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Catalytic Transformation of Ethanol over Microporous Vanadium Silicate Molecular Sieves with MEL Structure (VS-2)

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The transformation of ethanol was carried out over vanadium silicate molecular sieves with MEL topology (VS-2) with different Si/V atomic ratios in the temperature range 523–623 K. The reaction was performed in a fixed-bed down-flow reactor at atmospheric pressure. Acetaldehyde, diethyl ether, and ethylene were the major products along with small amounts of acetone, acetic acid, ethyl acetate, and carbon oxides. The conversion increased while the selectivity toward acetaldehyde decreased with increase in reaction temperature. The kinetics of the reaction (at 5% conversion) indicated a nearly first-order dependence of the rate of formation of the major products on ethanol. The formation of acetaldehyde is suggested to be mainly through the involvement of the vanadyl species (V=O) while diethyl ether production is controlled by the simultaneous involvement of V=O and V–O–Si associated with vanadium in the lattice. The intrinsic activity of vanadium incorporated into the zeolite framework is nearly 10 times that of the vanadium present in the impregnated sample. The nature of the sites involved in the formation of the different products, as elucidated from spectroscopic techniques (NMR and ESR), and the possible reaction mechanisms are proposed. © 1997 Academic Press

INTRODUCTION

Selective oxidation of ethanol to value-added chemicals has deserved recently an increasing technological interest in connection with the utilization of biomass as a chemical source (1). Although silver-based catalysts are commercially used, a number of metal oxides have been tested for this reaction in order to find a substitute for this commercial catalyst (2). Among the oxides screened, molybdenum- and vanadium-based catalysts are the promising candidates for the above reaction (3). Oyama and co-workers (4) have studied the oxidation of ethanol over silica-supported vanadium oxide catalysts. No remarkable change in the activity was observed with vanadium loading and particle size of the catalyst indicating that the reaction is structure insensitive. Quaranta *et al.* (5) have extended the earlier study by supporting V_2O_5 on a TiO_2-coated SiO_2 support. A good improvement in both activity and selectivity (to acetaldehyde) was observed for the V–Ti–Si catalyst when compared to both V–Si and V–Ti catalysts. The enhanced activity was attributed to the interactive nature of the TiO_2 support and good molecular dispersion. Very recently, selective dehydrogenation of ethanol was carried out over V_2O_5 supported on α-Al_2O_3 (6). An improved selectivity for acetaldehyde was observed, accounted for on the basis of greater heat dissipation and catalyst bed isothermicity.

Isomorphous substitution of vanadium in the framework of zeolite and molecular sieves results in new materials with remarkable catalytic properties particularly in partial oxidation reactions (7–12). Such incorporation of vanadium into zeolite lattices creates isolated active centers in an ordered matrix, responsible for such unusual reactivity. This has been well documented in the literature by projecting the differences in the activity of incorporated and impregnated (supported) vanadium in zeolites (8a, 13, 14). Wan *et al.* (15) have studied the oxidation of ethanol over the transition metal incorporated microporous aluminophosphate molecular sieve $AlPO_4$-5. VAPO-5 exhibited more acidic behavior yielding mainly diethyl ether and ethylene with small amount of acetaldehyde. Bellusi *et al.* (15) have studied the oxidation of methanol over V-containing MFI silicalites. V silicalites showed a higher activity than V_2O_5 supported on silica with similar selectivity for formaldehyde and the difference in the activity was explained based on the different sorption strengths.

The present investigation is concerned with the oxidation of ethanol over vanadium-containing silicalite with MEL structure (VS-2) and its postmodified forms with different Si/V atomic ratios. This study is aimed at delineating the intrinsic activity of vanadium in the zeolite lattice with that present in the extra framework positions and to identify the sites involved in the formation of the various reaction products.

EXPERIMENTAL

Catalyst Preparation and Characterization

The VS-2 samples were synthesized by a hydrothermal method using tetrabutyl ammonium hydroxide as the

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structure directing agent and $VOSO_4$ as the source of vanadium (12b). The as-synthesized samples were calcined in air at 773 K for 10 h (VS2-Cal). The calcined materials were treated with an aqueous ammonium acetate (IN) solution at 333 K for 12 h to remove extralattice vanadium (VS2-E). The extracted samples were exchanged with $NaNO_3$ (IN) solution at 333 K for 12 h to remove the Brønsted acidic sites (VS2-ENa). After extraction and exchange, the samples were again calcined at 773 K for 8 h. V-Sil-2 was prepared by impregnating V_2O_5 on pure silicalite-2 at 333 K for 6 h and the resulting sample was oven dried (383 K) and calcined at 773 K for 8 h. Two vanadosilicate samples, designated as VS2-A and VS2-B were used in these studies. The preparation of these samples has already been described in detail in our earlier publication (12b; samples B and C, therein). VS2-A and VS-B samples were prepared under identical synthesis conditions, except that different V concentrations were used. The calcined, extracted (with NH_4OAc), and extracted and exchanged (with $NaNO_3$) samples of VS2-A and only the extracted sample of VS2-B were employed for the catalytic studies. In addition silicalite-2 and V_2O_5-impregnated silicalite-2 (V–Sil-2) were also used.

Catalytic Studies

The reactor system employed for the present study was a bench top reaction system (BTRS, Autoclave Engineers U.S.A), which is a fixed-bed continuous down-flow stainless-steel reactor (5 cc) operating under steady-state conditions. Ethanol was fed through a HPLC liquid injection pump (Alcott, Model 760) and air was passed using a mass flow controller (Brooks, Model 5896). The reactants were mixed and vaporized in a preheated oven maintained at 393 K and passed through the reactor (6 mm i.d.). The temperature around the reactor was maintained by a temperature-controlled furnace. The outlet of the reactor was directly connected to a gas chromatograph (HP-5890 Series II) through a heated transfer line which was maintained at 393 K. An eight-port sampling valve was used to inject a known amount of the product mixture or reactant (250 μl) to the GC using nitrogen as the carrier gas. The products were analyzed using a capillary column (cross-linked methyl silicone gum, 50 m × 0.2 mm) and a FID. The carbon oxides in the samples were estimated using another GC (Shimadzu, 15-A) using a POROPAK-Q column (2 m × 0.3 mm) and a TCD.

Air after drying through a trap-containing molecular sieve (4A) and doubly distilled ethanol (>99%) were used for the reaction. A reactant gas mixture of 3 vol% C_2H_5OH in air [5.3 cc/170 cc; WHSV of ethanol (mass of ethanol passed in 1 h/mass of the catalyst) = 2.6 h^{-1}]. The concentration of ethanol in air was well below the lower explosion limit. Two-hundred fifty milligrams of the catalyst (mesh size 22–30) was employed for the reaction. The catalyst was initially activated at 673 K for 3 h in air and cooled to the reaction temperature. Reproducible results were obtained after each set of experiment indicating the establishment of the steady state without noticeable deactivation of the catalyst. A stable activity without much deactivation was observed for a long time period (~10 h). Carbon and oxygen mass balances of 100 ± 5% were obtained for most of the experiments. Rate, when expressed as turnover rate, was calculated as the number of molecules of ethanol converted per vanadium atom per second.

RESULTS AND DISCUSSION

Table 1 summarizes the elemental composition of the samples synthesized. It is clear from Table 1 that nearly 90% loss of vanadium was observed for VS2-A-Cal upon extraction with NH_4OAc indicating that vanadium is predominantly present in extralattice positions (12b). The influence of temperature on the conversion of ethanol over various vanadium silicalite samples is presented in Fig. 1. For comparison purposes, the reactivity of silicalite and V-impregnated silicalite are also included in Fig. 1. Table 2 summarizes the conversion and selectivities obtained for all the catalysts. During the reaction, on all the catalysts, acetaldehyde, diethyl ether, and ethylene were observed as minor products. A comparison of the activity of VS2-A-Cal and its postmodified forms indicates that VS2-A-Cal and VS2-A-ENa samples possess similar activities, while VS2-A-E possesses a lower activity. Figures 2a–2d show the plot of selectivity to the major products at constant conversion levels (10 and 50%). VS2-A-Cal and VS2-A-ENa samples exhibit a similar selectivity pattern and favor the dehydrogenation reaction (acetaldehyde formation), whereas the extracted sample (VS2-A-E) favors the primary dehydration product, namely diethyl ether (Figs. 2a and 2b). Furthermore, the selectivity to acetaldehyde decreases with an increase in reaction temperature for the former samples while it is not affected much for the later sample (Table 2). At higher temperatures, however, the selectivity for the secondary dehydration product, ethylene, is enhanced with a loss in the selectivity of acetaldehyde and diethyl ether.

TABLE 1

Chemical Composition of the Samples Used in the Studies

Catalyst	Pretreatment	V/Si + V ($\times 10^{-3}$)	Si/V
VS2-A-Cal	Calcined at 773 K for 10 h	7.46	133
VS2-A-E	NH_4OAc extraction at 333 K for 12 h	0.7	1427
VS2-A-ENa	Extraction + exchange with 1 *N* $NaNO_3$ at 333 K for 12 h	0.7	1427
VS2-B-Cal	Calcined at 773 K for 10 h	4.1	243
VS2-B-E	NH_4OAc extraction of VS2-B-Cal	2.4	415
V-Sil-2	Impregnation with V_2O_5	9.8	101
Sil-2	Calcined at 773 K for 10 h	0.0	$\propto$

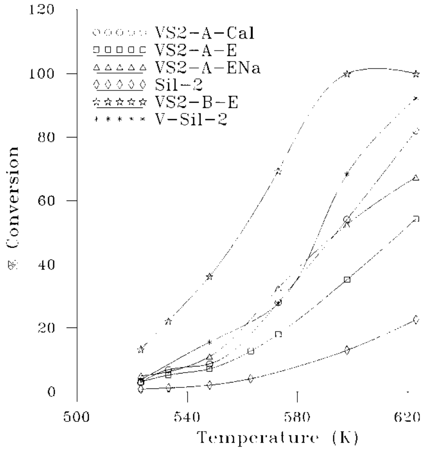
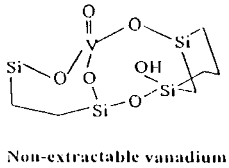


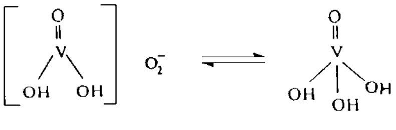
FIG. 1. Variation of total conversion with temperature over various catalysts.

The selective oxidation of ethanol over supported metal oxide surfaces has been studied extensively (17–19). The important steps involved in the reaction are: (i) adsorption and activation of ethanol on the active metal site and (ii) decomposition of the ethoxide species (rate-determining step) to form different products. However, the selective formation of any specific product is essentially controlled by the nature of the active sites present on the surface ($M=0$, M–O–M and M–O–M', where M is the active metal ion and M' is the support) (20). In the case of vanadium-containing silicalite (VS-2) and its postmodified forms, it is evident from Fig. 1 that the addition of vanadium into the silicalite matrix enhances the activity indicating the active participation of vanadium. Although vanadium is the active site on all these catalysts, a different selectivity pattern is observed suggesting that the products are produced through the decomposition of the ethoxide intermediate adsorbed on energctically different active sites. It was confirmed through spectroscopic techniques (12b) that VS2-E contains vanadium in a distorted tetrahedral environment (in +5 state) incorporated into the zeolite lattice (1), while VS2-A-Cal contains vanadium in +5 oxidation state present mainly in extra framework positions in a symmetric tetrahedral environment (II).



Non-extractable vanadium

I



Extractable vanadium

II

The lower activity (conversion of ethanol) of VS2-A-E in comparison with VS2-A-Cal is due to a lower concentration of vanadium in the former sample (Fig. 1). However, if one were to normalize the conversion on the basis of the V content of the samples, the activity of VS2-A-E is larger than that of VS2-A-Cal indicating a higher intrinsic activity of the V species in the latter catalyst (k_{Torr}, Table 3). The finding here of an enhanced activity with V concentration does not have a linear dependence on the overall rate because of the presence of different types of V centers with different intrinsic activities.

The selectivity pattern indicates (Fig. 2) that the calcined sample favors acetaldehyde while the extracted sample favors diethyl ether. Correlating with the species present in these samples, it is quite probable that V=O (associated with both extralattice and lattice vanadium) is responsible for the aldehyde formation and both the V=O and the V–O–Si are responsible for ether formation. This is in accordance with the results reported by Trifiro *et al.* (21) on methanol oxidation, who claimed V=O bond is the active site whose labilisation (reducibility) plays a crucial role in controlling the selectivity of the oxidation products.

TABLE 2

Oxidation of Ethanol over Various Catalysts

Catalyst	Temp. (K)	% Conversion	Selectivity (%)			
			C_2H_4	CH_3CHO	$(C_2H_5)_2O$	Others[a]
VS2-A-Cal	523	2.9	21	73	3	2
	548	8.8	18	82	—	—
	573	28.1	16	77	7	—
	598	54.2	30	67	3	—
	623	82.1	33	60	7	—
VS2-A-E	523	3.1	10	35	55	—
	548	7.3	14	37	49	—
	573	18.1	29	31	40	—
	598	35.3	52	29	19	—
	623	54.7	52	34	14	—
VS2-A-ENa	523	5.1	16	80	4	—
	548	11.1	14	77	9	—
	573	32.6	20	73	6	3
	598	52.6	21	61	7	11
	623	67.4	39	61	—	—
VS2-B-E	523	13.3	4	49	49	—
	548	36.3	7	43	50	1
	573	69.4	21	43	35	12
	598	100	50	33	5	3
	623	100	74	18	5	—
V-Sil-2	523	3.8	8	92	—	—
	548	15.6	11	88	1	—
	573	27.8	21	76	3	—
	598	68.4	21	77	2	—
	623	92.4	28	69	3	—
Sil2	523	0.8	4	51	45	—
	548	2.2	5	45	50	—
	573	4.8	8	33	59	—
	598	13.1	17	32	51	—
	623	22.7	30	30	40	—

[a] Mostly acetone, acetic acid, ethyl acetate, and methanol.

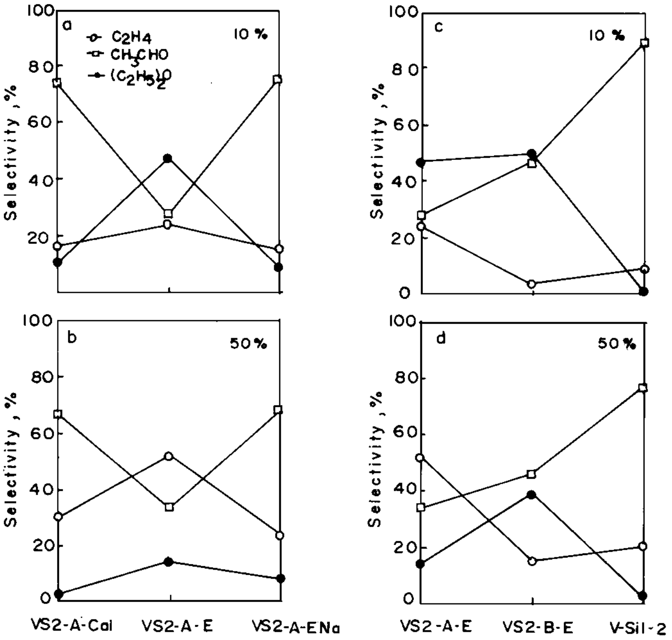


FIG. 2. Variation of selectivity of major products at constant conversion over various catalysts.

TABLE 3

Kinetic Parameters for the Oxidation of Ethanol over Various Catalysts

Catalyst	Temp. (K)	ln k^{a}	E_{app} (kJ/mol)	k_{Torr} ($\times$ 10^{-3}) (s^{-1})^{b}
VS2-A-Cal	523	−3.511	122.5^{c}	3.7
	533	−2.587	(116.4)^{d}	8.9
	548	−2.338		11.2
	563	−1.301		27.2
	573	−0.939		35.7
VS2-A-E	523	−3.442	94.1	42.3
	533	−2.883	(133.5)	72.3
	548	−2.541		99.6
	563	−1.913		174.6
	573	−1.509		247.0
VS2-A-ENa	523	−2.923	109.0	69.6
	548	−2.080	(115.2)	151.4
	573	−0.726		444.8
VS2-B-E	523	−1.875	135.3	52.7
	533	−1.254	(132.5)	88.1
	548	−0.562		144.0
	563	0.385		236.0
	573			275.3
V-Sil-2	523	−3.231	113.8	3.7
	548	−1.685	(109.4)	15.1
	573	−0.954		26.9

[a] Calculated employing first order rate expression.

[b] Turnover rate calculated as number of molecules of ethanol converted per vanadium atom per second.

[c] E_{app} calculated based on the conversion of ethanol.

[d] E_{app} calculated based on the acetaldehyde formation.

According to them, the activity of the catalyst is directly connected with the metal oxygen double bond which opens with the addition of an H atom from the alcohol, which in turn, leaves a free valence on the metal used for bonding with the dehydrogenated molecule (oxyreductive mechanism). A similar perception was realized on MoO_3-based catalysts for ethanol oxidation in which it was suggested that Mo=O sites were responsible for acetaldehyde formation (22–25). The catalytic activity of the VS2-A-ENa sample is similar to that of the calcined sample. The objective of the exchange of VS2-A-E with Na^+ ion was to remove the weakly Brønsted acidic sites associated with the defect centers created with V incorporation (12c), thereby increasing the selectivity toward acetaldehyde. In fact, a threefold increase in the selectivity was observed especially at low conversions, upon exchange (Fig. 2; Table 2).

In order to understand the kinetics of the reaction over these samples, it is essential to know the order dependence of ethanol on the rate of formation of the major products (C_2H_4, CH_3CHO, and $(C_2H_5)_2O$). Figure 3 shows the logarithmic plot of partial pressure of ethanol with turnover rate. Here the turn over rates were calculated assuming all V atoms (present both at internal and external surface) are accessible for the reactant molecule. The above assumption is valid in the case of zeolite molecular sieves (such as the MEL) in which all the framework V ions are accessible through the pore system. Besides, the small amount of the extraframework V species are expected to be well distributed (dispersed) on the large surface area (∼400 m^2/g). A linear dependence with slope nearly equal to unity is observed for all the three products. Extending the analysis, Arrhenius plots were constructed and the apparent activation energy values, E_{app}, were calculated for both total conversion and acetaldehyde formation.

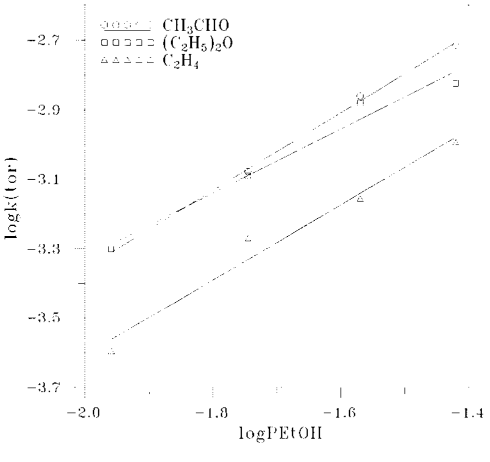


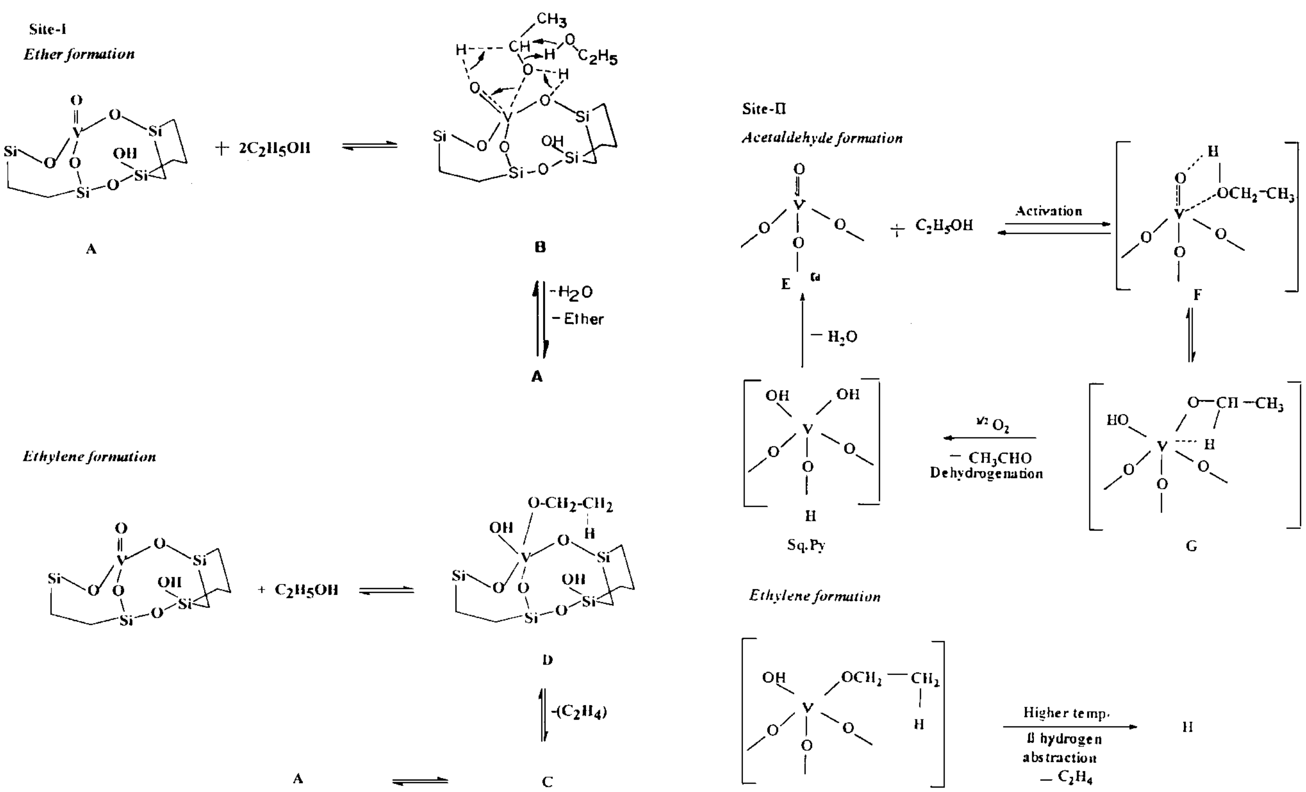
FIG. 3. Effect of partial pressure of ethanol on the reaction rate for various products over VS2-A-Cal.

Comparison of the catalysts with different Si/V atomic ratios indicate that an increase in the concentration of incorporated vanadium in the zeolite lattice increases the catalytic activity (Table 2). Although the impregnated catalyst contains nearly four times the concentration of the vanadium present in the VS2-B-E sample, a lower activity is observed indicating the higher intrinsic activity of incorporated vanadium. Figures 2c and 2d are a plot of the selectivity of the major products for the catalysts with different Si/V atomic ratios at constant conversion. Among the samples, the impregnated catalyst shows a maximum selectivity for acetaldehyde and a minimum selectivity for diethyl ether at both lower and higher conversions. The V-containing molecular sieves possess a higher selectivity for diethyl ether and nearly similar selectivity for acetaldehyde. As in the case of the earlier set of samples (postmodified forms), a higher selectivity for ethylene was observed at the higher conversion.

In contrast to the earlier set of samples (Figs. 2a and 2b) the increase in the activity is directly proportional to vanadium concentration. Similar turnover rates are observed (Table 3) for VS2-A-E and VS2-B-E which indicates that the nature of vanadium present in both the samples are similar, even though the V concentrations are different. Furthermore, with an increase in vanadium concentration, though a substantial increase in the apparent activation energy for total conversion is observed, the E_{app} values for acetaldehyde formation are nearly the same (Table 3). A comparison of the activity between the impregnated sample V-Sil-2 and VS2-B-E indicates that, despite a higher concentration of vanadium in the former sample, the activity is lower by an order of magnitude (Tables 2 and 3). This clearly demonstrates the higher intrinsic activity of the vanadium incorporated in the zeolite lattice when compared to the extralattice vanadium. The selectivity pattern indicates, in general, a higher selectivity for diethyl ether at low conversions and at higher temperature and higher conversions, the secondary dehydration reaction leading to ethylene is favored more over all the catalysts (Table 2). The involvement of acidity apart from redox property in controlling the selectivity of the products has been observed in various catalytic transformations over V-containing compounds (26, 27). In all these cases, the possible influence of vanadium, which by itself can act as a Lewis acid site, cannot also be ignored. However, the selectivity to acetaldehyde is not affected much at both conversions (10 and 50%), indicating that the sites responsible for aldehyde formation are not perturbed by an increase in the temperature (Table 2). In general, the selectivity pattern appears to be considerably influenced by the acidity of the catalyst (around the active site). Ai(28) has observed a linear correlation during the oxidation of methanol over V_2O_5-based catalysts between formaldehyde formation and the acidity of the catalyst, suggesting that the oxidation activity is largely governed by the activation of the methanol on the acidic sites rather than on the oxidation function. However, on V-containing silicalites for ethanol oxidation, the dual functionality, namely the nature of the vanadium center (redox property) and the acidity around the active site controls this overall selectivity. In the case of V-impregnated silicalite, a selectivity pattern similar to VS2-A-Cal was observed, indicating that the sites involved in the product formation on these samples are similar. Furthermore, the turnover rates calculated based on number of vanadium atoms are also similar for VS2-A-Cal and V-Sil-2 (Table 3). In essence, the nature of VS2-A-Cal and V-Sil-2 samples are similar which is quite understandable as more than 90% of the vanadium resides outside the lattice in the former sample.

The partial pressure effect of ethanol for acetaldehyde formation over VS2-A-Cal at 523 K shows (Fig. 3) a rate dependence corresponding to first order rate expression. The E_{app} values are calculated based on Arhhenius equation [a linear plot of $\ln(x/1-x)$ vs $1/T$ or $\ln(x_1/1-x)$ vs $1/T$, where x is the conversion of ethanol and x_1 is the formation of acetaldehyde] are given in Table 3. The E_{app} (aldehyde) values of samples containing framework V species (VS2-A-E and VS2-B-E) are similar ($\sim$130 kJ mol^{-1}) while the values for the other samples (VS2-A-Cal, VS2-A-ENa, and V-Sil-2) containing extraframework species are also similar though of a lower magnitude (110–120 kJ mol^{-1}; Table 3). This suggests that the formation of acetaldehyde is less favorable over samples containing only framework V atoms. Though the similarity of E_{app} (aldehyde) values for VS2-A-E and VS2-B-E are understandable, the reasons for the difference in the E_{app} (conversion) are not clear. The E_{app} (conversion) values are similar for the other three samples containing mainly nonframework V atoms (Table 3).

A recent molecular orbital study by Weber (29) showed that during the oxidative dehydrogenation of methanol over metal oxide surfaces (V and Mo), the initial destination of the hydrogen would seem to be the metal and not an oxygen ligand (in opposition to proton transfer) because the hydrogen and the metal develop a bonding interaction, while the hydrogen and any of the adjacent oxygens develop an antibonding interaction and this transfer is the rate-limiting step of the reaction. Extending the argument for the oxidation of ethanol, the C–H bond breaking should be accompanied by a partial hydride transfer to the active center, vanadium. In the present series of catalysts, the higher selectivity of acetaldehyde observed over VS2-A-Cal and V-Sil-2 indicates that the labilisation of V=O bond is more facile in species II compared to species I (shown earlier). It is likely that both the V=O and Si–O–V linkages are involved in the ether formation and hence higher selectivity of ether is observed for VS2-A-E and VS2-B-E samples. Based on these observations, a mechanism can be



SCHEME 1. Plausible reaction mechanism for the formation of products during the transformation of ethanol.

proposed for the formation of products resulting from the decomposition of ethanol (Scheme 1).

CONCLUSION

Oxidation of ethanol over vanadium substituted molecular sieves yields acetaldehyde, diethyl ether, and ethylene as major products. The kinetics of the reaction indicate a first-order dependence of the rate of formation of major products on alcohol. Although vanadium is the active center in controlling the reaction, a marked difference in the selectivity pattern is observed in these samples attributable to the nature of vanadium and its acidity. It is presumed that the V=O centers are responsible for aldehyde formation while both V=O and Si–O–V linkages are responsible for the formation of ether. The intrinsic activity of the vanadium incorporated in the zeolite lattice is remarkably high in comparison with vanadium present in the extralattice positions.

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