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**SYNTHESIS OF HMS AND ITS APPLICATION
IN ODH OF ETHANE**

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The contribution deals with the synthesis of hexagonal mesoporous silica containing aluminum, silica and titanium. Catalytic performance of vanadium species supported on hexagonal mesoporous silica containing aluminum, silica and titanium was compared in the oxidative dehydrogenation of ethane. The supports and the vanadium based catalysts were characterized by using of UV-Vis DR spectroscopy, N₂-isotherm, SEM and X-ray diffraction.

Introduction

Recently, the increasing need of upgrading low-cost feedstock has greatly prompted the research on the selective oxidation reactions of light alkanes, as an alternative to the use of the more expensive olefins. The great attention has been paid to the oxidative dehydrogenation (ODH) of alkanes, mainly of ethane and propane, to give the corresponding alkenes [1] as a thermodynamically favored

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process. Dehydrogenation, fluid catalytic cracking and thermal cracking currently produce ethene and propene. Nevertheless, these processes have some disadvantages such as thermodynamic limitation, coke formation and often catalysts regeneration [2].

The review of Cavani *et al.* [3], showed that the vanadium species supported on the mesoporous materials, such as materials of M41S family, belong among suitable catalysts in oxidative dehydrogenation of light alkanes [3]. M41S group is a typical member of mesoporous molecular sieves, which possesses uniform hexagonal channels ranging from 5 to 60 nm and a very narrow pore-size distribution [4]. Its large internal surface area ($> 800 \text{ m}^2 \text{ g}^{-1}$) allows dispersion of a large number of catalytically active centers. Its thick framework walls (3-10 nm) also provide high hydrothermal stability. One type of mesoporous materials that are of particular interest is the hexagonal mesoporous silicas (HMS), which are claimed to have larger pores, to be more stable and to have thicker pore walls than their MCM-41 counterparts [5]. The unique features (well-defined structure and variability of the pore diameter) associated with the HMS molecular sieve render it a promising candidate as support for various catalysts. More importantly, the synthesis of HMS materials offers additional advantages of the cost-reduction by employing a less expensive and nontoxic surfactant and mild reaction conditions.

Supported vanadium oxides have been extensively studied as selective catalysts in ODH reactions [2,6,7]. It has been established that parameters such as the oxidation state, coordination number, aggregation state and reducibility of vanadium species, distance between active sites or the acid/base properties of the catalysts have to be taken into account in order to explain the observed catalytic behavior. Furthermore, this behavior also seems to be influenced by the vanadium loading since the degree of aggregation of the VO_4 units depends on this. According to the literature the best catalytic performance and selectivity on desired products in ODH reaction of alkanes has been attributed to the presence of isolated tetrahedral V(V) species, whereas polymeric and bulk vanadium species could favor undesired reactions, leading to the formation of carbon oxides. These mesoporous materials usually exhibit a great versatility in terms of both chemical nature and structural characteristics. Thus, the synthesis, characterization and catalytic properties of V-doped mesoporous silica have been extensively reported [8-10].

This work is focused on the study of (i) the synthesis of HMS and the role of process conditions, (ii) the meaning of the presence of Ti, Al and Si atoms in a mesoporous silica framework and finally (iii) the catalytic performance of prepared vanadium-containing hexagonal mesoporous silica catalysts in the oxidative dehydrogenation of ethane.

Experimental

Four different Si-HMS materials were prepared and labeled as Si-HMS-I, Si-HMS-II, Si-HMS-III and Si-HMS-IV. In general, the Si-HMS-I, Si-HMS-II, Si-HMS-III and Si-HMS-IV materials were prepared by dissolving the particular amount of dodecylamine (n_{DDA} , $M = 185.35 \text{ g mol}^{-1}$, density 0.806 g ml^{-1}) in the mixture of appropriate amount of ethanol (n_{EtOH} , $M = 46.07 \text{ g mol}^{-1}$, density 0.789 g ml^{-1}) and redistilled water (n_{water}); solution 1. After stirring for 20 min, calculated amount of tetraethyl orthosilicate (n_{TEOS} , $M = 208.33 \text{ g mol}^{-1}$, density 0.933 g ml^{-1}) in ethanol (solution 2) was added drop-wise and stirred. The reaction mixture was stirred at $70 \text{ }^\circ\text{C}$ for various times (18-42 h) under static conditions. Table I contains the conditions of the synthesis of Si-HMS-I, -II, -III and IV, i.e. the exact amounts of each reaction component and the time of aging of each support. The solid product was filtered, washed with redistilled H_2O and finally calcined in air at $450 \text{ }^\circ\text{C}$ for 8 hours.

Table I The specific surface area and the conditions of the synthesis of Si-HMS-I, Si-HMS-II, Si-HMS-III and Si-HMS-IV materials, i.e. the time of aging and the amounts of dodecylamine, tetraethyl orthosilicate, ethanol and water

Matrix	Solution 1		Solution 2			t	S_{BET}
	$n_{(\text{DDA})}$ mol	$n_{(\text{TEOS})}$ mol	$n_{(\text{EtOH})}$ mol	$n_{(\text{H}_2\text{O})}$ mol	$n_{(\text{EtOH})\text{-added}}$ mol	h	$\text{m}^2 \text{ g}^{-1}$
HMS-I	0.10	0.25	3.85	40127	-	18	490
	0.10	0.25	3.85	40127	-	24	646
	0.10	0.25	3.85	40127	-	36	549
	0.10	0.25	3.85	40127	-	48	515
HMS-II	0.07	0.25	2.33	7.39	-	18	780
	0.07	0.25	2.33	7.39	-	36	650
HMS-III	0.10	0.25	2.46	40127	1.39	18	582
HMS-IV	0.07	0.25	2.46	40127	1.39	18	840
	0.07	0.25	2.46	40127	1.39	36	877

Al-HMS-IV with Si/Al=30 ($903 \text{ m}^2 \text{ g}^{-1}$) and Al-HMS-IV with Si/Al=10 ($1161 \text{ m}^2 \text{ g}^{-1}$) were prepared by dissolution of particular amount of dodecylamine in the mixture of appropriate amount of ethanol and redistilled water. After stirring for 20 min, a calculated amount of tetraethyl orthosilicate (TEOS) was added drop-wise and stirred. At the same time 8.3 mmol (Si/Al=30) or 25 mmol (Si/Al=10)

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the reaction system. The reaction mixture was stirred at 70 °C for 18 h under static conditions. The solid product was filtered, washed with redistilled H_2O and finally calcined in air at 450 °C for 8 hours.

Ti-HMS-IV (20 wt. % Ti, 1100 m^2g^{-1}) was prepared by dissolution of the particular amount of dodecylamine in the mixture of appropriate amount of ethanol and redistilled water. After stirring for 20 min, a calculated amount of tetraethyl orthosilicate was added drop-wise and stirred. At the same time 50 mmol of tetraethyl orthotitanate was added to the reaction system. The reaction mixture was stirred at 70 °C for 18 h under static conditions. The solid product was filtered, washed with redistilled H_2O and finally calcined in air at 450 °C for 8 hours.

V-Si-HMS (2.9 wt. % V), V-Al-HMS (3.57 wt. % V) and V-Ti-HMS (2.97 wt. % V) catalysts were prepared by impregnating Si-HMS, Al-HMS and Ti-HMS with a solution of vanadyl acetylacetonate in ethanol. After impregnation, the catalysts were filtered and dried for 24 hours at room temperature. Calcination was carried out for 8 hours in the temperature range from 600 °C in air.

Structure and crystallinity of synthesized mesoporous support was verified by X-ray diffraction and scanning electron microscopy (Fig. 1). The specific surface area of HMS materials (Table I) and vanadium-based catalysts was measured by means of nitrogen sorption at isotherm. The N_2 adsorption isotherms were measured at -196 °C using the through-flow chromatographic method. The relative pressure of nitrogen was varied in range 0.01-0.3. The specific surface area was determined by the fitting of the experimental data to the BET isotherm.



Fig. 1 SEM image of Si-HMS-IV

UV-Vis diffuse reflectance spectra of the dehydrated granulated (0.25-0.50 mm) materials were recorded using a GBS CINTRA 303 spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated with Spectralon and Spectralon as a reference. Dehydration of vanadium-based catalysts was carried out in a stream of oxygen (450 °C) followed by its

evacuation [11].

Oxidative dehydrogenation of ethane was carried out in a quartz through-flow micro-reactor at 600 °C and atmospheric pressure, with 200 mg of the catalyst (0.25-0.50 mm). The reaction mixture consisting of 8 vol. % C₂H₆, 2.5 vol. % O₂ and the rest of He was introduced at the flow-rate of 100 ml min⁻¹ (W/F 0.06 g_{cat} s ml⁻¹). Concentrations of CO₂, CO, O₂ and hydrocarbons were measured by means of an on-line connected gas chromatograph Shimadzu GC 17A [12].

Results and Discussion

Synthesis of HMS

Tanev and Pinnavaia firstly reported the synthesis of hexagonal mesoporous silica in 1995 [13]. After that, various modifications were published for the synthesis of HMS with the aim of increasing of the specific surface area and the crystallinity of HMS. Literature, for example, reported and discussed the role of structure direct agent, time of aging, dilution of TEOS in ethanol [14-18]. Based on these information, four different modifications of the preparation of hexagonal mesoporous silica were chosen as the most effective ones to be compared in our laboratory.

Two variables were chosen in the synthesis procedure, i.e. the time of aging (18-42h) and the composition of reaction gel (the amount of dodecylamine, the molar ratio of the individual compounds and the dilution of TEOS in ethanol). The conditions of the synthesis of hexagonal mesoporous silica materials are summarized in Table I. The Si-HMS-II and Si-HMS-IV materials were synthesized using a lower amount of dodecylamine (n_{DDA}) in comparison with the Si-HMS-I and Si-HMS-III materials. Moreover, the Si-HMS-III and Si-HMS-IV materials were synthesized using the diluted solution of TEOS in ethanol (solution 2). Si-HMS-I was synthesized according to the procedure described by Tanev and Pinnavaia [13]. Si-HMS-II was prepared by dissolving of a smaller amount of dodecylamine (n_{DDA}) in solution 1 leading to the different molar ratio between dodecylamine and tetraethyl ortosilicate in comparison to that of HMS-I and HMS-III. HMS-III was prepared by using the dissolved TEOS in ethanol (solution 2). The synthesis of HMS-IV combined both HMS-II and HMS-III procedures, i.e. the procedure was using the smaller amount of DDA and diluted TEOS in ethanol.

The X-ray powder diffraction patterns and the specific surface area of the synthesized Si-HMS-I, -II, -III and -IV supports are shown in Fig. 2 and Table I, respectively. The powder X-ray diffraction patterns showed the characteristic low angle diffraction peak indexed as d_{100} reflection characteristic for hexagonal lattice, typical for hexagonal mesoporous structure [19]. The specific surface area reached its maximum value between 18-24 h as it was observed for Si-HMS-I and

Si-HMS-II materials (Table I). At the aging time above 36 h, the specific surface area (Table I) and the crystallinity (Fig. 3) of Si-HMS materials decreased, as it is illustrated for Si-HMS-I, due to the transformation of silica gel to amorphous silica. Only in the case of HMS-IV the value of the specific surface area was preserved above 18 h. Slightly higher specific area was reached for Si-HMS-IV materials (S_{BET} 877 $\text{m}^2 \text{g}^{-1}$) with 36 hours of the aging time compared to Si-HMS-IV with 18 hours (840 $\text{m}^2 \text{g}^{-1}$). Nevertheless, as the difference is negligible and the value of the specific surface area generally decreased above 18 hour time of aging, we suggested to keep the time of synthesis up to 18 h. If all the Si-HMS materials were compared, the highest value of specific surface area was observed for Si-HMS-IV materials (Table I). Si-HMS-IV had the S_{BET} 840 $\text{m}^2 \text{g}^{-1}$ after 18 hour of the aging time. The specific surface area increased as well as the low angle diffraction became more narrow in the order HMS-IV > HMS-II > HMS-III > HMS-I. Thus, the high specific surface area and the crystallinity were achieved by using a smaller amount of DDA (the procedures Si-HMS-II and Si-HMS-IV). The dilution of tetraethyl orthosilicate in ethanol (solution 2) did not lead to any significant change in the specific surface area and the crystallinity if the Si-HMS-I and Si-HMS-III procedures and Si-HMS-II and Si-HMS-IV procedures are compared.

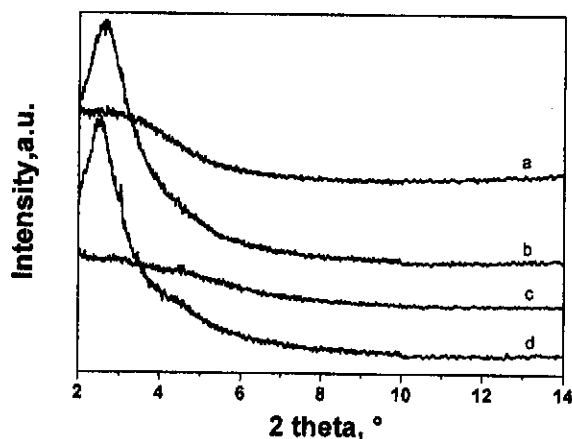


Fig. 2 XRD patterns of prepared Si-HMS-I (a), Si-HMS-II (b), Si-HMS-III (c) and Si-HMS-IV (d) materials

Figure 4 shows XRD patterns of Ti-HMS-IV (1100 $\text{m}^2 \text{g}^{-1}$), Al-HMS-IV with Si/Al=30 (903 $\text{m}^2 \text{g}^{-1}$), Al-HMS-IV with Si/Al=10 (1161 $\text{m}^2 \text{g}^{-1}$) and Si-HMS-IV (840 $\text{m}^2 \text{g}^{-1}$) materials. No significant difference in the specific surface area of Al-HMS-IV, Ti-HMS-IV and Si-HMS-IV supports was observed. The XRD patterns are in agreement with the literature reports for Al-HMS and Ti-HMS materials. The low angle XRD patterns only showed the first order diffraction in-

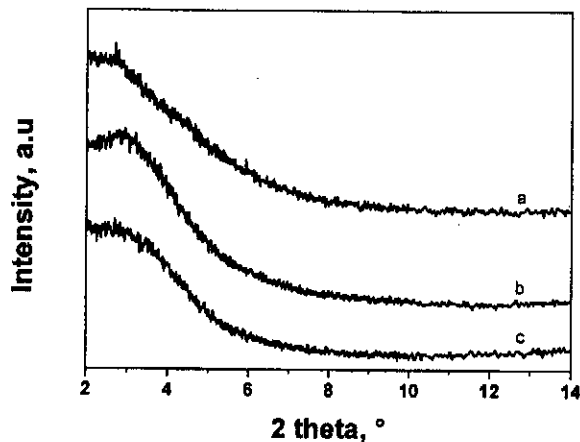


Fig. 3 XRD patterns of Si-HMS-I prepared by using of (a) 18 h, (b) 24 h and (c) 42 h time of aging

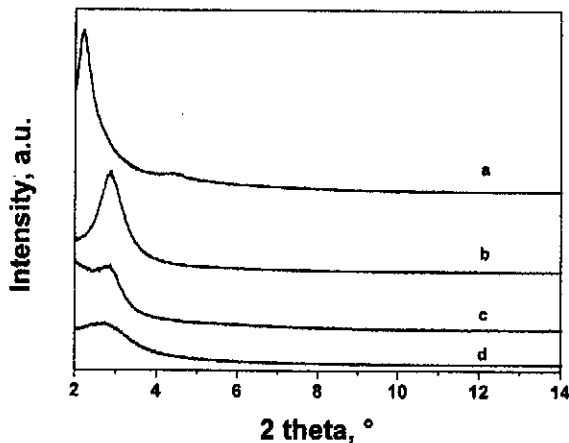


Fig. 4 XRD patterns of prepared (a) Si-HMS-IV, (b) Al-HMS-IV Si/Al=30, (c) Al-HMS-IV Si/Al=10 and Ti-HMS-IV

dicating that all the materials possess a mesoporous hexagonal structure. The incorporation of Al and Ti into the Si-HMS structure led to a shift of the d_{100} reflection to higher reflection angles, a decrease in the intensity, and a slight broadening of the reflection peak. It indicates that the mesoporous structure of Al-HMS-IV and Ti-HMS-IV was less uniform, which means a partial destroying the hexagonal lattice in comparison with Si-HMS-IV material. It means that Ti or Al was introduced into the framework without any changes in structure of the support. Therefore, it can be considered that properties of substituted supports are influenced only by electronegativity i.e. acidity of substituted elements (Si, Al, Ti).

Role of Si, Al and Ti Atoms in Activity of Vanadium Based HMS Catalysts in ODH of Ethane

In general, it is known that the acid-base properties affect the catalytic properties of vanadium-based catalysts in the ODH of ethane and propane [3]. While acid materials are more effective in the ODH of ethane, the inert matrix is required in ODH of propane. Therefore, the role of surface acidity in HMS containing aluminum and titanium atoms was studied. Titanium usually adopts a tetrahedral coordination within the framework of the HMS material, while Al ions are tetrahedral with one OH-group exposed toward the surface, generating a distortion in the framework of the HMS material. Gonzalez *et al.* [20] reported that the acidity increases in the order Al-MCM-41 > Ti-MCM-41 > Si-MCM-41.

The V-Si-HMS-IV, V-Al-HMS-IV and V-Ti-HMS-IV catalysts were prepared with a similar vanadium content (ca 3 wt. %). The vanadium content of 3 wt. % was chosen on the basis of our previous research, where we found out that the ideal vanadium-based catalysts in the ODH of ethane contained between 2 and 4 wt. % vanadium, not containing the vanadium oxide like species. All vanadium-based catalysts showed a similar distribution of vanadium species as it is seen from the UV-Vis spectra (Fig. 5). The UV-Vis bands below 400 nm could be attributed to the monomeric and oligomeric tetrahedrally coordinated vanadium species [12]. The UV-Vis bands characteristic for vanadium oxide species (UV-Vis band at 490 nm) and the V^{4+}/V^{3+} species were not observed in the UV-Vis spectra of V-Si-HMS-IV, V-Al-HMS-IV and V-Ti-HMS-IV catalysts. We previously discussed that the presence of vanadium oxide like species decreases the activity and selectivity of vanadium-based catalysts in the ODH of ethane [11].

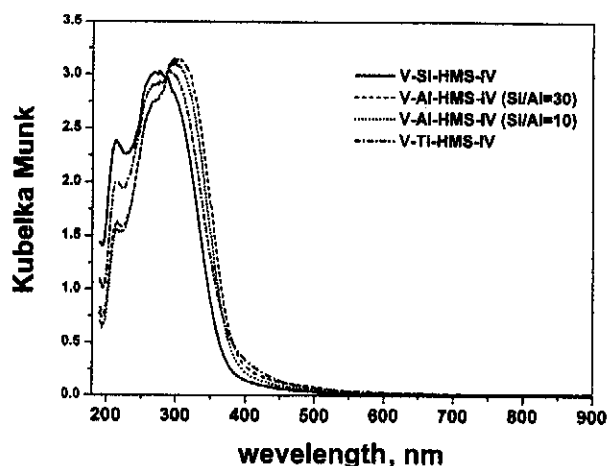


Fig. 5 DR UV-Vis spectra of dehydrated V-Si-HMS-IV, V-Al-HMS-IV Si/Al=30, V-Al-HMS-IV Si/Al=10 and V-Ti-HMS-IV materials

Figure 6 shows the dependence of the selectivity to ethene on the ethane conversion for V-Si-HMS-IV, V-Al-HMS-IV and V-Ti-HMS-IV catalysts. Firstly, it is clearly seen that the ethane conversion decreased with increasing content of aluminium, i.e. V-Si-HMS-IV > V-Al-HMS-IV (Si/Al=30) > V-Al-HMS-IV (Si/Al=10). Thus, the conversion of ethane surprisingly decreased with the increasing acidity of the support. Secondly, the conversion of ethane increased in the order of V-Si-HMS-IV > V-Al-HMS-IV > V-Ti-HMS-IV. The conversion of ethane again decreased with the increasing acidity of the support material. Although the comparison of the conversion of ethane and the acidity is in contrast to the general accepted results that the acid materials are more effective in the ODH of ethane, the important role of vanadium species has to be kept in mind. All vanadium-based catalysts were prepared with a similar distribution of vanadium species. Nevertheless, it can be concluded that the increasing acidity of support results in a small shift in the maximum of the UV-Vis band at ca 315 nm to the higher wavelength (Fig. 5). Thus, the changing acidity of the Si-HMS, Al-HMS and Ti-HMS materials would affect the reactivity of vanadium species.

As the selectivity of the catalysts has to be compared at the same value of the conversion of ethane, the activities of V-Al-HMS-IV (Si/Al=10) and V-Si-HMS-IV were compared at the same value of the conversion of ethane (ca 20 %). At iso-conversion experiment (the conversion of ethane ca 20 %), V-Al-HMS-IV (Si/Al=10) was more selective to ethene compared to the V-Si-HMS-IV.

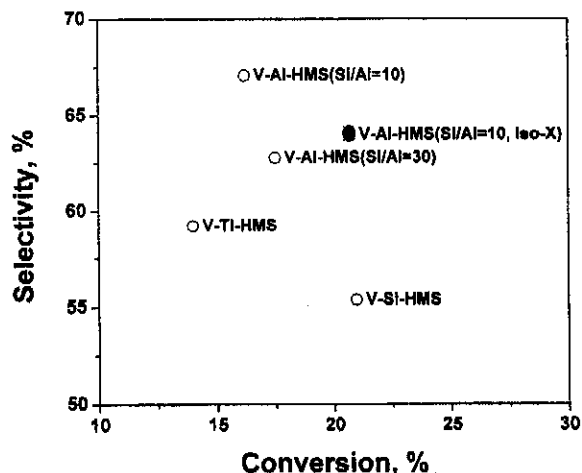


Fig. 6 Dependence of the selectivity to ethene on the conversion of ethane in ODH of ethane over V-Si-HMS-IV, V-Al-HMS-IV (Si/Al=30), V-Al-HMS-IV (Si/Al=10) and V-Ti-HMS-IV; gas composition 7.5 % ethane, 2.5 % O₂ and He, 600 °C, 200 mg catalysts, total flow-rate 100 ml min⁻¹ (open circles). The activity of V-Al-HMS-IV (Si/Al 10) at the ethane conversion 20 % (solid circle)

Although the V-Al-HMS-IV catalyst exhibited lower conversion of ethane in ODH of ethane, it was more selective to ethene in comparison with Si-HMS-IV. It should be mentioned that the selectivity to the desired product is the most desired property of catalyst with respect to its industrial application. Thus the application of V-Al-HMS-IV is more preferable compared to the V-Si-HMS-IV.

Conclusion

Synthesis of hexagonal mesoporous silica was investigated in order to obtain the highest specific surface area which is essential to get good dispersion of active species on surface of the catalyst. It was found that the specific surface area and the crystallinity increase with the decreasing amount of dodecylamine (lower molar ratio of dodecylamine and tetraethylorthosilicate). On the other hand, dilution of added tetraethyl orthosilicate did not affect the resulting properties of hexagonal mesoporous silica materials.

The ethane conversion decreased with the increasing acidity of supporting material, i.e. V-Si-HMS-IV > V-Al-HMS-IV (Si/Al=30) > V-Al-HMS-IV (Si/Al=10) and V-Si-HMS-IV > V-Al-HMS-IV > V-Ti-HMS-IV. The changing acidity of supporting material also slightly changed the coordination of vanadium species and thus probably its activity. In the iso-conversion experiment, V-Al-HMS-IV (Si/Al=10) was more selective to ethene compared to the V-Si-HMS-IV. As the selectivity to the desired product is one of the most desired properties of catalyst with respect to its industrial application, the application of V-Al-HMS-IV is more preferable compared to the V-Si-HMS-IV.

Acknowledgements

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