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Characterization of silica-supported vanadia-promoted rhodium catalysts by ^{51}V-NMR spectroscopy

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Vanadium oxide promoted Rh/SiO_2 catalyst precursors which were calcined at 573, 773, 973 and 1173 K, were characterized by ^{51}V-NMR. V_2O_5 is present in all materials and $RhVO_4$ is formed at 1173 K. An additional interaction species with vanadium in distorted tetrahedral oxygen environment is found after calcination at 973 K. These phases might have relevance for catalytic promotion of reduced Rh° metal catalysts by VO_x. In addition, distorted tetrahedral VO_4 species which are capable of interacting with water molecules (V_2 species) and distorted octahedral species having water molecules in their coordination sphere (V_5 species) have been detected.

Keywords: Rhodium; vanadia; promoter effect; ^{51}V-solid state NMR

1. Introduction

Vanadium promoted rhodium catalysts are among the most selective catalysts for the synthesis of C_{2+}-oxygenates from syngas [1]. These catalyst materials, including vanadia-supported rhodium [2–4] and silica-supported rhodium promoted by vanadia [5,6] have therefore been investigated extensively in the past.

Important factors which seem to critically determine activity and selectivity of these catalyst materials are the noble metal dispersion and the metal-promoter interaction. It has been argued that the formation of C_{2+}-oxygenates favourably proceeds at the metal-promoter perimeter [3,7–12]. Therefore several attempts have been made to bring the noble metal and the promoter oxide into close contact on support surfaces by choosing appropriate synthetic routes. One possibility involves anchoring suitable metal complexes as precursors onto support surfaces so that promoter and noble metal atoms are directly bound to each other or connected via common ligands. This approach was applied by Yermakov et al. [13] using group VIII metals modified (promoted) by group IV ions. Alternatively, heteronuclear organometallic cluster compounds can be used as precursors for the synthesis of promoted catalysts [14]. Finally, it has been suggested to be advantageous for intimate metal-promoter contact formation, if the two components were integrated in ternary oxide precursor compounds such as e.g. $RhVO_4$ [15,16],

In the present study, we have prepared silica-supported vanadia-promoted rhodium catalysts by impregnation techniques at fixed metal loading and constant Rh/V atomic ratio. The materials were calcined at 573, 773, 973 and 1173 K, so as to possibly produce ternary oxide precursors [17,18]. Since solid state ^{51}V-NMR spectroscopy has proved to be an extremely valuable technique for the structural characterization of vanadia-containing catalytic materials [19–26], we have characterized the catalysts by ^{51}V-NMR. The results are reported here.

2. Experimental

CATALYST PREPARATION

Vanadia-silica was prepared by impregnation of the silica support (Alpha Products, specific surface area $S_{\mathrm{BET}} = 400$ m^2/g) with an aqueous solution of NH_4VO_3 so as to give samples with a nominal vanadium content of 8 wt% V. These precursor materials were thermally decomposed by heating in air at 773 K for 3 h. The decomposition procedure was followed by calcination in air for 7 h at four different temperatures, namely 573, 773, 973 and 1173 K.

For preparation of the VO_x-promoted rhodium catalysts, "NH_4VO_3/SiO_2" after decomposition at 773 K was used. This material was impregnated with a methanol solution of $RhCl_3$ (Johnson Matthey Chemicals Ltd.) and dried at 383 K for 12 h. This procedure–after grinding the dry material in an agate mortar–was followed by calcination in air at four different temperatures, namely 573, 773, 973, and 1173 K. The samples had nominal metal concentrations of 8 wt% V and 4 wt% Rh corresponding to a V/Rh atomic ratio of 4.

NMR-SPECTROSCOPY

^{51}V-NMR spectra were recorded on a MSL-400 Bruker NMR spectrometer at 105.2 MHz (magnetic field 9.4 T). The pulse duration was 2 μs. The delay time between pulses for static NMR spectra was 10 s, so as to obtain the correct relation between intensities of different lines, some of which have a long T_1. For ^{51}V magic angle spinning (MAS) spectra the delay time was decreased to 1 s to increase signal-to-noise ratio. The spectral range was 250 kHz.

To obain the high-resolution ^{51}V MAS-NMR spectra, samples were rotated at frequencies between 2 and 5 kHz. Values of the isotropic chemical shift δ_{iso} have been determined from MAS spectra obtained at different rotation frequencies. The accuracy of δ_{iso} measurements was ± 5 ppm.

Prior to the measurements of static ^{51}V-NMR spectra, the samples were placed in quartz sample tubes and evacuated at 573 K during 8 h. The measurements were performed in sealed sample tubes. Samples with adsorbed H_2O were prepared by contacting the evacuated samples with water vapour over night.

Prior to measurements of MAS spectra the evacuated sample tubes were opened in a glove box and the samples were transferred to the plastic mushroom rotors.

The chemical shifts were measured relative to $VOCl_3$ as an external reference.

3. Results and discussion

The assignment of ^{51}V-NMR spectra can be based on a large body of spectra of V reference compounds having well-defined structures [19,25].

Fig. 1 shows the ^{51}V-NMR spectra of V/SiO_2 (fig. 1-A) and Rh/V/SiO_2 (fig. 1-B) samples which were calcined at temperatures between 573 K and 1173 K in air and then evacuated at 573 K during 8 hours. Two types of lines can be

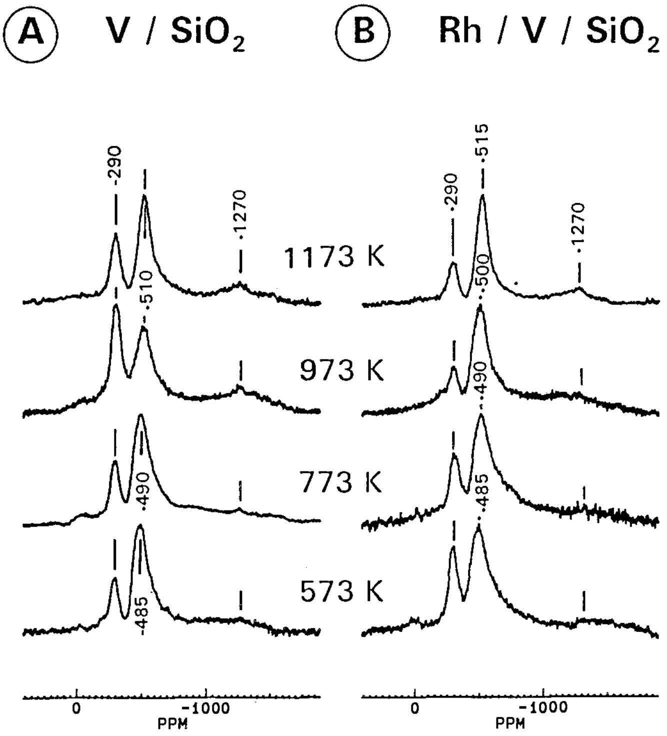

Fig. 1. ^{51}V-NMR spectra of V/SiO_2 (A) and Rh/V/SiO_2 (B) catalysts as function of calcination temperature.

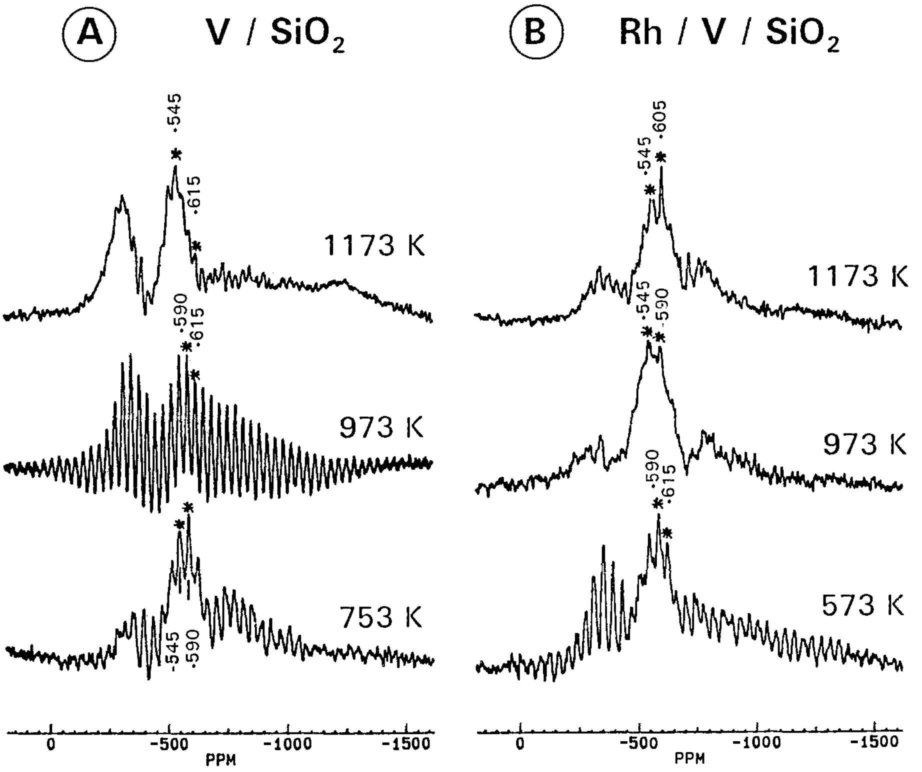

Fig. 2. ^{51}V-NMR-MAS spectra of V/SiO_2 (A) and $Rh/V/SiO_2$ (B) catalysts as a function of calcination temperature. Asterisks (*) indicate the position of δ_{iso}.

distinguished in these spectra. The line (A) with axial anisotropy of the chemical shift tensor ($\delta_{\perp} = -290 \pm 5$ ppm, $\delta_{\parallel} = -1270 \pm 10$ ppm) is due to vanadium in distorted octahedral environment. A second line (B) appears at −485 to −520 ppm. The peak position of the latter line shifts to high field as the calcination temperature increases. Also the relative intensities of lines (A) and (B) depend on calcination temperature. For V/SiO_2 samples the intensity of line (A) increases, while that of line (B) decreases as the calcination temperature increases from 573 to 973 K (fig. 1–A). On the contrary, for $Rh/V/SiO_2$ catalysts the increase of calcination temperature in the same range results in the increase of the intensity of a line B at the expense of line A (fig. 1–B).

After calcination of the samples at 1173 K the relative intensity of line A in the sample V/SiO_2 decreases (fig. 1–A) while for the $Rh/V/SiO_2$ sample the intensity of this line slightly increases (fig. 1–B).

The use of magic angle spinning (MAS) provides more detailed information on the types of V species present in catalysts since it improves the resolution of the spectra and allows one to measure the isotropic chemical shift values of individual lines (fig. 2). Parameters of ^{51}V-NMR lines together with their attribution to different V environments [19,25] are summarized in table 1.

Table 1
Parameters of ^{51}V-NMR lines observed in V/SiO$_2$ and Rh/V/SiO$_2$ catalysts and their attribution to different V species

Species	$\delta_1(\pm 10)$ (ppm)	$\delta_2(\pm 10)$ (ppm)	$\delta_3(\pm 10)$ (ppm)	$\delta_{iso}(\pm 5)$ (ppm)	$\Delta\delta = \delta_1$-δ_3 (ppm)	Line width (kHz)	Type of local environment	Attribution of lines
V_1	−290	−290	−1270	−615 [a]	~ 1000	4	distorted octahedra	V_2O_5
V_2	−440	−480	−850	−590 [a]	~ 400		surface distorted tetrahedra	VO_4 interacting with H_2O
V_3	−460	−515	−595	−545 [a]	~ 140		distorted tetrahedra	VO_4 encapsulated in the pores of SiO_2, observed for samples calcinated at 1173 K
V_4				−605 [a]	< 100		almost regular tetrahedra	$RhVO_4$
V_5	−310	−310	−1270	−625 [b]	~ 950	7	distorted octahedra	octahedra having H_2O molecules in the coordination sphere

[a] δ_{iso}-measured from MAS spectra at different rotation frequencies (accuracy ±5 ppm).

[b] δ_{iso}-estimated as $1/3(\delta_1 + \delta_2 + \delta_3)$, accuracy ±10 ppm).

The axially anisotropic line A, which is manifested by a set of side bands in MAS spectra, can be attributed to surface V species with a well defined structure (denoted V_1 in table 1). Since the parameters ($\delta_{\perp}$, $\delta_{\parallel}$, δ_{iso}) of this line for evacuated samples coincide with those for crystalline V_2O_5 [25], it can be unambiguously attributed to surface phase of vanadium pentoxide. A detailed analysis of the MAS spectra (fig. 2) shows that in general line B is composed of three different lines, the relative intensities of which depend on sample composition and treatment temperature.

In the samples calcined at 573 K, the main contribution to line B is from distorted VO_4 tetrahedra (V_2 in the table 1) having nearly axial anisotropy of chemical shifts, with $\delta_{iso} = -590 \pm 5$ ppm and $\Delta\delta \cong 400$ ppm (fig. 2–B). Unlike V_1, the MAS spectrum of V_2 species does not have a well resolved set of side bands, most probably due to irregularities in the structure of V_2 species. For the samples calcined at 1173 K a line with $\delta_{iso} = -545$ ppm and $\Delta\delta \cong 140$ ppm from tetrahedral V_3 species, having a smaller distortion of VO_4 tetrahedra prevails (fig. 2–A, B). The MAS spectrum of this sample has a poor resolution of the side bands, most probably caused by the same reason as for V_2.

For samples calcined at 773 and 973 K, line B represents a superposition of lines from V_2 and V_3 species, with the percentage contribution of V_3 species increasing at 973 K.

For the $Rh/V/SiO_2$ sample calcined at 1173 K a narrow isotropic line of relatively low intensity with $\delta_{iso} = -605$ ppm was observed (fig. 2–B) indicating a regular environment of V atoms in these species (denoted V_4 in table 1). Most probably this line can be attributed to formation of Rh orthovanadate $RhVO_4$. Although the ^{51}V-NMR spectra of this compound have not yet been reported, it is expected to have an isotropic line since the orthovanadates of the trivalent elements have regular VO_4 tetrahedra in their structure [27].

Water adsorption on the samples of the V/SiO_2 and $Rh/V/SiO_2$ series results in the partial disappearance of line B (component attributed to V_2 species) in the spectra samples calcined at 573, 773 and 973 K (fig. 3). In contrast, no changes of the spectra were observed for samples calcined at 1173 K (i.e. V_3 species are not influenced by H_2O adsorption). Simultaneously with the disappearance of V_2 species a new line with axial anisotropy of the chemical shift tensor appears in the spectra (fig. 3–A, B, 573, 773, and 973 K). This line has greater line width compared with that from V_2O_5 most probably due to dipolar interactions of vanadium nuclei with water protons. We suppose that it belongs to vanadium atoms having water molecules in their coordination sphere. The experiments with H_2O adsorption also show that a part of the V_2 species in the samples calcined up to 973 K must be attributed to surface VO_4 tetrahedra, while the V_3 species in samples calcined at 1173 K as well as the V_1 species in the samples under study must be ascribed to bulk V species or encapsulated V species which do not interact with H_2O molecules. Calcination at 1173 K results most probably in an excapsulation of a significant proportion of supported

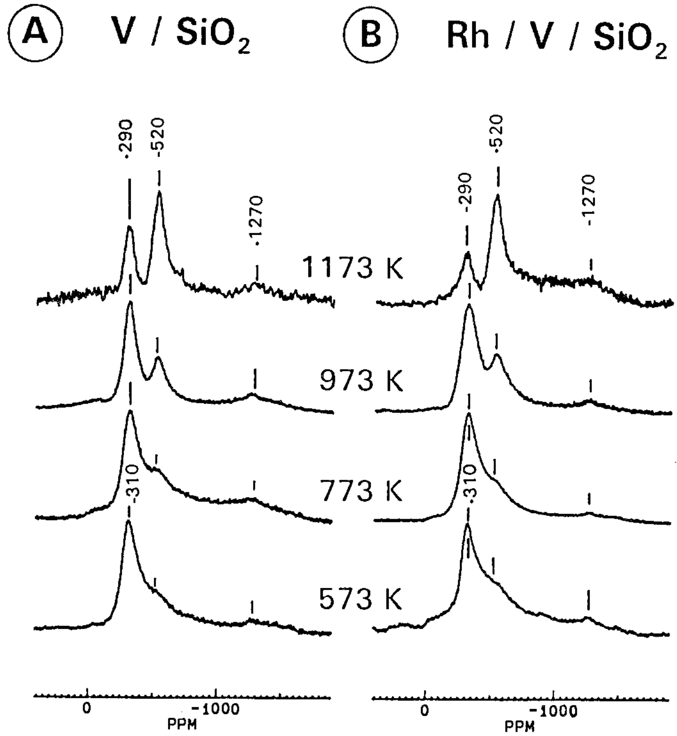

Fig. 3. Effects of H_2O adsorption on ^{51}V-NMR spectra of V/SiO_2 (A) and $Rh/V/SiO_2$ (B) catalysts, precalcinated at different temperatures.

tetrahedral V species inside SiO_2 pores and makes V species inaccessible for interaction with water molecules.

An interesting observation is the different temperature behaviour of V/SiO_2 and $Rh/V/SiO_2$ samples on calcination between 573 and 973 K (compare fig. 1–A and fig. 1–B). Indeed, for catalysts containing Rh the relative amount of V in tetrahedral coordination increases with treatment temperature, while for V/SiO_2 samples the effect of the calcination temperature is opposite (increase of temperature decreases the concentration of tetrahedral V species). It might be argued that the difference in the behaviour of V/SiO_2 and $Rh/V/SiO_2$ samples on calcination is due to the formation of Rh orthovanadate $RhVO_4$, in which V has a tetrahedral coordination. However, the sharp NMR line of $RhVO_4$ has not been observed in the spectra of samples calcined below 1173 K. The different behaviour of V/SiO_2 and $Rh/V/SiO_2$ can probably be explained by an incorporation of Rh atoms in the structure of surface V species, which may result in an increased thermal stability of these samples.

Thus, the analysis of ^{51}V-NMR, static and MAS spectra reveals five different V sites, in V/SiO_2 and $Rh/V/SiO_2$ catalysts, namely (see table 1):

V_1: ($\delta_{iso} = -615$ ppm, $\Delta\delta \sim 1000$ ppm) are the distorted octahedral V species in V_2O_5;

V_2: ($\delta_{iso} = -590$ ppm, $\Delta\delta \sim 400$ ppm) with nearly axial anisotropy of chemical shift belong to V in distorted VO_4 tetrahedra, having one V–O bond shorter than the others;

V_3: ($\delta_{iso} = -545$ ppm, $\Delta\delta \sim 140$ ppm) belong to slightly distorted VO_4 tetrahedra;

V_4: ($\delta_{iso} = -605$ ppm, $\Delta\delta < 100$ ppm) belong to V in almost regular tetrahedra; most probably in $RhVO_4$ orthovanadate;

V_5: ($\delta_{iso} = -625$ ppm, $\Delta\delta = 950$ ppm) belong to octahedral V species produced from tetrahedral ones after H_2O adsorption.

It is interesting to note that the structural data obtained in the present study compare very well with XRD results [28]. V_2O_5 (V_4 species) was found at all calcination temperatures in both V/SiO_2 and $Rh/V/SiO_2$ samples by both techniques, ^{51}V-NMR and XRD. $RhVO_4$ (V_4 species) was also detected by both techniques for the highest calcination temperature of 1173 K in $Rh/V/SiO_2$. Complementary information is provided by ^{51}V-NMR for $Rh/V/SiO_2$ calcined at 973 K. Species V_3 is detected by NMR which seems to be due to a species in which VO_4 distorted tetrahedra are interacting with rhodium ions. This phase is X-ray amorphous and not detected by XRD. Also species V_2 and V_5 were not seen by XRD.

4. Conclusions

The data presented demonstrate the potential ^{51}V-NMR for the structural characterization of supported catalysts. Clearly, several V species with distinct local environments were detected in $Rh/V/SiO_2$. In particular, species are characterized for the materials calcined at the highest temperatures of 973 and 1173 K in which VO_4 tetrahedra interact with rhodium ions. At 1173 K the corresponding phase is $RhVO_4$, which could also be detected by XRD. These phases might well be relevant for the catalytic properties of reduced catalysts in that they may guarantee the formation of Rh^{0} metal contact with VO_x promotor oxides.

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