

Synthesis, characterization and activity studies of vanadia catalysts supported on sol–gel derived $\text{Al}_2\text{O}_3\text{--ZrO}_2$ mixed oxide

Jhansi L. Lakshmi, Timothy R.B. Jones, Mohamedkamal Gurgi, Jack M. Miller *

Department of Chemistry, Brock University, Saint Catharines, Ontario, Canada L2S 3A1

Received 4 July 1999; accepted 4 August 1999

Abstract

A series of catalysts with vanadia contents varying between 4 and 18 wt.% were prepared using sol–gel derived alumina–zirconia mixed oxide as a support. The catalysts were characterized employing ^{51}V , ^1H solid-state MAS NMR, diffuse reflectance FT-IR and BET surface area measurements. The activities of the catalysts were tested for the partial oxidation of ethanol. ^{51}V NMR studies indicated the presence of tetrahedral vanadate species at all the loadings studied except in the catalyst with a V_2O_5 loading of 18 wt.%, in which six coordinated vanadia species was observed. Upon outgassing treatment of the calcined catalysts, a new tetrahedral species was observed, indicating the presence of water molecules or hydroxyl groups in the coordination sphere of vanadium. The ^1H MAS NMR studies showed the peaks corresponding to hydroxyl groups of alumina and zirconia. With increase in vanadia loading there was a decrease in the intensity of the basic hydroxyl groups of alumina showing the preferential reaction of vanadia with these groups. The DRIFT studies of the catalysts indicated the vibrations corresponding to agglomerates of V_2O_5 only in the sample with highest V_2O_5 content. Ethanol partial oxidation studies of the catalysts showed acetaldehyde as the major product with traces of ether, acetic acid, ethyl acetate, CO_x , etc. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sol–gel $\text{Al}_2\text{O}_3\text{--ZrO}_2$; Vanadia catalysts; Solid-state NMR; DRIFT; Ethanol oxidation

1. Introduction

Supported vanadia catalysts have been extensively employed for catalyzing partial oxidation, ammoxidation, alkylation reactions, etc. [1–3]. The commercial supports such as alumina, silica, titania and zirconia were usually used for dispersing the active vanadia phase. Synthesis, characterization and activity studies have been

reported on vanadia catalysts supported on sol–gel derived mixed oxides $\text{Al}_2\text{O}_3\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--TiO}_2$, $\text{TiO}_2\text{--SiO}_2$ catalytic applications [4–6]. Also, there are a number of reports in the literature on the modification of the thermally stable, high surface area supports such as Al_2O_3 , or SiO_2 with the transition metal oxides such as TiO_2 , ZrO_2 [7–9], etc. The modified supports thus produced are inexpensive, possess high surface area and thermal stability and retain the unique properties of the modifying oxide — surface acid–base and redox characteristics. The

* Corresponding author. Tel.: +1-905-688-5550 ext. 3402; fax: +1-905-684-2277; e-mail: jmillerspartan.ac.brocku.ca

characterization techniques such as X-ray diffraction, electron spin resonance, FT-Raman, FT-IR, ^{51}V solid-state NMR, etc., were usually employed for the structural elucidation studies of the supported vanadia catalysts. In recent years ^{51}V solid-state NMR has become a routine characterization tool for the structural analysis of vanadia species in supported catalysts [10–12]. The nature of vanadia species in the catalysts were found to depend on the V_2O_5 loading of the catalysts, surface area of the support, calcination temperature and pretreatment conditions of the catalysts. Solid-state ^{51}V NMR studies on heterogeneous catalysts often become complicated due to the influence of dipolar, quadrupolar and chemical shift interactions, resulting in the complicated peak shapes [10,11]. ^{51}V NMR spectra are mainly influenced by chemical shift interactions at high magnetic field strengths, as dipolar and first order quadrupolar interactions are independent of magnetic field B_0 , the influence of second order quadrupolar interactions on the peak position and shape can be minimized at high magnetic field $B_0 > 7$ T. The presence of V^{4+} ions in the catalysts were found to broaden the NMR peaks resulting in the overlapping of the signal due to V^{5+} species [10]. ESR investigations on the calcined vanadia catalysts revealed the presence of a very low percentage of V^{4+} species [2].

In our earlier investigations, we used ^1H MAS NMR and diffuse reflectance FT-IR techniques to identify different kinds of hydroxyl groups present in sol–gel supports and vanadia catalysts. Active vanadia phase was found to react with basic hydroxyl groups of the supports which usually appear in the upfield region. Numerous ^1H MAS NMR studies have been reported on the support materials such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 and the modified and mixed oxides such as $\text{TiO}_2/\text{Al}_2\text{O}_3$, $\text{TiO}_2/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$, $\text{Al}_2\text{O}_3\text{--SiO}_2$, etc. [13–15]. The ^1H MAS NMR studies of the sol–gel derived mixed oxides and V_2O_5 supported on $\text{Al}_2\text{O}_3\text{--TiO}_2$ and $\text{ZrO}_2\text{--SiO}_2$ sol–gel mixed oxides were reported in our earlier investigations [16–18]. In the pre-

sent study, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{--ZrO}_2$ catalysts were characterized employing the techniques ^{51}V , ^1H solid-state NMR, diffuse reflectance FT-IR and BET surface area measurements. Diffuse reflectance FT-IR technique provided limited information regarding the variation in surface vanadia species, this may be due to the transparent nature of the alumina component of the support. The activities of the catalysts were determined using ethanol partial oxidation as a test reaction.

2. Experimental

Alumina–zirconia mixed oxides were synthesized using 2,4-pentane dione as the complexing agent. The details of the preparation method are given elsewhere [16]. The solvents from Caledon Laboratory and the chemicals from Aldrich were used as received. Aluminum tri(*sec*-butoxide) (0.1 mol) and Zirconium *n*-propoxide (0.1 mol) were dissolved in 200 ml of *n*-propanol followed by heating at 343 K to get a clear solution. The complexing agent — 2,4-pentane dione (0.5 mol/mol alkoxide) was added to this clear solution followed by hydrolysis with deionized water (6.9 mol/mol alkoxide). The transparent gel obtained was aged at ambient temperature for 12 h. The solvent was removed at 383 K, and after drying, the mixed oxide was finely powdered and then calcined at 773 K to remove the organic residues. A series of catalysts with vanadia contents varying between 1 and 18 wt.% were prepared by impregnating alumina–zirconia support with a methanolic solution of vanadium (III) acetylacetonate (Gelest). Methanol was evaporated slowly to dryness in a rotary evaporator. The resulting material was dried at 383 K overnight followed by calcination at 773 K for 5 h. Vanadia catalysts supported on alumina (BET surface area $325\text{ m}^2/\text{g}$) and commercial ZrO_2 (Aldrich, BET surface area $30\text{ m}^2/\text{g}$) were synthesized using a similar preparation procedure. The BET surface areas, pore volumes and pore size distributions

of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$, Al_2O_3 and ZrO_2 supports, BET surface areas of the catalysts and vanadia contents of the catalysts are included in Table 1. The vanadia contents of the catalysts were estimated by Inductively Coupled Plasma (ICP) analysis using Perkin Elmer Optima 3300 DV ICP-OES spectrometer after calibrating the instrument with NIST traceable standards. A weighed sample was digested in hot concentrated nitric acid until the dissolution was complete and then the solution was diluted to $\sim 2\%$ (V/V HNO_3) prior to analysis. The BET surface areas, pore volumes, and pore size distributions of the alumina, zirconia and alumina–zirconia supports and BET surface areas of the catalysts and vanadia contents estimated from ICP analysis are given in Table 1.

BET surface areas were determined using a Coulter SA 3100 instrument and an automated gas volumetric method employing nitrogen as the adsorbate at 77 K. Samples were outgassed under vacuum at 473 K for 1 h immediately prior to analysis. ^{51}V and ^1H solid-state MAS NMR experiments were carried out on a Bruker Avance DPX 300 multinuclear FT-NMR instrument. A standard bore Bruker MAS/CPMAS probe with 4 mm zirconia rotors was used. The samples were dehydrated at 623 K for 30 min in a flow of He in BET apparatus and then immediately transferred to a N_2 atmosphere glove

bag and packed in zirconia rotors prior to recording the ^{51}V NMR and ^1H MAS NMR spectra. ^{51}V static and MAS spectra were obtained at 78.9 MHz with a pulse length of 1 μs and relaxation delays of 1 s over a spectral window of 149 kHz. Because of sweep width limitation of our NMR spectrometer, baseline distortions were observed in the ^{51}V NMR spectra of the catalysts. Chemical shifts were referenced to external VOCl_3 . MAS spectra were recorded at variable spinning speeds ranging from 6 to 10 kHz. The samples were spun typically at 10 kHz in air and 540 FIDs were collected for each sample. ^1H MAS NMR spectra were recorded at 300 MHz with a 30° pulse length of 3 μs with 1-s delay between the pulses over a spectral window of 12 kHz. The chemical shifts in ppm were referenced to external TMS using neat *p*-dioxane as secondary reference. The samples were spun at 10 kHz and 124 FIDs were accumulated for each sample. DRIFTS spectra were acquired using a SPECTRATECH DRIFT accessory “THE COLLECTOR” in an ATI Mattson Research Series FT-IR spectrometer (KBr beamsplitter, DTGS detector, spectral range 6000–400 cm^{-1}). DRIFT spectra of calcined and outgassed catalysts were obtained; 512 scans were accumulated for calcined catalysts and 1024 scans were obtained for the outgassed samples. The cal-

Table 1
BET surface areas, pore size distributions and vanadia contents of the catalysts

Catalyst	Code	V_2O_5 (wt.%) ^a	BET surface area (m^2/g)	Pore volume and pore size distribution of the supports
$\text{Al}_2\text{O}_3\text{-ZrO}_2$	Al–Zr	–	218	0.18 cm^3/g , 3–6 nm
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-ZrO}_2$	V/Al–Zr 1	4.2	183	–
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-ZrO}_2$	V/Al–Zr 2	7.3	173	–
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-ZrO}_2$	V/Al–Zr 3	9.8	167	–
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-ZrO}_2$	V/Al–Zr 4	12.0	157	–
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{-ZrO}_2$	V/Al–Zr 5	17.9	156	–
Al_2O_3	Al	–	325	0.47 cm^3/g , 6–10 nm
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	V/Al	11.5	260	–
ZrO_2	Zr	–	30	0.14 cm^3/g , 10–80 nm
$\text{V}_2\text{O}_5/\text{ZrO}_2$	V/Zr	8.0	18	–

^aEstimated from ICP analysis.

cined catalysts outgassed at 350°C for min in a flow of He, and then cooled to room temperature before recording the DRIFT spectra.

Activity studies for the partial oxidation of ethanol were carried out at atmospheric pressure in a fixed bed microcatalytic reactor interfaced to a gas chromatograph with a six-way gas sampling valve. A 200 mg of catalyst diluted with equal amount of 0.5 mm glass beads was held at the middle of a 6-mm o.d. Pyrex reactor on a layer of quartz wool. The details of the experimental conditions for activity studies are discussed in detail elsewhere [18]. The activity per site (turnover frequency, TOF) was calculated for various catalysts from the total moles of ethanol converted per mole of vanadium atom per second, assuming that all the surface vanadia atoms are participating in the reaction.

3. Results and discussion

The ^{51}V solid-state NMR spectra of the calcined catalysts are shown in Fig. 1. Type ‘A’ species with a chemical shift at ~ -310 ppm (perpendicular component δ_{\perp}) and the corresponding parallel component (δ_{\parallel}) at -1270 ppm observed in the catalyst V/Al–Zr 5 with a highest V_2O_5 loading of 18 wt.% indicating the presence of octahedral vanadia species. Type ‘B’ species at ~ -550 ppm corresponding to tetrahedral vanadia species can be seen in all the catalysts. In the samples V/Al–Zr 3 and 4 in addition to a major percentage of Type ‘B’ species, Type ‘A’ species were also noticed. Fig. 2 shows the ^{51}V solid-state NMR spectra of the catalysts evacuated at 623 K for 30 min. The chemical shifts are given in Table 2. The peak at ~ -740 ppm (Type ‘C’) observed in all the samples can be attributed to tetrahedral VO_4^{3-} species. This species might have formed due to the removal of water molecules or hydroxyl groups from Type ‘B’ species of the calcined catalysts [10,11]. Type ‘A’ species observed at -310 ppm in the catalyst V/Al–Zr 5 corresponds to six coordinated vanadia species.

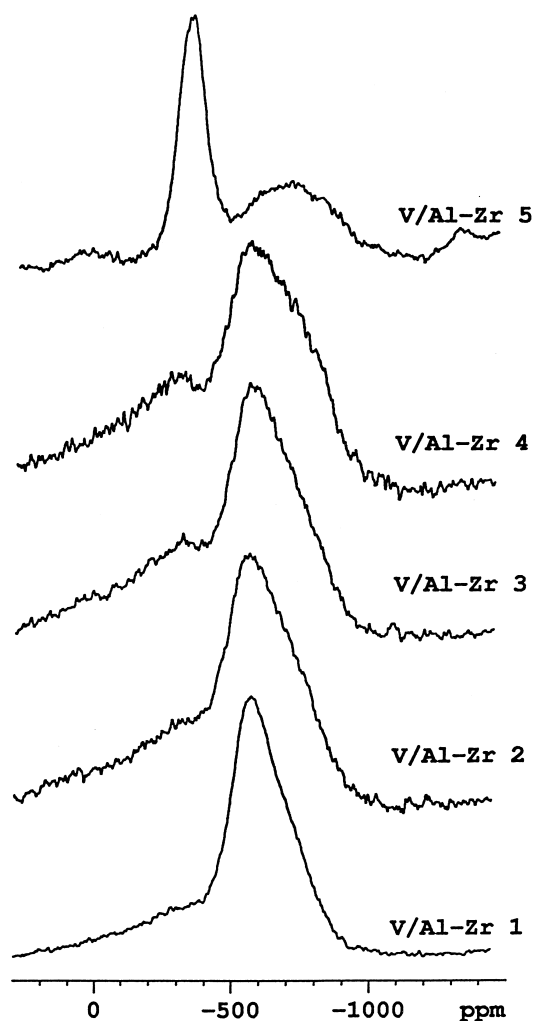


Fig. 1. 78.9 MHz ^{51}V solid-state NMR spectra of the calcined catalysts.

Lapina et al. [11,19] in their ^{51}V NMR studies on calcined $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts have assigned the peak at -520 to -590 ppm to vanadium atoms in distorted tetrahedral environment with water molecules in its coordination sphere, the peak at -750 ppm to isolated VO_4^{3-} tetrahedra and the peak at -350 ppm was attributed to polynuclear vanadium species in a distorted octahedral environment. The tetrahedral species ($\delta = -520$ ppm) were found to result in the formation of isolated tetrahedral ($\delta = -750$ ppm) species by the removal of water molecules. Similar observations were

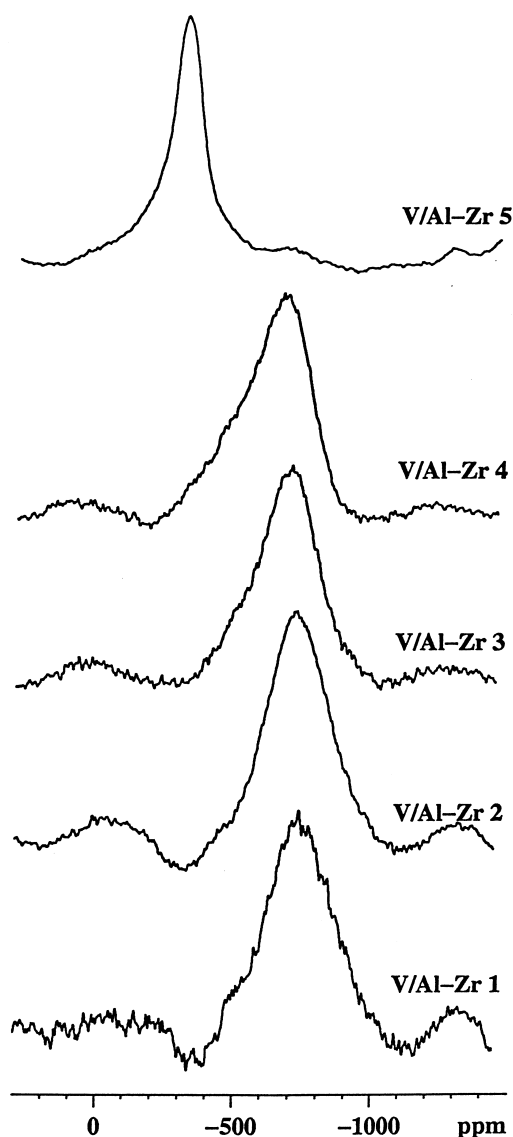


Fig. 2. 78.9 MHz ^{51}V solid-state NMR spectra of the calcined catalysts outgassed at 623 K for 30 min.

made by Eckert and Wachs [10] in their ^{51}V NMR studies on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts. In the case of vanadia catalysts supported on mixed oxides such as $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$, zirconia component of the support was found to show stronger influence in determining the coordination of vanadia species in the ^{51}V NMR studies on catalysts [11] as the chemical shifts were found to be much different from ^{51}V chemical

shifts of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. In our earlier investigations on V_2O_5 supported on sol-gel derived $\text{Al}_2\text{O}_3\text{-TiO}_2$ and $\text{ZrO}_2\text{-SiO}_2$ [17,18], we observed that ^{51}V chemical shifts of the catalysts correspond to vanadia species in interaction with both the components of the support material.

^{51}V MAS NMR spectra of the catalysts acquired at a spin rate of 10 kHz are shown in Fig. 3. It can be seen from the figure that there is not much influence of MAS on the width of the peaks at lower loadings, which may be due to wide chemical shift distribution. This behavior can be explained based on large quadrupole coupling constants and chemical shift parameters [10,11]. In the sample V/Al-Zr 5, the spinning side band pattern is similar to that of V_2O_5 indicating the presence of vanadia clusters. Thus the ^{51}V MAS NMR studies of the catalysts indicate highly dispersed tetrahedral vanadia species at low and medium loadings and amorphous aggregates of V_2O_5 in the case of V/Al-Zr 5 catalyst.

Fig. 4 shows the ^1H MAS NMR spectra of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ support and the catalysts. The spectra were deconvoluted into Voigt line shapes [13] using the GRAMS/32 software and are given in Fig. 5. The chemical shifts of various peaks are given in Table 2. Deconvolution of the ^1H MAS NMR signal of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ resulted in five components corresponding various hydroxyl groups with the peaks centers at -0.3 , 1.9 , 3.3 , 4.5 and 7.6 ppm. The peak at -0.3 ppm can be attributed to the terminal/basic hydroxyl groups coordinated to octahedral

Table 2
 ^1H MAS NMR chemical shifts of the catalysts

Catalyst	^1H chemical shift (ppm)
Al-Zr	-0.3 , 1.9 , 3.3 , 4.5 , 7.6
V/Al-Zr 1	0.2 , 2.3 , 3.6 , 5.2 , 7.8
V/Al-Zr 2	0.3 , 3.0 , 5.2 , 8.1
V/Al-Zr 3	0.2 , 3.2 , 5.7 , 8.2
V/Al-Zr 4	0.2 , 3.3 , 5.7 , 8.3
V/Al-Zr 5	0.2 , 3.4 , 7.7

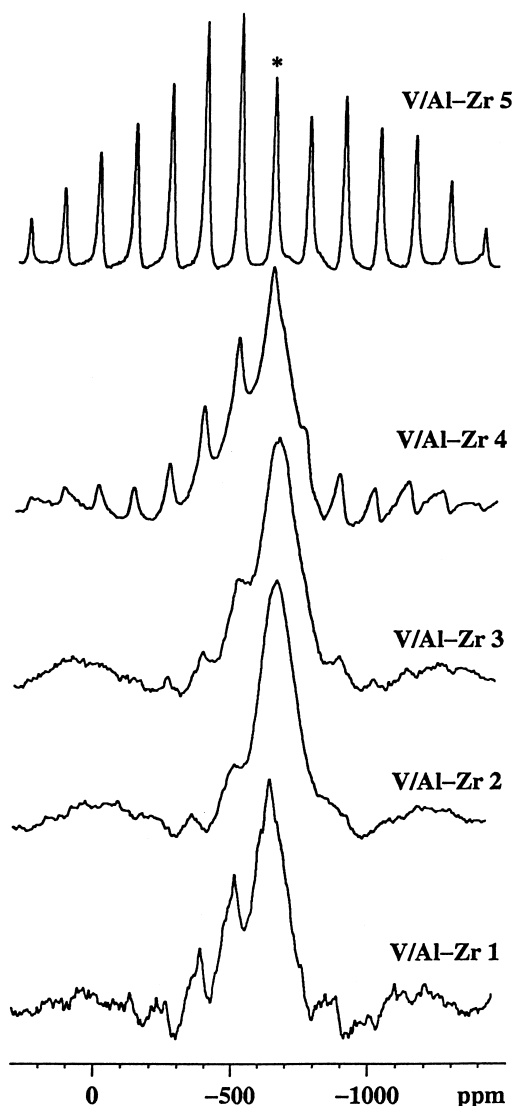


Fig. 3. 78.9 MHz ^{51}V MAS NMR spectra of the calcined catalysts outgassed at 623 K for 30 min (spin rate 10 kHz), * isotropic chemical shifts.

alumina [14,20]. The peaks at 1.9, 3.3 and 4.5 ppm may correspond to overlapping resonances from Al–OH and Zr–OH hydroxyl groups. In the previous ^1H MAS NMR investigations [14,20] on alumina, the peaks at upfield were attributed to terminal or basic hydroxyl groups and the peaks at downfield were attributed to acidic or bridged hydroxyl groups. Mastikhin et al. [21] and Mastikhin and Zamaraev [22], in their ^1H NMR studies on zirconia support, ob-

served the peaks at 4.8 and 2.4 ppm corresponding to hydroxyl groups of ZrO_2 , the peaks at low field were assigned to terminal –OH and the ones at high field to the bridged OH groups. Riemer et al. [15] observed peaks at 1.6 and 3.86 ppm for the ZrO_2 support obtained from calcination of $\text{Zr}(\text{OH})_4$. ^1H MAS NMR investigations were reported earlier on zirconia modified silica, titania modified alumina/silica to determine the types of hydroxyl groups [20,23]. In the case of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts, a decrease in the intensity of

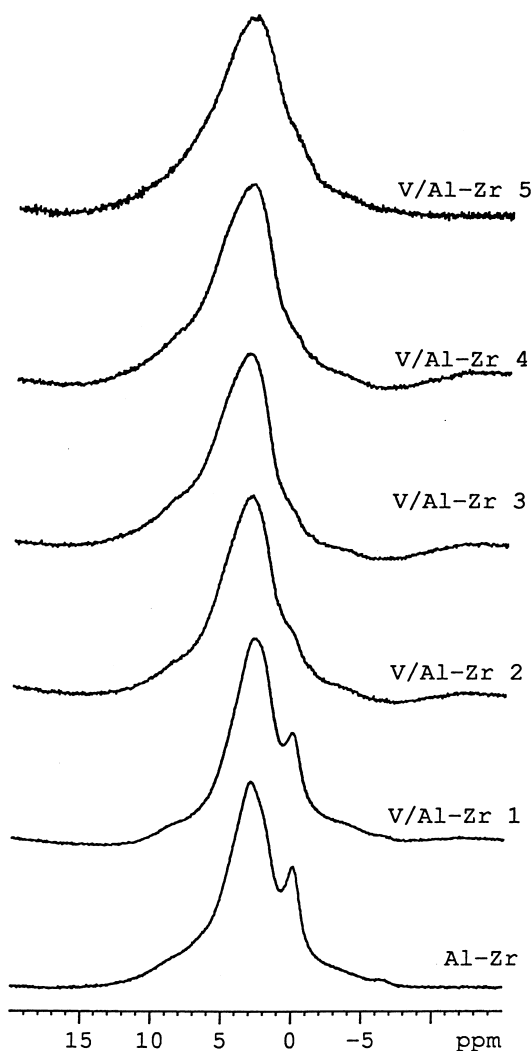


Fig. 4. ^1H MAS NMR spectra of the calcined catalysts outgassed at 623 K for 30 min (spin rate 10 kHz).

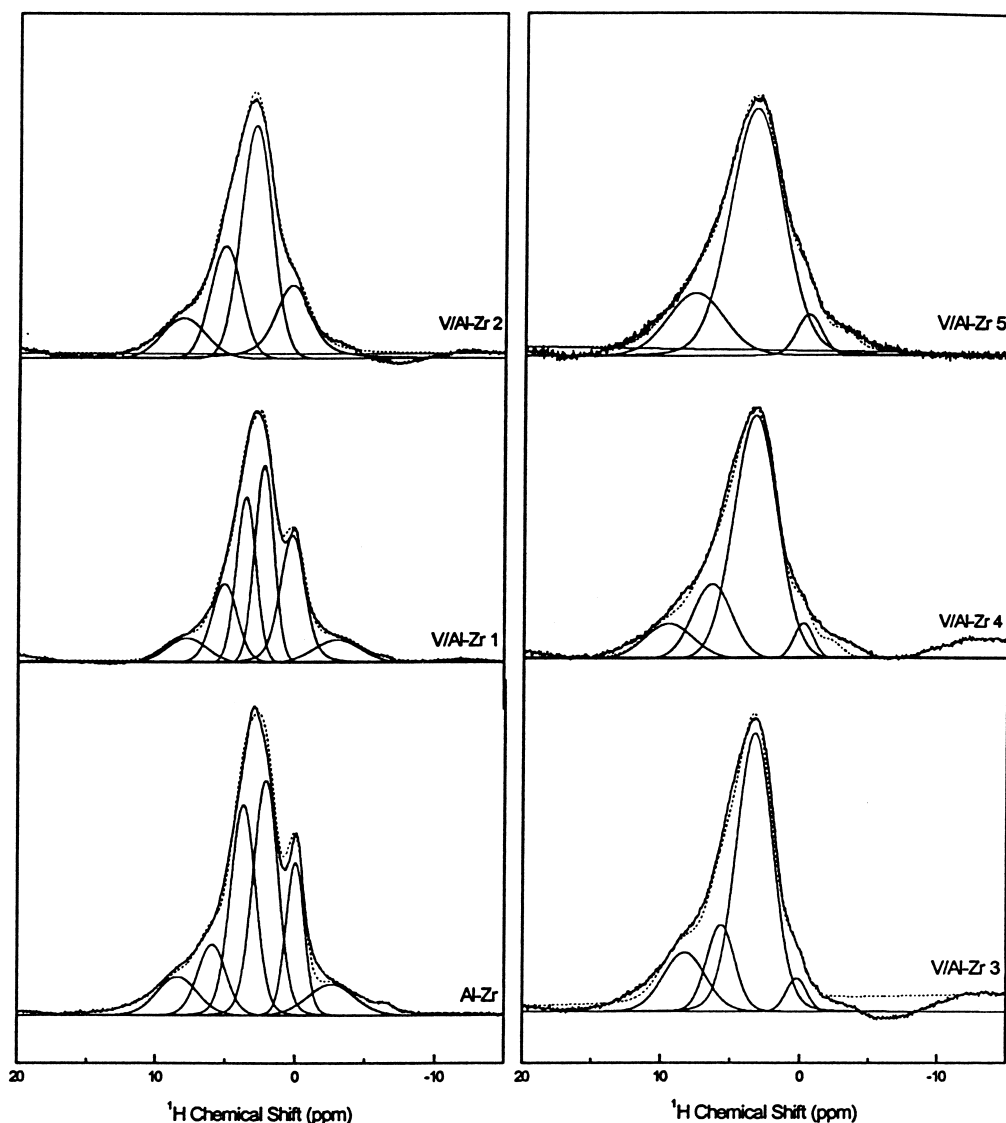


Fig. 5. The deconvoluted ^1H MAS NMR spectra of the Al-Zr and V/Al-Zr catalysts. (—) Experimental spectrum. (---) Curve fitted spectrum.

the peaks corresponding to basic hydroxyl groups was observed [24]. The present ^1H NMR data indicate the preferential reaction of vanadia with the basic hydroxyl groups of the mixed oxides. It can be seen from Fig. 4 that with increase in vanadium loading, there is a decrease in the intensity of the resonance at -0.3 ppm corresponding to basic hydroxyl groups of alumina.

The diffuse reflectance FT-IR spectra of the calcined catalysts in $1200\text{--}400\text{ cm}^{-1}$ region are shown in Fig. 6. Due to the opaque nature of alumina component of the support no significant vibrations corresponding to dispersed vanadia species could be seen in the catalysts. The vibration at 550 cm^{-1} observed in Al-Zr support and vanadia catalysts correspond to Al-O bending vibrations [25]. In the catalyst V/Al-Zr

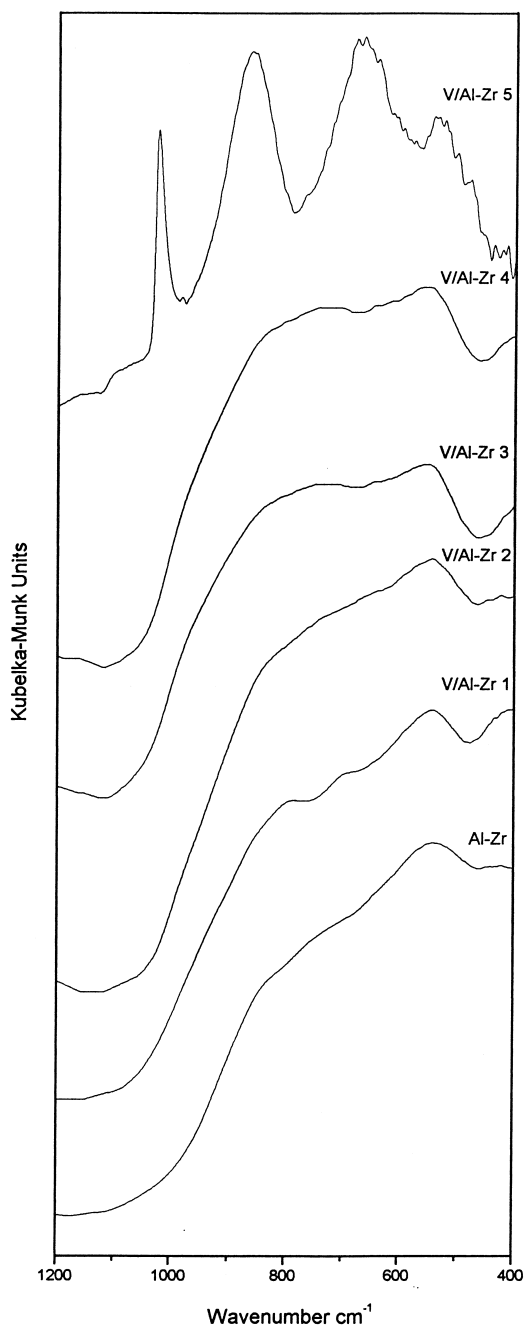


Fig. 6. Diffuse reflectance FT-IR spectra of the calcined catalysts in the skeletal vibration region ($1200\text{--}400\text{ cm}^{-1}$).

5, the vibrations at 1022 and 862 cm^{-1} can be attributed to stretching vibrations of $\text{V}=\text{O}$ and $\text{V}-\text{O}-\text{V}$ bonds [26]. The DRIFT spectra of catalysts remained unchanged upon outgassing treatment in the skeletal vibration region, except

for a decrease in the intensities of the 1022 and 862 cm^{-1} bands in the V/Al-Zr 5 catalyst. The DRIFT studies of the catalysts are in conformity with ^{51}V NMR studies indicating the presence of V_2O_5 agglomerates only in the V/Al-Zr 5 catalyst with high vanadia loading. The DRIFT spectra of the evacuated catalysts in the hydroxyl region ($4000\text{--}2000\text{ cm}^{-1}$) are shown in Fig. 7. The broadness of the IR bands

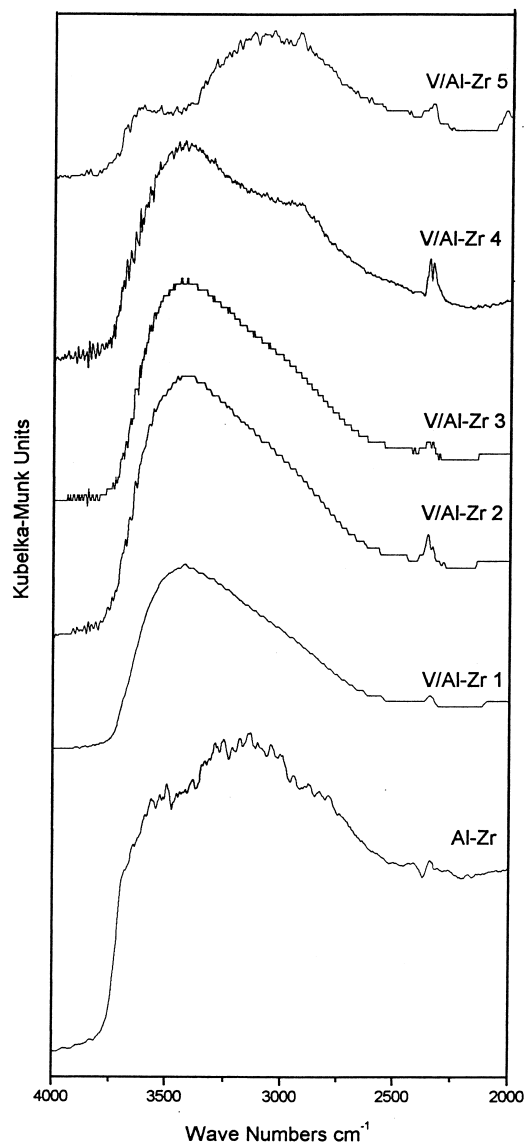


Fig. 7. Diffuse reflectance FT-IR spectra of the outgassed (at 623 K for 30 min) catalysts in the hydroxyl region ($4000\text{--}2000\text{ cm}^{-1}$).

suggest the presence of chemisorbed water, in the support and the catalysts. Similar observations were made by Turek et al. [27], they attributed the broad peak to chemically adsorbed water interacting with the surface hydroxyl groups of the catalysts pretreated at 300°C. However, Eberhardt et al. [28], in their IR studies on V/Al₂O₃ catalysts, have observed the vibrations corresponding to various hydroxyl groups of alumina, by treating the support and the catalysts at 450°C for 4 h. They have shown that the most basic surface hydroxyls exhibit high IR frequency and sequential consumption of hydroxyl groups starting with most basic hydroxyl groups with increase in V₂O₅ content of the catalysts. In the Al–Zr mixed oxide support, the vibrations at 3563, 3163 cm⁻¹ were observed with a broad shoulder

at 2900 cm⁻¹. In our earlier DRIFT studies on Zr–Si sol–gel mixed oxide supported vanadia catalysts, we attributed these bands to Zr–OH vibrations [18]. However, there may be overlap of vibrations from Al–OH groups in this region [28]. It can be seen from the figure that with an increase in vanadia loading, the vibration at 3563 cm⁻¹ became less intense indicating preferential consumption of these hydroxyl groups, and in the catalysts V/Al–Zr 1, 2, 3 and 4, only a broad band centered at 3446 cm⁻¹ could be seen. In the catalyst V/Al–Zr 5 with highest V₂O₅ loading IR bands at 3637 and 3063 cm⁻¹ could be seen. The IR band at 3637 cm⁻¹ may correspond to V–OH vibrations [28].

The activities of the V/Al, V/Zr and V/Al–Zr catalysts and the supports were tested using ethanol oxidation as a probe reaction. The

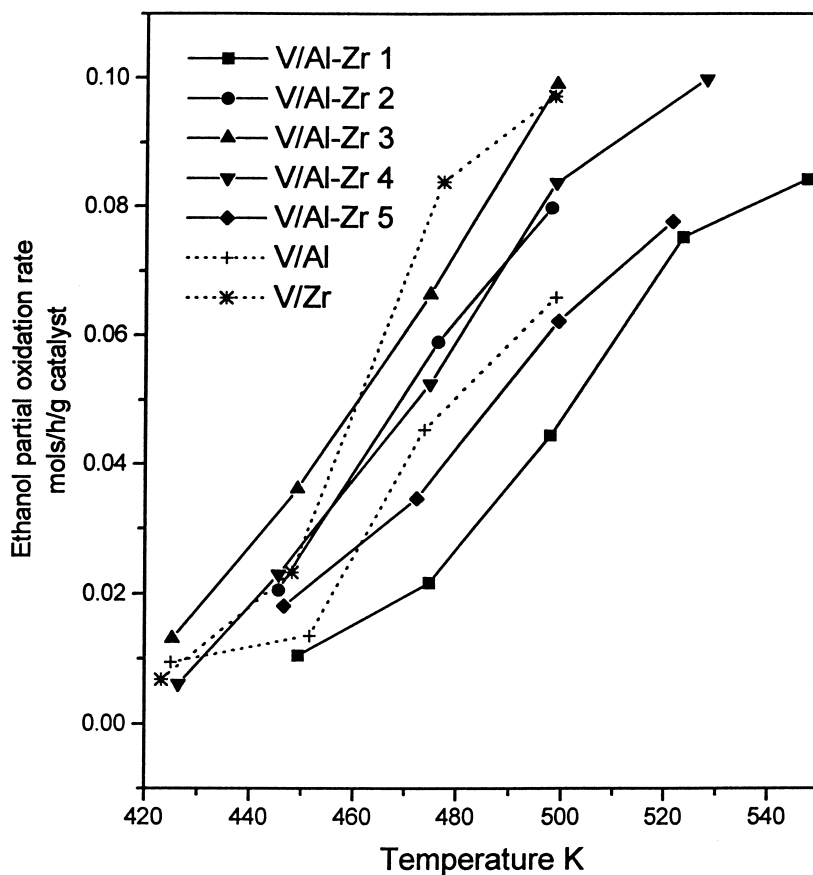


Fig. 8. Ethanol partial oxidation rates of the catalysts as a function of reaction temperature (reaction conditions are given in Section 2).

Table 3
TOFs for the ethanol partial oxidation on the V/Al–Zr, V/Al, V/Zr catalysts at a reaction temperature of 448 K

Catalyst	TOF (s ⁻¹) ^a
V/Al–Zr 1	0.6
V/Al–Zr 2	0.7
V/Al–Zr 3	0.9
V/Al–Zr 4	0.5
V/Al	0.3
V/Zr	0.7

^aBased on the amount of vanadia loaded.

partial oxidation rates of various catalysts are shown in Fig. 8 as a function of reaction temperature. The activities of the catalysts increased with increase in reaction temperature. It can be seen from the figure that there is not

much difference in the reaction rates of the V/Al–Zr catalysts which indicates structure insensitive nature of the ethanol partial oxidation reaction [18,29,30]. The TOFs of the catalysts calculated from the amount of V₂O₅ present in the catalysts are given in Table 3. In the case of V/Al–Zr 5 catalyst, the TOF was not calculated as V₂O₅ microcrystallites were noticed from characterization studies of this catalyst. It can be seen from the table that the TOFs of V/Al–Zr, V/Zr catalysts are about two times higher than the V/Al catalyst, indicating the zirconia-like nature of alumina–zirconia support in determining the catalytic activity. Quaranta et al. [30] obtained high ethanol partial oxidation rates and acetaldehyde selectivities for the V₂O₅/TiO₂/SiO₂ catalysts in comparison to

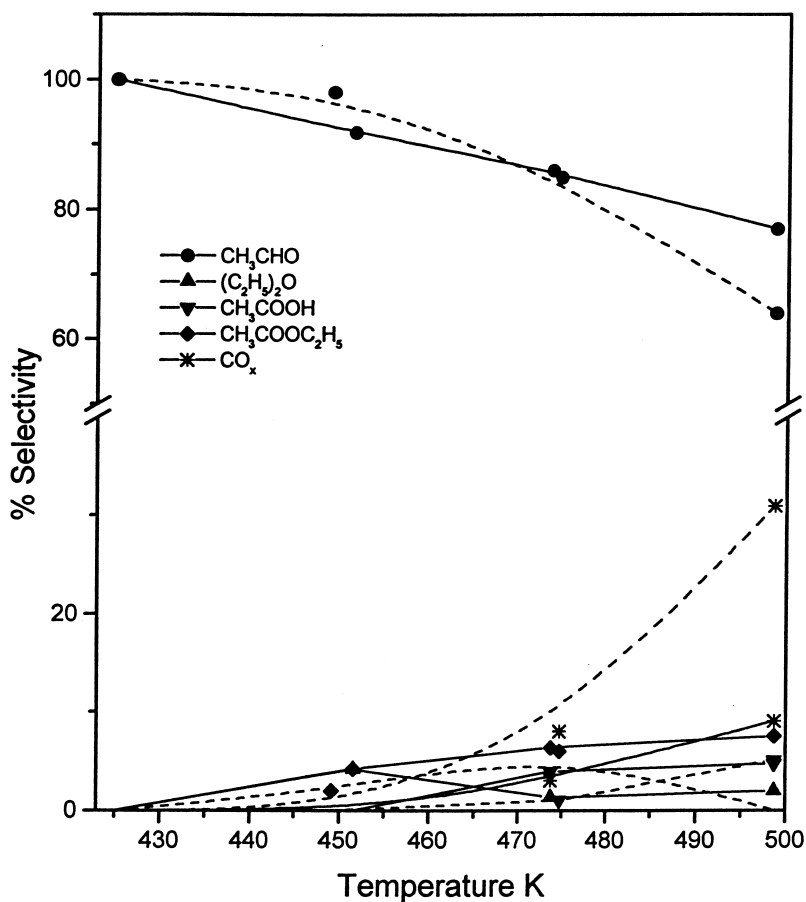


Fig. 9. The % selectivities of V/Al (—) and V/Al–Zr 3 (---) catalysts as a function of reaction temperature.

the vanadia catalysts supported on silica or alumina, which was attributed to the vanadia species in interaction with the titania component of the titania modified silica support. Alumina support at a reaction temperature of 250°C exhibited a very high conversion of 65%, with 85% selectivity to ether and ~12% ethylene selectivity. Zirconia and Al–Zr mixed oxide supports at a reaction temperature of 250°C showed less than 2% conversion with total selectivity to acetaldehyde and traces of acetic acid.

The % selectivity to various products observed for the V/Al and V/Al–Zr 3 catalysts are shown in Fig. 9 as function of reaction temperature. The reactivity data for the V/Zr catalyst was included in our recent report [18]. At low reaction temperatures and low conversion levels primarily acetaldehyde was obtained as major product in both the catalysts. With increase in reaction temperature significant selectivity to ether, acetic acid, ethyl acetate and CO_x was observed. The alumina support which showed the presence of only dehydration product upon vanadia impregnation exhibited almost total selectivity to dehydrogenation product acetaldehyde which indicates the predominance of the redox property of the V/Al catalyst over the acid–base characteristics. V/Zr catalyst exhibited significant selectivity to acetic acid at total conversion where as V/Al–Zr 3 catalyst exhibited higher CO_x selectivity at total conversion level.

4. Conclusions

Our present and previous studies [16–18] indicated that the sol–gel derived mixed oxides are promising materials for dispersing and stabilizing the active vanadia phase. We have employed the characterization techniques — ⁵¹V solid-state NMR and DRIFT spectroscopic studies to differentiate various kinds of hydroxyl groups and vanadia species present in the support and the catalysts, and the influence of

increasing vanadia loading in the catalysts. ⁵¹V NMR studies of the calcined and outgassed catalysts indicated the presence of water molecules in the coordination sphere of vanadia. ⁵¹V NMR studies of the catalysts showed the presence microcrystalline V₂O₅ species only at a highest vanadia loading in the sample V/Al–Zr 5. DRIFT studies of the catalysts were in conformity with ⁵¹V NMR studies as the vibrations corresponding to V=O and V–O–V species were seen only in the V/Al–Zr 5 catalyst. ¹H MAS NMR studies and DRIFT studies of the outgassed catalysts indicate the preferential reaction of vanadia with the basic or terminal hydroxyl groups followed by the bridged or acidic hydroxyl groups of the Al₂O₃–ZrO₂ mixed oxide. The ethanol partial oxidation studies indicated zirconia-like nature of the alumina–zirconia support in determining the activities of the catalysts. The lower oxidation activity of the V/Al–Zr 5 can be attributed to the presence of V₂O₅ microcrystallites as observed from the spectroscopic studies. Further investigations on the effect of in-situ addition of vanadia to the alumina–zirconia sol are progress to study the effect of surface or framework vanadia species in determining the catalytic activity.

Acknowledgements

We would like to thank NSERC, Canada for financial support. Thanks are due to Prof. Ian Brindle for ICP analysis and Tim Jones for his help during NMR investigations.

References

- [1] G.C. Bond, S.F. Tahir, Appl. Catal. 71 (1991) 1.
- [2] G. Deo, I.E. Wachs, J. Haber, Crit. Rev. Surf. Chem. 4 (1994) 141.
- [3] G.C. Bond, J.C. Vedrine, Catal. Today 20 (1994) special issue.
- [4] P.S. Iyer, H. Eckert, M.L. Ocelli, M. Stencel, Fluid Catalytic Cracking II: Concepts in Catalyst Design, 1992, p. 242.

- [5] H.K. Matralis, M. Ciardelli, M. Ruwet, P. Grange, *J. Catal.* 157 (1995) 368.
- [6] B. Handy, A. Baiker, M. Schraml-Marth, M.A. Wokaun, *J. Catal.* 133 (1992) 1.
- [7] A. Kytokivi, E.-L. Lakomaa, A. Root, H. Osterholm, J.-P. Jacobs, H.H. Brongersma, *Langmuir* 13 (1997) 2717.
- [8] Z. Dang, B.G. Anderson, Y. Amenomiya, B.A. Morrow, *J. Phys. Chem.* 99 (1995) 14437.
- [9] L.J. Lakshmi, E.C. Alyea, S.T. Srinivas, P.K. Rao, *J. Phys. Chem. B. Mater.* 101 (1997) 3324.
- [10] H. Eckert, I.E. Wachs, *J. Phys. Chem.* 93 (1989) 6786.
- [11] O.B. Lapina, V.M. Mastikhin, A.A. Shubin, V.C.N. Krasilnikov, K.I. Zamaraev, *Prog. NMR Spectrosc.* 24 (1992) 457.
- [12] R.H.H. Smits, K. Seshan, A.P.M. Kentgens, *J. Phys. Chem.* 99 (1995) 9169.
- [13] H. Kraus, R. Prins, *J. Catal.* 164 (1996) 260.
- [14] E.C. DeCanio, J.C. Edwards, J.W. Bruno, *J. Catal.* 148 (1994) 76.
- [15] T. Riemer, D. Spielbauer, M. Hunger, G.A.H. Mekhemer, H. Knozinger, *J. Chem. Soc. Chem. Commun.* 10 (1994) 1181.
- [16] J.M. Miller, L.J. Lakshmi, *J. Phys. Chem. B. Mater.* 102 (1998) 6465.
- [17] J.M. Miller, L.J. Lakshmi, *J. Mol. Catal.* 144 (1999) 451.
- [18] J.M. Miller, L.J. Lakshmi, *J. Catal.* 184 (1999) 68.
- [19] O.B. Lapina, V.M. Mastikhin, L.G. Simonova, Yu.O. Bulgakova, *J. Mol. Catal.* 69 (1991) 61.
- [20] V.M. Mastikhin, V.V. Terskikh, O.B. Lapina, S.V. Filiminova, M. Seidl, H. Knozinger, *Solid State NMR* 4 (1995) 369.
- [21] V.M. Mastikhin, A.V. Nosov, V.V. Terskikh, K.I. Zamaraev, *J. Phys. Chem.* 98 (1994) 13621.
- [22] V.M. Mastikhin, K.I. Zamaraev, *Appl. Magn. Reson.* 1 (1990) 295.
- [23] V.M. Mastikhin, V.V. Terskikh, O.B. Lapina, S.V. Filiminova, M. Seidl, H. Knozinger, *J. Catal.* 156 (1995) 1.
- [24] V.M. Mastikhin, A.V. Nosov, V.V. Terskikh, K.I. Zamaraev, I.E. Wachs, *J. Phys. Chem.* 98 (1994) 13621.
- [25] J.M. Saniger, N.A. Sanchez, J.O. Flores, *J. Fluorine Chem.* 88 (1998) 117.
- [26] M. Sanati, A. Andersson, *J. Mol. Catal.* 59 (1990) 233.
- [27] A.J. Turek, I.E. Wachs, E. De Canio, *J. Phys. Chem.* 96 (1992) 5000.
- [28] M.A. Eberhardt, M. Houalla, D.M. Hercules, *Fresenius' J. Anal. Chem.* 350 (1994) 570.
- [29] S.T. Oyama, G.A. Somorjai, *J. Phys. Chem.* 94 (1990) 5022.
- [30] N.E. Quaranta, J. Soria, V. Cortes Corberan, J.L.G. Fierro, *J. Catal.* 171 (1997) 1.