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Alkali-Loaded Silica, a Solid Base: Investigation by FTIR Spectroscopy of Adsorbed CO_2 and Its Catalytic Activity

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FTIR spectra (298 K) of CO_2 adsorbed on SiO_2-supported Li_2O, Na_2O, K_2O, and Cs_2O were studied. An absorption band around 2345 cm^{-1} and two sets of bands, one at around 1675 and 1325 cm^{-1} and another at around 1640 and 1375 cm^{-1}, indicate the presence of monodentate and bidentate types of adsorbed CO_2 species. These bands are absent in the spectrum of CO_2 adsorbed on pure SiO_2. Therefore, it is concluded that both of these species are associated with alkali metal oxides on the SiO_2 surface. The characteristic pairs of absorption bands shift to lower wave numbers with increasing basicity of the metal oxide. Isopropanol mainly undergoes dehydrogenation into acetone over the catalysts. In the methylation of phenol by methanol these catalysts exhibit good activity and ∼100% selectivity for the O-alkylated product, anisole.

INTRODUCTION

Alkali metal oxides supported on magnesium oxide (1) and calcium oxide (2–7) have been used as basic catalysts. Rubidium and cesium oxides exhibit super base characteristics with Hammet basicity function $H_- > +26$ (8). Supported alkali metal oxide catalysts have been tested in reactions like oxidative methylation of acetonitrile with methane to form acrylonitrile (2, 3), dehydrogenation of cumene (4), and partial oxidation of methane (5–7). Alkali-containing zeolite catalysts are active in a variety of reactions like isopropanol dehydrogenation (9), 1-butene isomerization (10–12), and side-chain alkylation of toluene with methanol (13, 14). Doskocil *et al.* (15) have examined Rb loaded on some metal oxides (MgO, TiO_2, Al_2O_3, and SiO_2) and reported that 2-propanol dehydrogenation activity decreases with increasing Sanderson intermediate electronegetivity of the support. The basicity of alkali metal oxides loaded on the support depends also on the acid–base properties of the support. Silica is a preferred support because of its neutral surface. A few studies on silica-supported alkali metal oxides are available in the literature (9, 12, 16). Despite these studies and many others, to our knowledge, comparative information on the basicity and catalytic activity of alkali metal oxide-loaded silica is not available in the literature.

In this study, we have supported Li_2O, Na_2O, K_2O, and Cs_2O on silica and characterized the basicity of the samples by FTIR spectroscopy of adsorbed CO_2 and temperature-programmed desorption (TPD) of CO_2. Their catalytic activities in the dehydrogenation of isopropanol and alkylation of phenol have been examined and correlated with their basicities.

EXPERIMENTAL

Fumed silica (Cab-osil, Fluka, surface area 166 m^2/g) was used as support for alkali metal oxides. The catalysts were prepared by impregnation with the metal acetate (Li, Na, K, and Cs) dissolved in a minimum amount of water (incipient wetness method). In a typical experiment to prepare Cs(0.375)SiO_2, 10 g fumed silica was added to 50 ml of a water solution containing 0.375 mmol/g of the Cs compound and mixed thoroughly. The mixture was evaporated to dryness with stirring at 353 K. The catalyst was further dried at 373 K (6 h) and calcined at 773 K (6 h) in air and stored in a closed container until used. A Cs–SiO_2 catalyst containing 1.5 mmol of Cs per gram of SiO_2 ($Cs^*(1.5)SiO_2$) was prepared by impregnating Cs_2SiO_3 and calcining at 773 K (6 h).

Temperature-programmed desorption (TPD) of CO_2 was carried out with 0.25 g of dried sample for each experiment. The sample was activated at 673 K in a flow of He (30 ml/min) and cooled to room temperature. Ultrahigh-purity CO_2 was passed for 1 h at room temperature at a flow rate of 25 ml/min, then flushed with He (30 ml/min) for 90 min and the temperature raised to 723 K at the rate of 5°/min in He flow (30 ml/min). The evolved CO_2 was estimated using a TCD (Zeton Altamira AM1-200) to obtain the TPD curves.

FTIR spectra of the samples in the region of structural vibrations were recorded using KBr pellets. For spectra of adsorbed CO_2, self-supported wafers were used. The

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sample was pressed into thin wafers (5–6 mg/cm^2), evacuated (10^{-5} mm) at 673 K, and cooled to 298 K to record the spectrum of the pure sample. Ultrapure CO_2 (99.999%, Linde Air) was then adsorbed on the sample at 5 mm equilibrium pressure for 1 h and another spectrum was recorded. Then part of CO_2 gas was pumped out to maintain an equilibrium pressure of 0.4 mm and the spectrum was recorded again. All the spectra were recorded using a Nicolet 60 SXB spectrometer with 2 cm^{-1} resolution, averaging over 500 scans.

Catalytic experiments were carried out in a vertical down-flow glass reactor (15 mm i.d.). All the reactions were carried out using 2-g charge of the catalyst in the form of granules (10–22 mesh). The reactor zone (~15 cm long) above the catalyst bed packed with ceramic beads served as the preheater. The reactor was placed in a temperature-controlled furnace (Geomecanique, France) with a thermocouple placed at the center of the catalyst bed for measuring the reaction temperature. The catalyst was activated in flowing air (20 ml/min) at 773 K for 3 h and flushed with N_2 before setting of the reaction temperature and start of the experiment. The feed (mixture of phenol and methanol) was passed using a syringe pump (Braun, Germany) with N_2 as carrier gas (18 ml/min). The product was collected in a water-cooled receiver and analyzed using a gas chromatograph (HP 5880 A; capillary column, HP-5, 50 m × 0.2 mm; FID). Product identification was done by GC-IR, GC-MS and NMR spectroscopy.

RESULTS AND DISCUSSION

The chemical composition, the surface area, and the amount of CO_2 adsorbed as determined by TPD and FTIR spectroscopic methods are presented in Table 1. The surface areas (Table 1) of the samples were calculated from an N_2 sorption isotherm (BET method). The surface areas decrease with an increase in metal loading and also with an increase in basicity of the metal. Surface areas were also calculated on an alkali free basis (Table 1). These values are also lower than that of pure SiO_2. The decrease in surface area is attributed to the "dissolution" of the surface by the alkali during impregnation, fusion of SiO_2 particles, and pore filling by the alkali oxides.

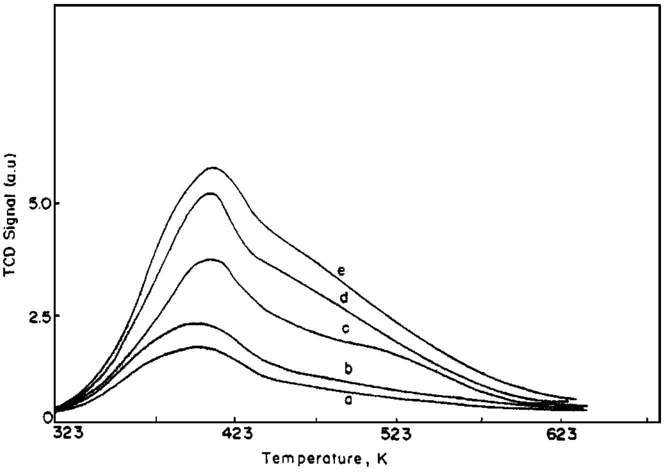

FIG. 1. TPD plots of CO_2 adsorbed on different Cs loaded samples. (a, b, c, d, e) refer to samples with Cs loading of 0.075, 0.375, 0.75, 1.5, and 2.25 mmole/g of silica, respectively.

Temperature-Programmed Desorption of Carbon Dioxide

The results of TPD of adsorbed CO_2 are presented in Table 1. The TPD plots of various Cs-loaded samples are given in Fig. 1. It was found that most of the CO_2 desorbed from the samples below 500 K with desorption peak maxima

TABLE 1

Physicochemical Properties of the Catalysts

Catalyst[a]	Metal loading as oxide (wt%)	Surface area[b] (m^2/g)	Surface area[c] (m^2/g)	S_{int}	Relative basicity: TPD of CO_2: mmole/g	Relative basicity: TPD of CO_2: Mole/mole metal	Relative basicity: FTIR[d]	Relative basicity: FTIR[e]
SiO_2	—	166	—	4.25	—	—	—	—
$Li(1.5)SiO_2$	2.25	104	164	3.98	0.062	0.041	92	102
$Na(1.5)SiO_2$	4.65	99	161	3.96	0.071	0.047	132	140
$K(1.5)SiO_2$	7.05	91	156	3.92	0.078	0.052	153	180
$Cs(0.075)SiO_2$	1.43	149	164	4.22	0.031	0.41	19	24
$Cs(0.375)SiO_2$	5.28	121	156	4.18	0.049	0.13	88	96
$Cs(0.75)SiO_2$	10.5	102	149	4.09	0.061	0.081	120	168
$Cs(1.5)SiO_2$	21.1	70	133	3.91	0.079	0.053	216	229
$Cs(2.25)SiO_2$	31.7	56	116	3.69	0.082	0.036	262	281

[a] The numbers in parentheses denote the millimoles of alkali metal loaded per gram of SiO_2.

[b] Measured by N_2 adsorption (BET method).

[c] Normalized to 100% silica.

[d,e] Relative band intensity of adsorbed CO_2 in FTIR spectra (1200–1750 cm^{-1}) at 0.4 and 5 mm equilibrium pressure, respectively.

in the range 375–425 K. Although CO_2 adsorbs weakly on the catalysts and desorbs easily, the TPD data do reveal some information concerning the basicity of the samples. At constant metal loading (1.5 mmol/g of SiO_2), the amount of adsorbed (actually desorbed) CO_2 increases with increasing basicity of the metal (Li to Cs). In addition, an increase in CO_2 adsorption is noticed with an increase in Cs_2O loading. However, the number of moles of CO_2 adsorbed per mole of alkali metal decreases with increases in Cs_2O loading. This is due to lower dispersion and cluster formation in samples containing higher amounts of Cs_2O. The intermediate electronegativity (S_{int}) of the samples calculated (17) on the basis of Sanderson's intermediate electronegativity principle decreases as expected with increasing basicity of the metal.

FTIR Spectroscopy: Framework Structure

The FTIR spectrum of pure silica shows strong bands due to tetrahedral framework vibrations of Si–O–Si linkages at 1106 and 807 cm^{-1}. As the Cs_2O loading increases, these characteristic bands shift systematically to lower wave numbers as can be noticed in Fig. 2. The bands at 1106 and 807 cm^{-1} in pure SiO_2 shift to 1097 and 794 cm^{-1} respectively in Cs(2.25)SiO_2 (31.7% Cs_2O) sample. In the case of cesium silicate, they appear at 1041 and 787 cm^{-1}, respectively (Fig. 2a). The shift indicates that Si–O–Si linkages are perturbed by the formation of Si–O–Cs linkages in the framework, suggesting the formation of a cesium silicate type of species at the surface. Doskosil *et al.* (15) have identified such an alkali silicate phase in the case of the Rb_2O/SiO_2 system from X-ray absorption studies.

Adsorption of Carbon Dioxide

In the past, supported alkali metal oxide catalysts have been prepared using both hydroxide and alkali metal acetate salts (18–21). The catalysts were finally calcined to obtain alkali oxides on the support. Inspection of those reports reveals that, when acetate was used to load the alkali metal oxide, the nature of the product depended on the basicity of the support. On highly basic supports like NaX, undecomposed alkali metal carbonate was detected on the surface, where as less basic supports like NaY, total decomposition of acetate to oxide was noticed. On the neutral SiO_2 support used by us, we believe that only metal oxides are formed on the surface. FTIR spectra of the samples activated to 673 K and cooled to 373 K under vacuum showed no bands characteristic of CO_3, indicating complete decomposition of acetate to oxide in the sample. CO_2, being amphoteric in nature, can be used to monitor both Lewis acid centers and Lewis base centers on metal oxides and zeolite surfaces. It is a linear molecule having D_4 symmetry and three fundamental vibrations, one stretching vibration ν_1, which is Raman

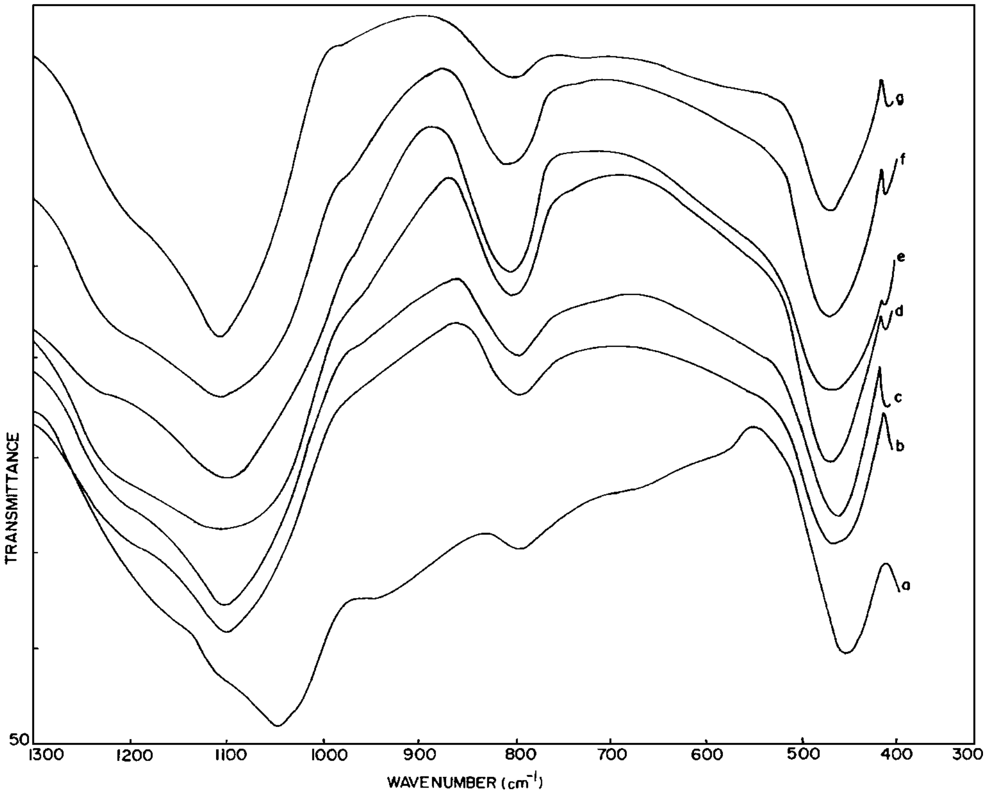

FIG. 2. FTIR spectra (298 K) of Cs_2O–SiO_2 samples in the framework region. (a) Cesium silicate and (b, c, d, e, f) samples with Cs loading of 2.25, 1.5, 0.75, 0.375, 0.075 mmole/g of silica, respectively and (g) pure SiO_2.

active appearing as a doublet at 1285 and 1388 cm^{-1} and two other IR-active vibrations, doubly degenerate deformation ν_2 at 667 cm^{-1} and the antisymmetric stretching ν_3 at 2349 cm^{-1} (22). The IR spectrum of adsorbed CO_2 varies distinctly from the gas phase spectrum, and three types of adsorption have been distinguished:

(1) On unreactive surfaces, the infrared spectrum of adsorbed CO_2 shows mostly the ν_3 vibration near 2349 cm^{-1}.

(2) The adsorption of CO_2 on reactive surfaces may give rise to several adsorbed species, such as carbonate, bicarbonate, and formate, which exhibit characteristic absorption bands (23–25).

(3) CO_2 can also function as a ligand in different complexes of transition metals as a highly perturbed structure. These CO_2 species have a characteristic pair of absorption bands in the region 1700–1200 cm^{-1}. This type of bond is formed when electrons are donated to a CO_2 molecule and a CO_2^- anion is formed, but such an anion is stable only at low temperatures.

Adsorption of CO_2 on pure SiO_2 shows a band only due to molecularly adsorbed CO_2 (ν_3, type 1) at 2349 cm^{-1} associated with changes in the band shapes of the hydroxyl groups on SiO_2. The hydroxyl groups on pure silica exhibit a sharp band at 3745 cm^{-1} and a broad band centered around 3550 cm^{-1}, which are perturbed by the adsorption of CO_2 (not shown). These hydroxyl groups are centers of CO_2 adsorption. No bands are observed in the carbonate region, 2000–1200 cm^{-1}. Similar reports have been made earlier by many workers (15, 26–28). CO_2 (at 298 K) was completely desorbed on evacuating the sample.

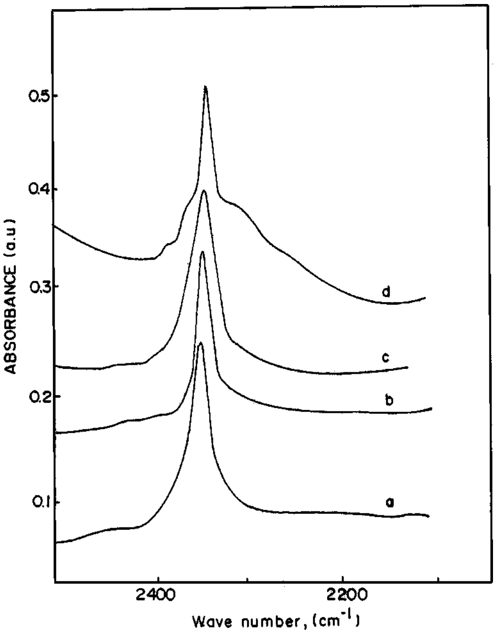

FIG. 3. FTIR spectra (298 K) of adsorbed CO_2 (0.4 mm equilibrium pressure of CO_2) in the region of anti-symmetric stretching on alkali metal (1.5 mmole/g) loaded silica: (a) Li_2O–SiO_2, (b) Na_2O–SiO_2, (c) K_2O–SiO_2, and (d) Cs_2O–SiO_2.

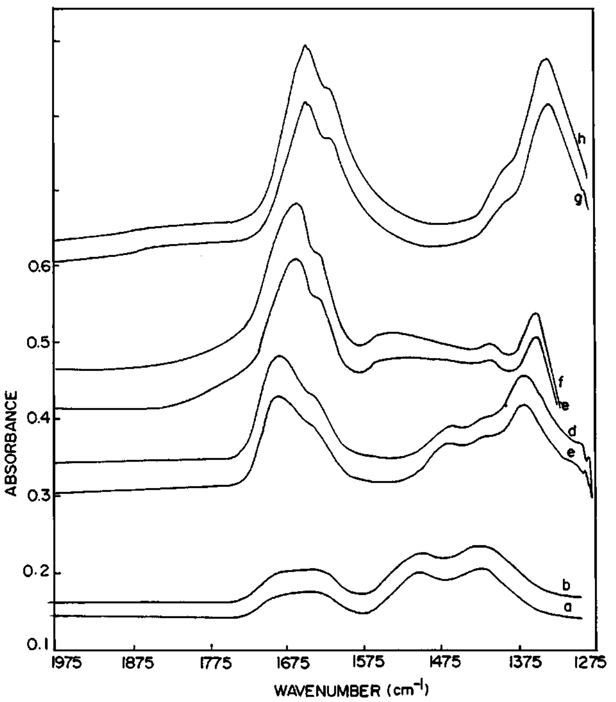

FIG. 4. FTIR spectra (298 K) of adsorbed CO_2 on alkali metal (1.5 mmole/g) loaded silica: (a, b) Li–SiO_2, (c, d) Na–SiO_2, (e, f) K–SiO_2 and (g, h) Cs–SiO_2. (a, c, e, g) for 0.4 mm and (b, d, f, h) for 5 mm equilibrium pressure, respectively.

IR spectra of adsorbed CO_2 on alkali metal-modified silica are shown in Figs. 3, 4, and 5. In Fig. 3, bands due to antisymmetric stretching ν_3 vibrations of physisorbed CO_2 on Li_2O-, Na_2O-, K_2O-, and Cs_2O-modified SiO_2 are seen; they appear, respectively, at 2348, 2346, 2342, and 2340 cm^{-1}. As the ionic radius of the alkali metal cation and the metal–oxygen bond length increases, the electron-donating ability (to adsorbed CO_2) increases and hence the ν_3 frequency shifts to a lower wave number, in accordance with the basicity of the alkali metal. In Fig. 4, the corresponding FTIR spectra in the region of carbonate vibrations (1975–1275 cm^{-1}) are presented. Adsorption of CO_2 produced two sets of bands. Each set consists of bands due to one anti-symmetric and one symmetric stretching vibration. The frequencies of these bands for Li_2O-, Na_2O-, K_2O-, and Cs_2O-loaded SiO_2 (1.5 mmol/g loading) are presented in Table 2. The relative intensity of these bands decreases with decreases in equilibrium pressure but persists even after evacuation. It is clear that the supported alkali metal changes the adsorptive property of SiO_2. The frequencies of these bands of adsorbed carbonate species decrease as the basicity of the alkali metal increases. The difference between the high- and the low-frequency bands varies from 258 to 319 cm^{-1} for anti-symmetric stretch and 154 to 234 cm^{-1} for symmetric stretch vibrations for

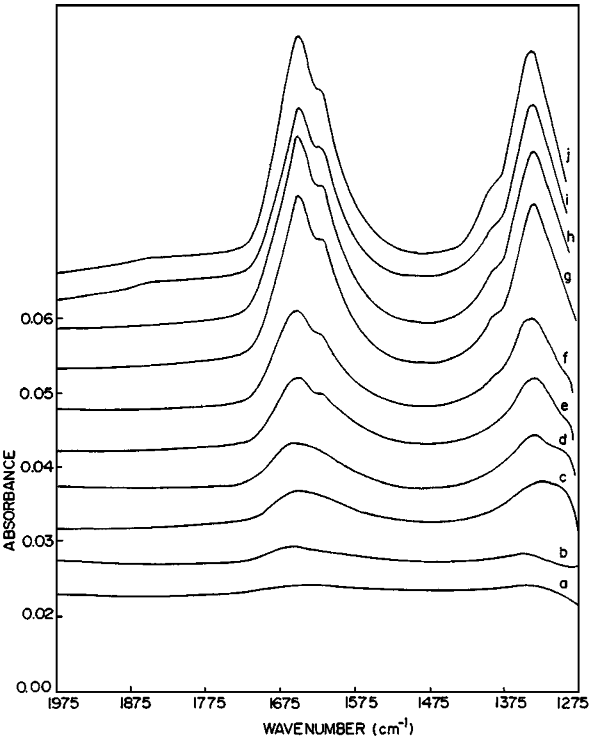

FIG. 5. FTIR spectra (298 K) of adsorbed CO_2 in the CO_3 vibration region on Cs_2O–SiO_2 samples with Cs loading of 0.075, 0.375, 0.75, 1.5 and 2.25 mmole/g; (a, c, e, g, i) at 0. 4 mm and (b, d, f, h, j) at 5 mm equilibrium pressure of CO_2, respectively.

different metal oxide-loaded samples. For samples containing different amounts of Cs_2O, the frequency variations are much less (Table 2). The assignment of these absorption bands is based on characteristic vibrations reported previously for CO_2 adsorption on metal oxides and alkali metal-modified metal oxides (24, 25).

Carbon dioxide is believed to adsorb on metals and basic oxides in many forms, such as the symmetrical, monodentate, bidentate, and bridged forms (25). The interaction of CO_2 is believed to be through the transfer of electronic charge to the CO_2 molecule from the metal or alkali metal oxide, which increases with the size of the metal ion. In metal oxides, simultaneous interaction of alkali cation and O^{2-} anion on adsorbed CO_2 takes place in bridged conformation. The increasing shift in the high- and low-frequency bands and increasing frequency difference between the bands on going from Li^+ to Cs^+ cation-modified SiO_2 samples indicate increasing interaction with CO_2. Solymosi and Knozinger (25) have proposed $\Delta\nu$ values of 0, 100, 300, and >400 for symmetrical, monodentate, bidentate, and bridged confirmations for adsorbed CO_2 species, respectively, on interacting surfaces. Going by this concept, the $\Delta\nu$ values observed for CO_2 on Li^+-, Na^+-, K^+-, and Cs^+-modified SiO_2 surfaces indicate the presence of mainly monodentate and bidentate types of adsorbed species. The concentration of bidentate species increases with the basicity of the alkali metal.

TABLE 2

$\Delta\nu$ Splitting for Different Forms of Carbonate[a]

	Antisymmetric			Symmetric		
Sample[b]	cm^{-1}	cm^{-1}	$\Delta\nu$	cm^{-1}	cm^{-1}	$\Delta\nu_3$
Li(1.5) SiO_2	1679	1421	258	1652	1498	154
Na(1.5) SiO_2	1683	1365	318	1643	1462	181
K(1.5) SiO_2	1663	1347	316	1633	1407	226
Cs(0.375) SiO_2	1652	1336	316	1617	1390	227
Cs(0.75) SiO_2	1651	1333	318	1619	1387	232
Cs(1.5) SiO_2	1648	1329	319	1618	1384	234
Cs(2.25) SiO_2	1645	1331	314	1617	1383	234

[a] Spectra recorded at 0.4 mm equilibrium pressure of CO_2 (298 K).

[b] The numbers in parentheses denote the millimoles of alkali metal loaded per gram of SiO_2.

Catalytic Activity

The catalytic activity of the samples was tested by carrying out the dehydrogenation of isopropanol and vapor phase methylation of phenol with methanol. The results of the dehydrogenation of isopropanol are presented in Table 3. Pure silica has negligible selectivity for acetone (a base-catalyzed product). Incorporation of alkali metal increases the selectivity to acetone formation. Both conversion and selectivity for acetone increase with the basicity of the metal. A small amount of the dehydration product propene was noticed over all the catalysts. The catalyst deactivated slowly with time presumably due to coke formation. At constant metal oxide loading, the activity is in the order $Li(1.5)SiO_2 < Na(1.5)SiO_2 < K(1.5)SiO_2 < Cs(1.5)SiO_2$.

The results of the alkylation of phenol with methanol are presented in Table 4. Turn over frequency (TOF) and

TABLE 3

Catalytic Activity in Isopropanol Dehydrogenation

Catalyst[a]	Conv. (mole %)	Selectivity (acetone)	Specific rate[b] (k) (mole. $s^{-1}g^{-1}$)	TOF[c] $\times 10^{-3}$ (w.r.t. alkali metal)
SiO_2	4.0	1.3	0.5×10^{-6}	—
$Li(1.5)SiO_2$	4.4	65.2	0.6×10^{-6}	0.77
$Na(1.5)SiO_2$	5.6	76.3	0.8×10^{-6}	1.16
$K(1.5)SiO_2$	6.8	83.7	0.9×10^{-6}	1.35
$Cs(1.5)SiO_2$	9.5	90.8	1.4×10^{-6}	1.93

Note. Conditions: Temperature = 723 K, WHSV (h^{-1}) = 3.14, time on stream = 1 h.

[a] The numbers in parentheses denote the millimoles of alkali metal loaded per gram of SiO_2.

[b] Calculated from the first-order rate equation $\ln(1/1 - X) = (W/F)k$, where W = catalyst weight, F = feed rate in mole s^{-1} and X = conversion.

[c] Moles of isopropanol conversion/mole of metal atom/s.

TABLE 4

Activities of the Catalysts in Phenol Methylation

Catalyst[a]	Conv. (%)	Selectivity (anisole)	Specific rate[b] (k) mol s^{-1} g^{-1}	TOF[c] $\times 10^{-3}$ (w.r.t. metal)
SiO_2	1.2	2.0	7×10^{-6}	—
Li(1.5) SiO_2	1.0	~100	7×10^{-6}	0.037
Na(1.5) SiO_2	9.2	~100	9×10^{-5}	0.33
K(1.5) SiO_2	23.5	~100	3.6×10^{-4}	0.85
Cs(0.075) SiO_2	10.6	~100	1.0×10^{-4}	7.30
Cs(0.375) SiO_2	34.2	~100	4.4×10^{-4}	4.98
Cs(0.75) SiO_2	46.7	~100	7.2×10^{-4}	3.37
Cs(1.5) SiO_2	64.3	~100	2.5×10^{-3}	2.34
Cs(2.25) SiO_2	66.9	~100	2.6×10^{-3}	1.63
Cs*(1.5) SiO_2[d]	27.5	~100	1.1×10^{-3}	1.00

Note. Conditions: temperature 633 K, time on stream = 1 h, WHSV (h^{-1}) = 2.66, phenol/methanol (mole) = 0.2, N_2 = 18 ml/min.

[a] The numbers in parentheses denote the millimoles of alkali metal loaded per gram of SiO_2.

[b,c] Same as footnotes *b* and *c* in Table 3.

[d] Catalyst prepared by impregnation of Cs_2SiO_3 instead of Cs acetate.

specific rate constants for the catalysts are also presented in the table. The activity of the catalysts increases with increasing metal loading as well as with the basicity of the alkali metal. The following general trends in the activity and selectivity of the catalysts are observed: (i) catalyst activity increases with the basicity of the catalyst, (ii) resonable correlation between basicity and CO_2 adsorption exists and (iii) pure silica possesses negligible O-alkylation selectivity, but exhibits very high O-alkylation selectivity when loaded with even a mildly basic alkali, Li_2O.

In order to understand the actual nature of the catalytic species (alkali silicate or oxide) present on the surface of the catalysts, a catalyst prepared by impregnation of Cs_2SiO_3 was also tested for catalyst activity. The catalyst (Cs*(1.5)SiO_2) was much less active (27.5% conversion compared to 64.3% over Cs(1.5)SiO_2; Table 4). It appears therefore that the major active species on the catalyst are the alkali oxides, although a small amount of silicate species may be present on the surface (see discussion on FTIR spectroscopy) and may also be contributing to catalytic activity to a limited extent.

CONCLUSIONS

Pure SiO_2 adsorbs CO_2 weakly and molecularly at 298 K. On alkali oxide-loaded SiO_2, $CO_2^{\delta-}$ species are formed on the alkali metal oxide, giving rise to characteristic pairs of absorption bands. The positions of all the bands shift to a lower wave number with a decrease in Sanderson's electronegativity and an increase in basicity of the alkali metal oxide. At ambient temperature, the surface complex transforms into a more stable bi-dentate carbonate species with increasing basicity of the alkali oxide. The activity of the catalysts increases with increasing basicity of the alkali metal (Li to Cs) in both isopropanol conversion and methylation of phenol with MeOH. In the decomposition of isopropanol, these catalysts produce mainly the dehydrogenated product acetone, and in the methylation of phenol with methanol these catalysts selectively produce the O-alkylated derivative, anisole.

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