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Influence of support composition on the structure and reactivity of strontium base catalysts

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Strontium was supported on a variety of carriers, including silica, alumina, titania and carbon, by impregnation and decomposition of an acetate precursor at 773 K. These supported samples were characterized by surface area measurements, stepwise temperature-programmed desorption of carbon dioxide and activity for the catalytic decomposition of 2-propanol. In some cases, infrared and X-ray absorption spectroscopy were used to identify surface species. Results from these techniques suggested that strontium supported on silica forms a weakly basic surface silicate phase that had low activity for 2-propanol dehydrogenation. On alumina and titania, strontium acetate decomposed to form supported basic carbonates that were moderately active for 2-propanol dehydrogenation. When rates are normalized by the base site density determined from CO_2 desorption, strontium supported on carbon was the most active sample for dehydrogenation of 2-propanol. These results suggest that the nature of supported alkaline earth catalysts is strongly dependent on the composition of the carrier.

Keywords: strontium, EXAFS, IR spectroscopy, CO_2 TPD, 2-propanol dehydrogenation, silica support, alumina support, titania support, carbon support

1. Introduction

Alkaline earth oxides have long been known to function as solid base catalysts. Recent work has demonstrated their potential for many reactions including double-bond isomerization, hydrogenation, alcohol dehydrogenation, amination, aldol condensation, Knoevenagel condensation and alkylation [1–3]. The selective alkylation of phenol with methanol over MgO to form 2,6-xylenol, discovered by General Electric in 1965, has now been commercialized [4]. These oxides also function as catalyst supports, promoters and stabilizers [5–8]. One method to increase the mechanical strength and the available surface area of these basic catalysts is to incorporate them on stable high surface area support materials. However, very little work has been done in this direction. Tsuji et al. [9] found that strong base sites were generated in the cavities of Y zeolite by the introduction of magnesium oxide. The resulting material showed activity for 1-butene isomerization and 1,3-butadiene hydrogenation, even at 273 K. The activity enhancement correlated to an increase in CO_2 adsorption for the supported catalyst compared to Y zeolite. Tsuji et al. propose that an occluded magnesium oxide lattice having considerable charge separation between Mg and O forms the strong base sites. They also tested the supported catalyst for the double-bond isomerization of allylbenzene [9]. Bulk MgO was active for the liquid phase reaction at room temperature, whereas MgO supported on Y zeolite was inactive. Their results suggest that internal diffusion of the reactant in the zeolitic micropore is very slow at the low reaction temperature, and that the active base sites are located in the zeolite cavities.

Even though much of the previous work on alkaline earth oxides involves MgO, oxides of elements lower in the periodic table are stronger bases and are potentially useful catalytic materials. In addition, little is known about the interaction of alkaline earth compounds with support materials commonly used in the catalysis community. Thus, in this work, strontium was incorporated on several supports and the resulting samples were characterized by X-ray and infrared spectroscopies as well as CO_2 adsorption capacity. The decomposition of 2-propanol to acetone was used to probe the surface reactivity of these base catalysts.

2. Experimental

2.1. Catalyst preparation

The supported Sr catalysts (approximately 5 wt% Sr) were prepared by incipient wetness impregnation of the carriers, namely fumed silica (Cab-O-Sil M-5), γ-alumina (Mager Scientific AP-312), titania (Degussa P25) and microporous carbon (kindly donated by Dow) with a solution of strontium acetate (Alfa 99.999%). Preliminary tests with strontium nitrate as a precursor showed that the compound was difficult to decompose. After impregnation, the materials were dried overnight at 373 K in air and subsequently calcined for 10 h at

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773 K in flowing air. The carbon sample was heated to 773 K in helium instead of air to avoid oxidation of the support. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN) and surface areas (BET) were obtained from dinitrogen adsorption isotherms measured at 77 K on a Coulter Omnisorp 100CX instrument after outgassing for 10–12 h at 573 K.

2.2. Catalyst characterization

Stepwise temperature-programmed desorption (STPD) of carbon dioxide. Stepwise TPD of preadsorbed CO_2 from the catalysts was used to estimate the number density of surface base sites on the materials. The experiments were performed with a Thermogravimetric Analyzer – TGA 2050 (TA Instruments). A catalyst sample (ca. 100 mg) was pretreated in situ by heating at 773 K in a flow of ultra-high purity He (BOC gases, 99.9999%) for 4 h to remove water and other surface adsorbates. After cooling to 303 K, the catalyst was exposed to carbon dioxide by flowing spectra clean CO_2 (BOC gases) for 2 h. The sample was then purged with He for 2 h to remove physisorbed CO_2. Stepwise desorption of CO_2 was carried out by heating the sample from 303 to 773 K in a series of successive temperature steps (303–373 K, 373–473 K, 473–573 K, 573–673 K, 673–773 K). The temperature in each step was increased at a rate of 10 K min^{-1}. The maximum temperature in each step was maintained for a period of 30 min and the amount of CO_2 desorbed was determined from the weight loss of the sample. The flow rates of He and CO_2 during the experiment were 100 ml min^{-1}.

X-ray absorption spectroscopy. The X-ray absorption spectra associated with the Sr K-edge of Sr/silica and bulk SrO were recorded in the transmission mode on beam line X23A2 at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York. The storage ring operated with an electron energy of 2.58 GeV with beam currents ranging from 100 to 300 mA. The ionization chambers were filled with Ar to optimize sensitivity. Sample powder consisting of a mixture of the Sr/silica and boron nitride (Alfa) was pressed into a self-supporting wafer and placed inside an in situ cell capable of both heating and cooling the wafer in controlled atmospheres. Pretreatment of the catalyst sample involved heating to 773 K in flowing He, after which the sample was cooled to liquid dinitrogen temperature for collection of spectra. The EXAFS data were processed with Macintosh versions of the University of Washington analysis programs. Strontium oxide (Aldrich 99.9%), compressed with boron nitride between two Kapton films and cooled to liquid dinitrogen temperature, was used as the reference material for structural information. A distance of 2.58 Å was assigned to the Sr–O distance in strontium oxide [10]. Curve fitting of the supported Sr sample was performed in the k-space region 2.9–9.5 $Å^{-1}$.

Fourier transform infrared spectroscopy. The FT-IR absorption spectra were recorded on a Bio-Rad FTS 60A spectrometer. Sample powders were pressed into self-supporting pellets and loaded into a cell. The catalysts were pretreated in situ in flowing dinitrogen (BOC gases, 99.999%) at 773 K for 2 h and then cooled to 303 K prior to recording of the spectra. A cold trap placed in a mixture of dry ice and acetone was used to remove any moisture that might be present in the dinitrogen. The IR spectra for strontium carbonate (Aldrich 99.995%) and strontium acetate were obtained by pressing the samples with KBr into pellets. All spectra were recorded with a resolution of 4 cm^{-1} and averaged over 256 scans.

Decomposition of 2-propanol. The catalytic activity of the samples for the decomposition of 2-propanol was evaluated in a single-pass fixed bed, quartz reactor. About 0.5 g of fresh catalyst with particle sizes ranging from 40 to 60 mesh were pretreated at 773 K in flowing He (BOC gases, 99.999%) for 90 min. The 2-propanol, dried over molecular sieves, was continuously fed using a syringe pump to give a 1 : 1 molar ratio with He as carrier gas. The total molar flow rate of the mixture was 0.15 mol h^{-1}. The product composition was determined using a Hewlett Packard HP-5890 series II gas chromatograph, fitted with an Alltech Carbowax column. The selectivity and turnover frequency for acetone formation were calculated using the following equations:

$$\text{selectivity to acetone} = \frac{\text{moles of acetone formed}}{\text{moles of 2-propanol reacted}},$$

$$\text{turnover frequency for acetone formation, } v_t = \frac{\text{rate of acetone formation (mol m}^{-2}\text{ s}^{-1})}{\text{total CO}_2\text{ chemisorbed by the catalyst (mol m}^{-2})}.$$

3. Results and discussion

The surface areas and CO_2 adsorption capacities of the bare supports and Sr-loaded supports are reported in table 1. Titania and alumina do not show any significant change in surface area upon incorporation of strontium. However, carbon and silica show a moderate decrease in surface area after Sr incorporation.

It is well-known that extremely high temperatures are required to activate strong base sites on oxides [1]. However, these sites are easily poisoned by trace contaminants. Therefore, we chose to examine the basic properties of supported materials formed by heating to the moderate temperature of 773 K. The decomposition profile of the strontium acetate precursor in flowing air is shown in figure 1. The mass of the sample at 773 K was 71% of its original value and corresponded to the formation of strontium carbonate, which was confirmed by X-

Table 1
Strontium contents and adsorption capacities of the catalysts

Sample	Sr (wt%)	Surface area ($m^2\,g^{-1}$)	CO_2 chemisorbed (10^{-6} mol m^{-2})	Excess CO_2 chemisorbed on Sr-loaded catalyst [a] (mol (mol Sr)$^{-1}$)
SiO_2	–	191	0.0	–
Sr/SiO_2	5.72	166	0.15	0.04
Al_2O_3	–	88	1.13	–
Sr/Al_2O_3	5.46	87	2.78	0.23
TiO_2	–	57	0.97	–
Sr/TiO_2	4.15	57	3.37	0.29
carbon	–	843	0.0	–
Sr/carbon	4.79	723	0.13	0.18

[a] Calculated from the difference in the CO_2 uptakes of pure supports and Sr-loaded supports.

ray diffraction (figure 2). The low loading of Sr on the supported Sr samples precluded the use of TGA to identify the existence of surface carbonates. Thus, FT-IR spectroscopy was used to characterize the Sr species on the surface.

Figure 3 shows the IR absorption spectra of the impregnated silica sample before and after calcination at 773 K. The spectrum of bulk strontium acetate is included for comparison. Bulk strontium acetate shows two broad peaks at about 1430 and 1560 cm^{-1}. These two peaks are also seen in the impregnated SiO_2 sample before calcination, but they are absent in the calcined sample. Since carbonates have strong features in this region of the IR spectrum, figure 3c provides excellent evidence that strontium acetate decomposed on silica gel at 773 K without forming surface carbonates.

Additional structural information in the vicinity of Sr in the Sr/SiO_2 sample was obtained from the Sr-K edge EXAFS of the supported sample. The k^3-weighted χ data and the resulting Fourier transform over the k-space region 2.9–9.5 Å^{-1} for bulk SrO are shown in figure 4. The analogous plots for the silica supported sample are shown in figure 5. The two peaks in the Fourier transform of bulk SrO at about 2 and 3.5 Å correspond to Sr–O and Sr–Sr distances (not corrected for phase shifts), respectively. The Sr–O peak at 2 Å in the Fourier transform has a lower intensity in the Sr/SiO_2 sample than in bulk SrO. Also, the Sr–Sr peak in bulk SrO is absent in the Sr/SiO_2 sample. These results indicate that either very small clusters of Sr oxide were synthesized on the surfaces of SiO_2 or a disordered surface silicate phase was formed. d'Espinose de la Caillerie et al. have detected the formation of an amorphous magnesium silicate after impregnation of Mg^{2+} cations onto silica at room temperature and moderately basic pH [11]. We suspect that our strontium on silica also formed a silicate phase. The Sr–O distance in bulk SrO, which has a rock salt structure, is 2.58 Å. Curve-fitting of the

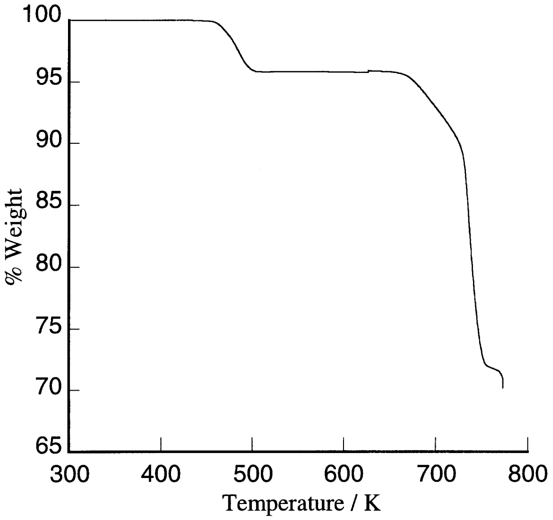

Figure 1. Decomposition of bulk phase strontium acetate in flowing air.

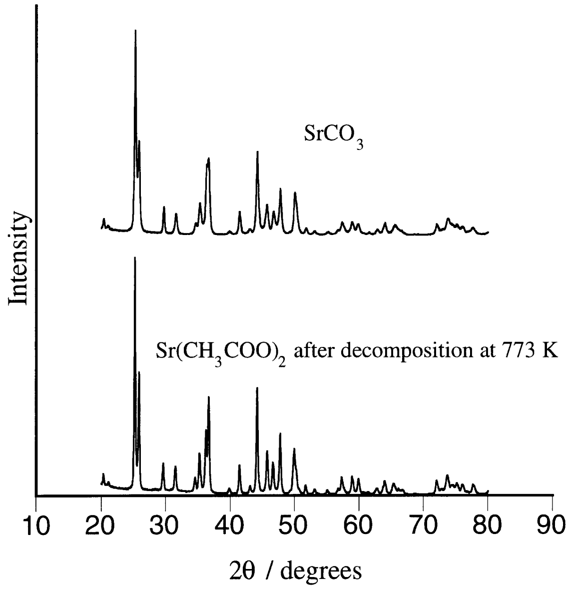

Figure 2. X-ray diffraction patterns of bulk $SrCO_3$ and decomposed $Sr(CH_3COO)_2$.

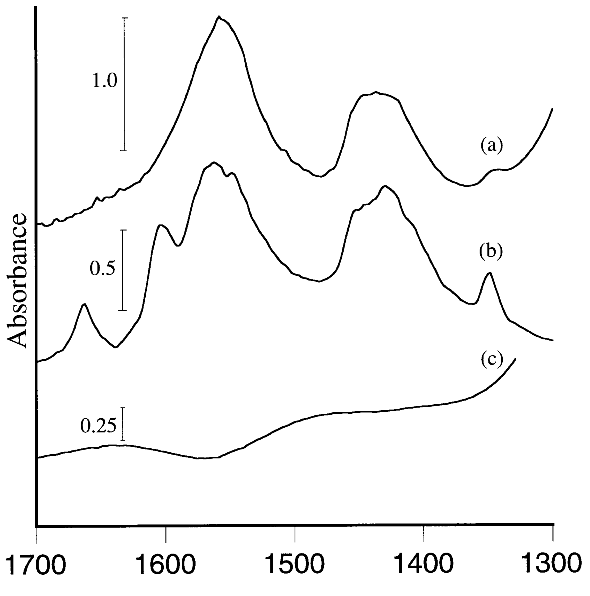

Figure 3. IR absorption spectra of (a) bulk strontium acetate; (b) strontium acetate impregnated on silica; (c) Sr/SiO$_2$ after calcination at 773 K.

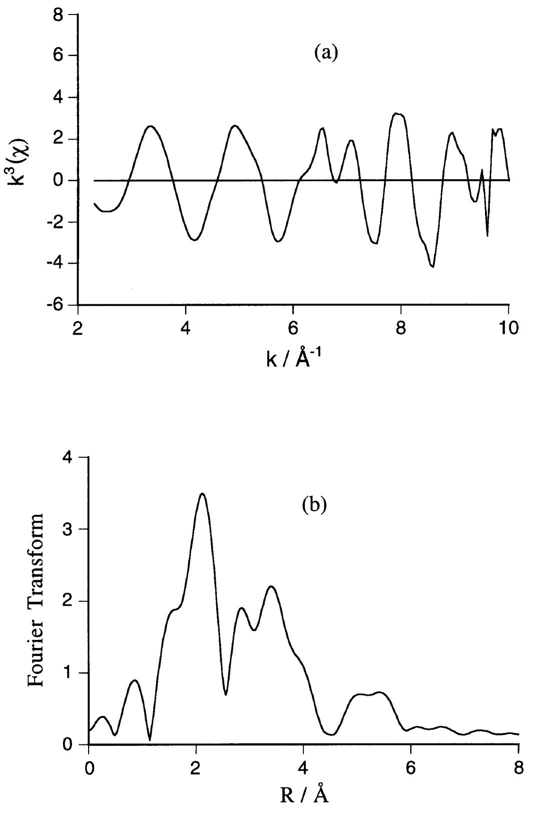

Figure 4. Sr-K edge EXAFS for bulk SrO. (a) $k^3(\chi)$ data; (b) radial structure function derived from Fourier transform of data shown in (a), not corrected for phase shift.

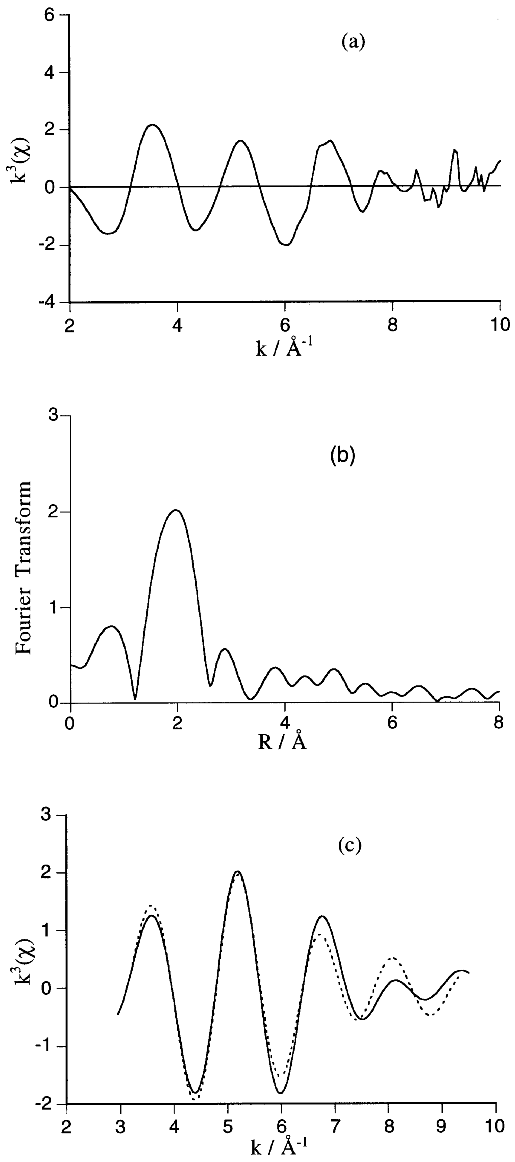

Figure 5. Sr-K edge EXAFS for Sr/SiO$_2$. (a) $k^3(\chi)$ data; (b) radial structure function derived from Fourier transform of data shown in (a), not corrected for phase shift; (c) Fourier-filtered EXAFS function and resulting curve fit (dotted line) used to calculate interatomic distance.

back transform of Sr/SiO$_2$ (figure 5c) gave a Sr–O distance of 2.54 Å. This contraction in the Sr–O distance is additional evidence for the strong interaction of Sr with a silica surface.

The IR absorption spectra for Al$_2$O$_3$ and TiO$_2$, before and after incorporation of Sr, are shown in figure 6. The spectrum for bulk SrCO$_3$ is also included for comparison. Pure alumina and titania do not exhibit any carbonate bands in their spectra after pretreatment in dinitrogen at 773 K. However, the Sr-loaded supports show the presence of carbonate species, even after pretreatment at 773 K. The most intense peak in the spectra

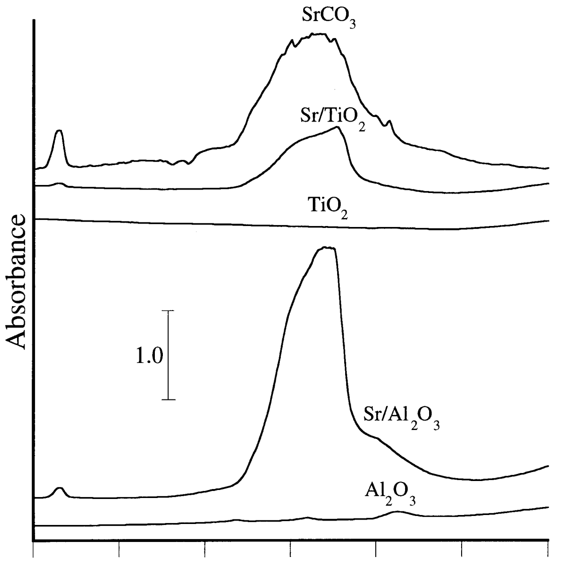

Figure 6. IR absorption spectra of bulk $SrCO_3$ in air at room temperature, alumina and titania (with and without Sr) at 303 K after pretreatment in dinitrogen at 773 K.

of Sr-loaded titania and alumina occurs at about the same wavenumber as that for bulk $SrCO_3$. The various carbonate bands seen in the spectra of the Sr-loaded titania and alumina are in good agreement with carbonate species observed after CO_2 adsorption on SrO, as reported by Xu et al. [12]. Our results from infrared spectroscopy clearly show that the form of Sr on silica was different from the carbonate forms observed on alumina and titania. Strong absorption of IR radiation by the carbon support prevented analysis of the Sr phase on carbon.

The base strength distributions obtained from STPD of CO_2 on the pure supports and Sr-loaded catalysts are shown in figure 7. Each bar represents the number of CO_2 desorption sites per gram measured in a corresponding temperature step. The results show that incorporation of Sr increased the CO_2 adsorption capacity of the materials. Pure carbon and silica did not adsorb CO_2 under our conditions and incorporation of Sr created new adsorption sites. However, the CO_2 uptake on Sr/silica was very low, indicating that few base sites were formed on that sample. Our results from IR and EXAFS spectroscopies of Sr/silica are consistent with the formation of a surface silicate phase rather than a basic supported oxide or carbonate. Strontium appeared to be equally well-dispersed on the surfaces of carbon, alumina and titania since the CO_2 uptakes per mole of added Sr on these samples were fairly similar. Most of the chemisorbed CO_2 was desorbed below 573 K, indicating that the basic sites on these catalysts were relatively weak.

The decomposition of 2-propanol at 593 K was used to probe the catalytic activity of the basic materials and results are presented in table 2. The rates of decomposition over pure titania and pure alumina were very high, but the predominant product was propene, probably indicating an abundance of acid sites on these materials. However, propene formation via an alkoxide intermediate is a possible alternate route over oxide catalysts [13]. On all the other samples, the conversion levels were differential ($< 15\%$) thus allowing for the calculation of rates. Strontium-loaded titania and alumina had lower rates and higher selectivities to acetone compared to the bare supports, suggesting a neutralization of acid sites on these oxide carriers upon incorporation of strontium. Based on CO_2 STPD results, new base sites were also formed by strontium addition. The turnover frequency for acetone formation, based on the amount of CO_2 chemisorbed on the catalysts, provided a simple approximation of the intrinsic activity of the basic sites on the surface. Previous work by Fishel and Davis shows that CO_2 adsorption capacity provides a good measure of the base site density for 2-propanol decomposition over Mg(Al)O catalysts [14]. Although 2-propanol decomposition on silica yields 99% propene, the activity of silica was much lower than titania and alumina. Even after addition of strontium, silica continued to exhibit low activity. However, the few sites that chemisorb CO_2 are apparently as active as those on Sr/Al_2O_3 as demonstrated by the similarity in turnover frequency. These catalysis results support the speculation that most of the added strontium on silica forms a silicate phase.

Untreated carbon shows some activity for the decomposition reaction and has a fairly high selectivity for acetone. This observation indicates the presence of some base sites on carbon, although these sites did not chemisorb CO_2 at our conditions. Apparently, these weak sites are capable of catalyzing the alcohol dehydrogenation reaction, without chemisorbing CO_2 at room temperature. Interestingly, Sr/carbon exhibits the highest activity and selectivity towards acetone formation.

Since carbonate species were detected on the surfaces of Sr/TiO_2 and Sr/Al_2O_3, the activity of bulk strontium carbonate was tested for 2-propanol decomposition. Despite its low surface area of 5 $m^2\ g^{-1}$, $SrCO_3$ showed activity per square meter comparable to Sr/TiO_2 and a very high selectivity to acetone, demonstrating a predominance of base sites on the surface. Bulk strontium oxide with a surface area of 2 $m^2\ g^{-1}$ showed an order of magnitude higher activity than strontium carbonate, with acetone as the predominant product. Evidently, the supported carbonate species can function as base catalysts, although they are likely much less active than the corresponding oxides. A recent report by Aramendia et al. shows that $BaCO_3$ is an active base catalyst for the Knoevenagel condensation reaction between benzaldehyde and malononitrile [15].

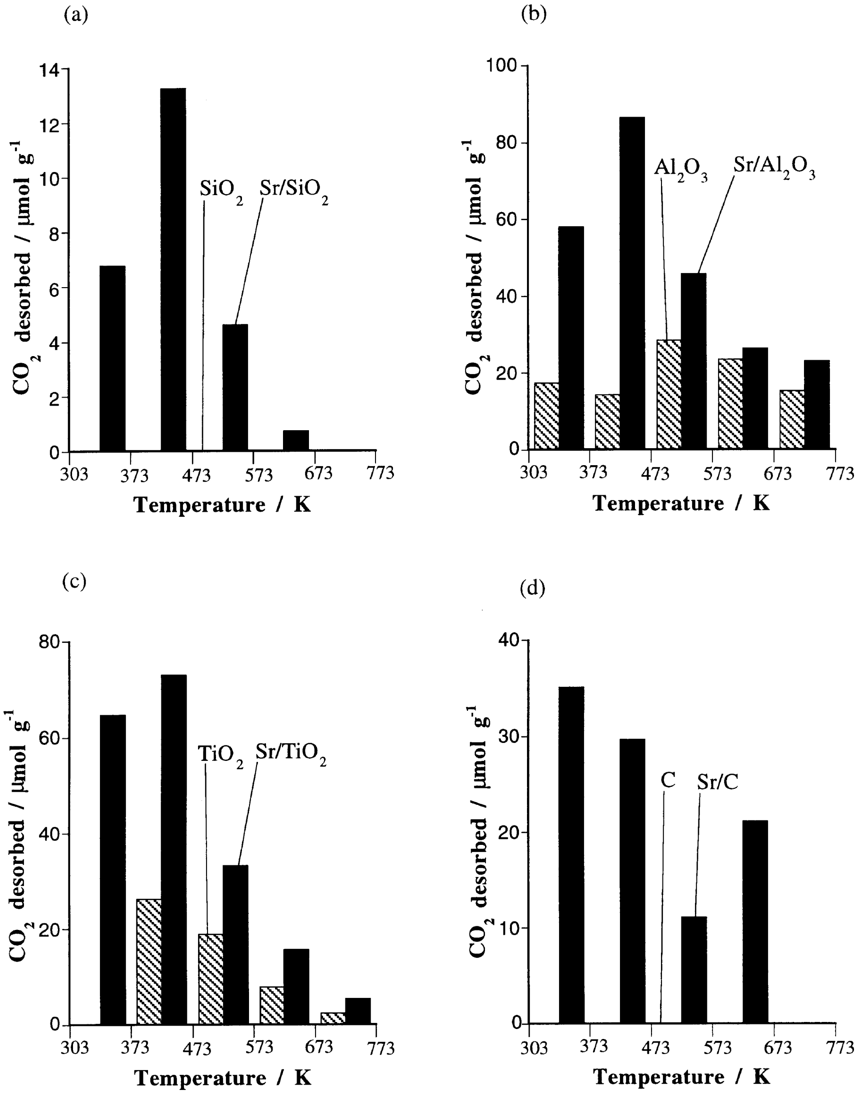

Figure 7. Base strength distribution obtained by STPD of CO_2 from 303 to 773 K on supports and Sr-loaded supports (a) silica, (b) alumina, (c) titania, (d) carbon. No CO_2 uptake was observed on the pure silica and carbon supports.

Table 2
Reaction rates for 2-propanol decomposition at 593 K

Catalyst	Rate of decomposition of 2-propanol (10^{-9} mol m^{-2} s^{-1})	v_t of acetone formation[a] (10^{-3} s^{-1})	Selectivity to acetone (%)
SiO_2	19.4	–	1.3
Sr/SiO_2	1.36	0.80	9.0
Al_2O_3	very high	–	0.2
Sr/Al_2O_3	8.74	0.97	30.3
TiO_2	very high	–	0.8
Sr/TiO_2	46.6	4.83	35.0
carbon	0.46	–	32.7
Sr/carbon	1.94	8.28	57.5
$SrCO_3$	41.8	–	93.5
SrO	735	–	91.5

[a] Based on total CO_2 uptake.

4. Conclusions

The nature of impregnated Sr species on the surfaces of various supports is a function of the type of support. On SiO_2, the most acidic of all the supports studied, strontium apparently forms a surface silicate phase, whereas on TiO_2 and Al_2O_3, strontium exists as a surface carbonate. On all of the supports studied, addition of strontium acetate followed by calcination at 773 K resulted in the creation of new basic sites as counted by CO_2 STPD. However, these sites are fairly weak. The strontium silicate material chemisorbed very little CO_2 per added Sr atom, indicating that few basic sites were created on this material. Results from 2-propanol dehydrogenation confirmed the basic character of the supported catalysts, with Sr/carbon exhibiting the greatest turnover frequency for acetone formation.

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References

[1] H. Hattori, Chem. Rev. 95 (1995) 537.
[2] H. Hattori, Stud. Surf. Sci. Catal. 78 (1993) 35.
[3] K. Tanabe, M. Misono, Y. Ono and H. Hattori, Stud. Surf. Sci. Catal. 51 (1989).
[4] W.F. Holderich, Stud. Surf. Sci. Catal. 75 (1993) 127.
[5] A.B. Stiles, Symposium on Catalyst Supports, Division of Petroleum Chemistry, Inc. American Chemical Society, New York City Meeting, August 1991.
[6] E. Ruckenstein and Y.H. Hu, Appl. Catal. A 133 (1995) 149.
[7] A.Z. Khan and E. Ruckenstein, Appl. Catal. A 102 (1993) 233.
[8] C.T. Fishel, R.J. Davis and J.M. Garces, J. Catal. 163 (1996) 148.
[9] H. Tsuji, F. Yagi, H. Hattori and H. Kita, Stud. Surf. Sci. Catal. 75 (1993) 1171.
[10] R.W.G. Wyckoff, *Crystal Structures*, Vol. 1 (Wiley, New York, 1965).
[11] J. d'Espinose de la Caillerie, M. Kermarec and O. Clause, J. Phys. Chem. 99 (1995) 17273.
[12] Y. Xu, L. Yu, C. Cai, J. Huang and X. Guo, Catal. Lett. 35 (1995) 215.
[13] K.S. Kim, M.A. Barteau and W.E. Farneth, Langmuir 4 (1988) 533.
[14] C.T. Fishel and R.J. Davis, Catal. Lett. 25 (1994) 87.
[15] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas and F.J. Romero, Chem. Lett. (1995) 279.