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Characterization of vanadia–silica and titania–silica aero- and xerogels by acid–base probe reactions

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The acid–base properties of 10 wt% V_2O_5–SiO_2 and 10 wt% TiO_2–SiO_2 binary mixed oxide aero- and xerogels were determined by studying the transformation of methyloxirane and 1-butane. The transformations (the isomerization of methyloxirane to propanal and the double-bond migration of 1-butene to form isomeric 2-butenes) indicate that all samples contain mainly acidic sites. Correlations are shown to exist between heteroconnectivity (derived from FTIR analysis) in conjunction with the textural properties and the catalytic performance.

Keywords: vanadia–silica, titania–silica, methyloxirane, 1-butene, ring opening, double-bond migration, acidity

1. Introduction

Since the discovery of silicalites, and particularly titanium-silicalites, as oxidation catalysts [1–3], silica-containing binary mixed oxides have been in the focus of great academic and industrial interest. Besides being excellent catalysts themselves they may also serve as catalyst supports [4].

Developments in recent years of various preparation procedures allow the synthesis of binary mixed oxides with desirable physical characteristics [4]. A highly controllable process, the solution–sol–gel (SSG) method provides an opportunity to prepare mixed oxides with advantageous morphological and chemical properties. A crucial step of the SSG technique, markedly affecting the properties of the resulting product, is the drying process. Supercritical drying results in aerogels, whereas xerogels are the product of conventional evaporative drying techniques. Due to the considerable shrinkage, occurring during conventional drying, xerogels are usually characterized by denser morphology with lower porosity and lower surface area. Moreover, characteristic differences are found in pore-size distribution. Xerogels usually reveal pronounced microporosity. Aerogels, in turn, are usually meso- to macroporous with little microporosity. This high accessibility of internal surface area is one of the prominent properties for the catalytic application of aerogels.

In earlier papers the thorough characterization of titania–silica [5–7] and vanadia–silica [8,9] mixed oxides over a wide composition range were disclosed. Their excellent catalytic properties for the epoxidation of alkenes were described in refs. [6,8,10–12]. In conjunction with this catalytic interesting redox functionality, information about the acidity and basicity of these solids is of crucial importance. Numerous transformations are known to be induced by solid acids and bases. Furthermore, the knowledge of acid–base properties is pertinent when such materials are used as catalyst carriers. A large variety of methods, none of them universal, have been developed for the characterization of acid–base functionality [13,14]. Of the various probe molecules, 2-propanol was used to study the effect of preparation parameters on titania–silica aero- and xerogels [7]. Temperature-programmed reaction and desorption in conjunction with XPS analysis revealed surface silica enrichment and significant differences in the dehydration temperature of 2-propanol. In the present paper, the acid–base properties of selected mixed oxides, determined by studying the transformation of two test molecules, are described.

2. Experimental

Two sets of binary mixed oxide samples, various forms of 10 wt% V_2O_5–SiO_2 and 10 wt% TiO_2–SiO_2, were used in the present study. These materials were prepared by low-temperature supercritical drying, high-temperature supercritical drying, or evaporative drying, resulting in low-temperature aerogels, high-temperature aerogels, or xerogels, respectively. Low-temperature supercritical drying was carried out by the semicontinu-

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ous extraction of the solvent with supercritical carbon dioxide at 313 K. The corresponding samples are denoted as 10VLT and 10TiLT. The samples prepared by high-temperature supercritical drying at 533 K are 10VHT and 10TiHT. The xerogel samples (10VX and 10TiX) were prepared by evaporative drying at 373 K. All samples were calcined in flowing air at either 673 or 873 K for 5 h. Further details on the preparation of the samples can be found in refs. [5,8,9]. A summary of relevant physicochemical data is given in table 1.

Catalytic measurements were carried out in a flow-type microreactor at 523 K in helium purified with an Alltech Oxy-Trap + Indicating Oxy-Trap. Fresh catalyst samples corresponding to 10 m^2 surface area were used in each measurement after a 1 h pretreatment at 673 K in helium. 1 μl liquid pulses of methyloxirane (FERAK product of 99% purity) or 375 μl gas pulses of 1-butene (Linde, 99.3%), delivered through a loop, were introduced into the microreactor connected to a GC (Carlo Erba Fractovap Mod G with a thermal conductivity detector). The products formed were frozen out into a metal loop by liquid nitrogen then flash-evaporated and analyzed by the GC. A 15 wt% 1,2,3-tris(2-cyanethoxy)propane + Reoplex 400 on Merck Kieselguhr column was used for product analysis in the case of methyloxirane (1.2 m, room temperature, 20 ml min^{-1} helium flow). The column used for analysis of the transformation of 1-butene was 15 wt% bis(2-methoxyethyl) adipate on Chromosorb P (6 m, room temperature, 20 ml min^{-1} helium). Calculations were made applying a DataApex Chromatography Station for Windows 1.5.

3. Results and discussion

Experimental data on the transformations of methyloxirane and 1-butene over the twelve catalyst samples are given in tables 2–5. Catalyst samples exhibited a slight deactivation (a few percent decrease in catalytic activity with increasing pulse number) during the transformation of 1-butene. No significant changes in selectivities were, however, detected. In contrast, deactivation in the transformation of methyloxirane over titania–silica oxides calcined at 673 K was more significant (a 50% drop in activity during the injection of five pulses). Again, selectivities were not affected. All data in tables are the average of five pulses.

3.1. Methyloxirane

In an earlier paper methyloxirane was shown to be an appropriate molecule to characterize the acid–base properties of oxide catalysts [16]. A correlation was found to exist between the selectivity of the ring-opening transformations (isomerization to propanal and acetone) and the acidity of the oxides. It was shown, for example, that WO_3 with the highest acidity of the oxides studied exhibited the highest selectivity for the formation of propanal. MgO, in turn, which is a highly basic oxide was the most selective for the formation of acetone. In the present study methyloxirane is found to yield propanal as the sole product (tables 2 and 3). This behavior is a clear indication that only acidic centers are involved in the ring-opening reaction. As to the catalytic activity of the different catalyst preparations, the low-temperature aerogels (10VLT and 10TiLT) always exhibit higher activity than their corresponding high-temperature counterparts (10VHT and 10TiHT) (tables 2 and 3) after calcination at both 673 K and 873 K. In addition, the activity of aerogel catalysts calcined at 873 K is always higher than that after calcination at 673 K. The activity of the xerogels is between the low-temperature and high-temperature aerogel samples.

The changes in activity of vanadia–silica mixed oxides can be correlated with the relative contribution of Si–O–

Table 1

Textural and structural properties of 10 wt% V_2O_5–SiO_2 and 10 wt% TiO_2–SiO_2 mixed oxides. (Data taken from refs. [5,8,9])

Samples	S_{BET} (S_t) [a] (m^2 g^{-1})	$V_{p(N2)}$ (V_t) [b] (cm^3 g^{-1})	$\langle d_p \rangle$ [c] (nm)	$S_{(Si-O-V)}/S_{(Si-O-Si)}$ [d]	Samples	S_{BET} (S_t) [a] (m^2 g^{-1})	$V_{p(N2)}$ (V_t) [b] (cm^3 g^{-1})	$\langle d_p \rangle$ [c] (nm)	$S_{(Si-O-Ti)}/S_{(Si-O-Si)}$ [e]
10VLT(673)	840(53)	1.8(0.0)	9(17)	0.11	10TiLT(673)	683(140)	1.7	10(55)	0.49
10VLT(873)	728(37)	1.7(0.0)	9(15)	n.d.[f]	10TiLT(873)	557(98)	1.4	10(50)	0.50
10VHT(673)	1060(0)	3.2(0.0)	12(15)	0.07	10TiHT(673)	598(0)	3.6	24(60)	0.14
10VHT(873)	840(14)	2.5(0.0)	12(16)	n.d[f]	10TiHT(873)	611(0)	3.7	24(50)	0.12
10VX(673)	698(245)	0.2(0.1)	1(< 2)	0.08	10TiX(673)	473(407)	0.03	0.3(1.5)	n.d.[g]
10VX(873)	586(189)	0.1(0.1)	< 1(< 2)	n.d.[f]	10TiX(873)	256(202)	0.02	0.3(1.5)	n.d.[g]

[a] (S_t), in parentheses, denotes specific micropore surface area derived from t-plot analysis.

[b] $V_{p(N2)}$ designates the Barrett–Joyner–Halenda cumulative desorption pore volume of pores in the maximum range 1.7–300 nm diameter [15]; (V_t), in parentheses, denotes specific micropore volume derived from t-plot analysis.

[c] $\langle d_p \rangle = 4V_{p(N2)}/S_{BET}$; in parentheses, the graphically assessed pore-size maximum of the pore-size distribution.

[d] Relative contribution of Si–O–V entities, estimated from the ratio of Si–O–V (930–939 cm^{-1}) and Si–O–Si (1205–1215 cm^{-1}) peak areas.

[e] Relative contribution of Si–O–Ti entities, estimated from the ratio of Si–O–Ti (930–939 cm^{-1}) and Si–O–Si (1205–1215 cm^{-1}) peak areas.

[f] n.d.: not determined since calcination was found to have no effect on Si–O–V and Si–O–Si values.

[g] 10TiX possesses “good” dispersion, as indicated by the FTIR-data on the raw aerogel. Moreover, the estimates for Si–O–Ti connectivity are virtually not influenced by the calcination temperature up to 873 K.

Table 2
Product distribution (in mol%) of the ring opening of methyloxirane on 10 wt% V_2O_5–SiO_2 catalysts

	10VLT		10VHT		10VX	
	673 K	873 K	673 K	873 K	673 K	873 K
methyloxirane	77	56	91	79	82	66
propanal	21	38	9	20	18	31
acetone	0	0	0	0	0	0
decomposition	2	6	0	1	0	3
conversion	23	44	9	21	18	34

V entities (table 1). These values calculated from the FTIR spectra are supposed to represent a semiquantitative measure of the proportion of Si–O–V species (heteroconnectivity) and, consequently, indicate a kind of mixing efficiency or estimate of vanadia dispersion. The activity values determined over vanadia–silica samples parallel the heteroconnectivity: the 10VHT(673) sample possessing the lowest proportion of Si–O–V entities exhibits the lowest activity in the ring opening of methyloxirane, whereas 10VLT(673) characterized by the highest mixing efficiency is the most active catalyst. Although calcination at 873 K was found to have virtually no effect on the heteroconnectivity compared to calcination at 673 K, the former catalysts proved to be superior in the catalytic transformation of methyloxirane.

As to the titania–silica aerogels (table 3), the results are similar to those of the vanadia–silica aerogels (table 2). The xerogel sample 10TiX calcined at 873 K, however, does not show any activity at all. This drastic decline might originate from the significant textural restructuring caused by the rise in calcination temperature from 673 to 873 K (table 1). In addition, mass transport may also be suspected to play a role in determining catalytic activity. This phenomenon can be expected to affect the behavior of microporous materials, that is xerogels. It appears, therefore, that the inactivity of 10TiX(873) is caused by mass transport limitations.

Table 3
Production distribution (in mol%) of the ring opening of methyloxirane on 10 wt% TiO_2–SiO_2 catalysts

	10TiLT		10TiHT		10TiX	
	673 K	873 K	673 K	873 K	673 K	873 K
methyloxirane	71	48	90	83	73	100
propanal	27	52	10	17	27	0
acetone	0	0	0	0	0	0
decomposition	2	0	0	0	0	0
conversion	29	52	10	17	27	0

Table 4
Product distribution (in mol%) and selectivity of the isomerization of 1-butene on 10 wt% V_2O_5–SiO_2 catalysts

	10VLT		10VHT		10VX	
	673 K	873 K	673 K	873 K	673 K	873 K
1-butene	39	72	75	84	37	44
trans-2-butene	29	13	11	7	33	28
cis-2-butene	32	15	14	9	30	28
cis/trans ratio	1.1	1.2	1.3	1.3	0.9	1.0
conversion	61	28	25	16	63	56

3.2. 1-butene

To establish a more reliable correlation between the physicochemical characteristics of the samples and their catalytic properties, a further test reaction was applied, i.e., isomerization (double-bond migration) of 1-butene. This reaction is frequently applied for the characterization of solid catalysts to gain information on their acidity–basicity [17].

As regards the effect of the drying method on the vanadia–silica samples, the activity changes observed in the isomerization of 1-butene parallel those found in the transformation of methyloxirane. Namely, 10VHT samples exhibit the lowest activity (table 4). This behavior means that the correlation between activity and mixing efficiency established for methyloxirane is valid for 1-butene as well. In the case of the titania–silica mixed oxides (table 5), the activity is lower and decreases in the order low-temperature aerogel, high-temperature aerogel, and xerogel, which is likely to reside in the superposition of vanadium dispersion and texture. As to the influence of calcination (tables 4 and 5) calcination at 873 K causes a decline in activity for 10VLT, 10VHT, 10VX, 10TiHT, and 10TiX.

The selectivity of isomerization, i.e., the ratio of cis-2-butene to trans-2-butene is considered to give information about acidity–basicity of solid catalysts. It is suggested that low cis/trans ratios (values between 1 and 2)

Table 5
Product distribution (in mol%) and selectivity of the isomerization of 1-butene on 10 wt% TiO_2–SiO_2 catalysts

	10TiLT		10TiHT		10TiX	
	673 K	873 K	673 K	873 K	673 K	873 K
1-butene	84	80	92	94	97	99
trans-2-butene	8	10	4	3	1	0.4
cis-2-butene	8	10	4	3	2	0.6
cis/trans ratio	1.0	1.0	1.0	1.0	2.0	1.5
conversion	16	20	8	6	3	1

are indicative of carbocations formed on Brønsted sites [17]. In contrast, selectivity values much higher than 2 indicate that isomerization is induced by basic centers.

Most selectivity values determined over the twelve samples are very close to 1 (tables 4 and 5) and even the highest values found for the two 10TiX catalysts are only 2 and 1.5. This finding is in agreement with that observed in the ring opening of methyloxirane and corroborates that all mixed oxide samples used in the present study possess Brønsted acid sites which induce carbocationic double-bond migration. A similar conclusion was drawn by Ko et al. [18,19] who studied the same reaction over titania–silica and zirconia–silica mixed oxides of a wide composition range (samples with 40–96 wt% TiO_2). They observed increasing cis/trans ratios with increasing titania content reaching the value of 2 at a composition of about 85 wt% TiO_2 and 15 wt% SiO_2. The lowest ratio (about 1.2) was measured over a sample containing 40 wt% titania.

The selectivity patterns of the different catalysts depend on both the composition and the drying method. Vanadia–silica aerogels, for example, give higher cis/trans ratios than titania–silica aerogels (tables 4 and 5). The selectivity of the corresponding xerogels, in turn, are opposite. In fact, titania–silica xerogels exhibit the highest cis/trans ratios. In addition, all vanadia–silica catalysts calcined at 873 K give slightly higher selectivity values than samples calcined at 673 K (table 4), whereas the opposite is true for the titania–silica catalysts (table 5).

4. Conclusion

In conclusion, the isomerization of methyloxirane and 1-butene was chosen to study the acid–base functionality of differently dried vanadia–silica and titania–silica sol–gel samples. Independent of the drying method and the composition, all samples contain mainly acidic sites. However, activities and selectivities are markedly influenced by the drying method and the presence of either vanadia or titania in the silica matrix. The estimates of heteroconnectivity derived from FTIR analysis in conjunction with the textural properties allow pertinent correlations with the catalytic performance in the probe reactions chosen.

The isomerization of methyloxirane and 1-butene unravel, however, differences in the acid–base properties which are not amenable by the physico-chemical data quoted. Mass transport phenomena, especially in the case of microporous materials, should also be taken into account, since the accessibility of the active sites of the samples prepared by various drying methods are certainly different. The different nucleophilic character of the two probe molecules is an additional important factor affecting reactivities. Since methyloxirane is an n-donor molecule, whereas 1-butene exhibits a π-donor character, the two molecules certainly probe different surface active sites. Finally, the difference in the method of determining surface areas and that used for studying the probe molecules (*static* nitrogen chemisorption versus *flow* experiments) can also lead to difficulties in interpretation. Further studies are clearly needed to get insight into the finer details of both the surface characteristics of mixed oxides and the behavior of these probe molecules.

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