measured in a temperature range of 575–625 °C at 1.8 bar for 3 h at each temperature step after reaching steady state within an induction period of 1 h. The reactant gas stream consisted of CH_4 and O_2 in the ratio 9:1 and the total flow rate was 300 ml·min^{-1} which corresponds to a modified GHSV of 360,000 l·kg^{-1}·h^{-1}.

An on-line gas chromatograph equipped with FID and TCD and a methanation unit was used to analyze the O_2, CH_4, C_2 (ethane + ethylene), CO, CH_2O and CO_2 content of the product gas stream at steady state. Two different columns were used, an Agilent J & W 113–3133, 30 m × 320 μm with 250 μl sample loop for FID and an Agilent J & W CP1306, 1.5 m × 1/16″ × 1 mm with 50 μl sample loop for TCD.

The calculation of the CH_4 conversion (X_{CH_4}), yield of products i (Y_i), selectivity to the products (S_i), space time yield of formaldehyde (STY_{CH_2O}) and reaction rate for formaldehyde (r_{CH_2O}) were made according to the following equations:

$$X_{CH_4} = \frac{n_{CH_4}^0 - n_{CH_4}^p}{n_{CH_4}^0} \cdot 100\%$$

(1)

$$Y_i = \frac{n_i^p - n_i^0}{n_{CH_4}^0} \cdot 100\%$$

(2)

$$S_i = \frac{Y_i}{X_{CH_4}} \cdot 100\%$$

(3)

$$STY_{CH_2O} = \frac{\dot{m}_{CH_2O}}{m_{catalyst}};$$
$$\dot{m}_{CH_2O} = Y_{CH_2O} \cdot \dot{n}_{CH_4} \cdot M_{CH_2O}$$

(4)

$$r_{CH_2O} = \frac{\dot{n}_{CH_2O}}{n_{V-atoms}}; \dot{n}_{CH_2O} = Y_{CH_2O} \cdot \dot{n}_{CH_4}$$

(5)

with n_i^0 as amount of a substance i fed to the reaction (e.g. also traces of CO_2 in the CH_4 feed), n_i^p as amount of substance i detected at the reactor outlet, $\dot{n}_{CH_4}$ molar flux of CH_4, $\dot{m}_{CH_2O}$ mass flux of CH_2O, $\dot{n}_{CH_2O}$ molar flux of CH_2O and $n_{V-atoms}$ total number of V atoms.

3. Results and discussion

3.1. Characterization of catalysts

The two precursors differently influence the final VO_x loading in V-MCM-41 which is reflected in different molar Si/V ratios, calculated from ICP-OES results (Table 1). The VO_x content in V-a is significantly higher than that of V-s, although, both catalysts originated from the same molar gel composition of 0.04 VO_x: 0.96 TEOS: 1.64 NH_3: 0.15 CTAB: 150 H_2O.

The XRD patterns of V-a and V-s showed signals of the diffraction planes (100), (110) and (200) typical for the hexagonal mesoporous structure of MCM-41 (Fig. S1a) [30,31]. The main (100) reflection is broad and the reflections (110) and (200) are only hillock-like bands pointing to low degree of short range order. It was inferred that the addition of V ions to the silica expands the unit cell and the main interplanar distance (d_{100}) when incorporated in the SiO_2 network because V(V) (0.495 Å) has a larger ion-radius than Si(IV) (0.4 Å) and the V−O bond distance (1.8 Å) is longer the Si−O bond distance (1.6 Å) [19]. In this study, the corresponding d_{100} spacing values of V-s and V-a are similar (data from XRD) and correlate with the pore diameters, which are also in the same range (from nitrogen sorption, Fig. S2). Obviously, the vanadium content in the materials has no influence on the pore size. Moreover, both catalysts possess a significant amount of reducible VO_x species (Table S1). Both facts imply a preferred localization of VO_x on the pore walls of the mesoporous silica.

Both catalysts possess surface areas of about 1000 m^2/g owing to the mesopores within the samples (Table 1). The STEM images of the catalysts are presented in Fig. 1. V-a shows only small areas of short-range order (Fig. S1b). V-s shows a higher degree of order and the hexagonal structure is visible. V_2O_5 particles were not detected in case of V-a, indicating a fine dispersity of V (Fig. 1a). In contrast, in sample V-s a local vanadium enrichment could be observed (Fig. 1b, red arrow)

Table 1
d-spacing, specific surface area (SSA), pore volume (PV), pore diameter, molar ratio of Si/V, and V-density of the catalysts.

Sample	d_{100}[a]/Å	SSA[b]/ m^2·g^{-1}	PV[b]/ cm^3·g^{-1}	d_{pore}[b]/Å	Si/V[c]	V-density[d]/V atoms·nm^{-2}
V-a	40.2	970	0.84	29.6	23.6	0.30
V-s	40.6	1029	0.88	31.0	35.5	0.24

[a] Calculated from XRD measurements.
[b] From nitrogen sorption experiments using the BET and BJH model.
[c] Values are calculated by ICP-OES and AAS results.
[d] Calculated from SSA$_{BET}$ and ICP-OES results.